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**Dihydroxylammonium 5,5'-bis-tetrazole-1,1'-diolate (TKX-50) Synthesis and Lab Scale Characterization**

Steve Nicolich\*, Philip Samuels, Dr. Reddy Damavarapu, Dr. Alex Paraskos, Edward Cooke, Dr. Victor Stepanov, Paula Cook, Dr. Kelley Caflin  
US Army Armaments Research, Development and Engineering Center

Dr. Raja Duddu  
Liedos

Explosives Development Branch  
Energetics, Warheads, and Manufacturing Technology Directorate  
Picatinny Arsenal, New Jersey 07806  
Email: [steven.m.nicolich.civ@mail.mil](mailto:steven.m.nicolich.civ@mail.mil); Phone: 973-724-3016

**ABSTRACT**

The Joint Insensitive Munitions Technical Program (JIMTP) began a directed study in fiscal year 2013 to evaluate the scale up of new molecules. Requirements for candidate consideration stated that the synthesis must be demonstrated multiple times at the 25 g batch size, small-scale safety test data including impact, friction and electrostatic discharge testing must be available and a measured crystal density is also required (pycnometry or x-ray). Thermal stability assessment via DSC, isothermal weight loss, or vacuum thermal stability (<2 cc gas/48hrs at 100°C) was additionally required. Based on the above criteria TKX-50 was picked as the JIMTP's FY14 Molecule of the Year.

Professor Tom Kloptke first published on the synthesis and properties of TKX-50, reporting a high measured density (1.877 g/cm<sup>3</sup> @ 298 K) with very good predicted and some limited measured performance properties (i.e. - significantly greater than RDX) [1]. The RDECOM Ordnance Environmental Program (OEP) looked at small scale synthesis of this new molecule and then transitioned to JIMTP. ARDEC has begun evaluating a new one-pot processes for TKX-50 production that will hopefully avoid the necessity of using toxic elemental chlorine gas during the production of the dichloroglyoxime precursor and will also avoid the isolation of any residual intermediate azide species formed during the reaction sequence.

TKX-50 has proven to be compatible with most energetics and binders. Studies are currently ongoing to evaluate the solubility of TKX-50 in various common solvents. This paper will discuss the synthesis, small scale sensitivity and performance properties of pure TKX-50 as well as in formulations.

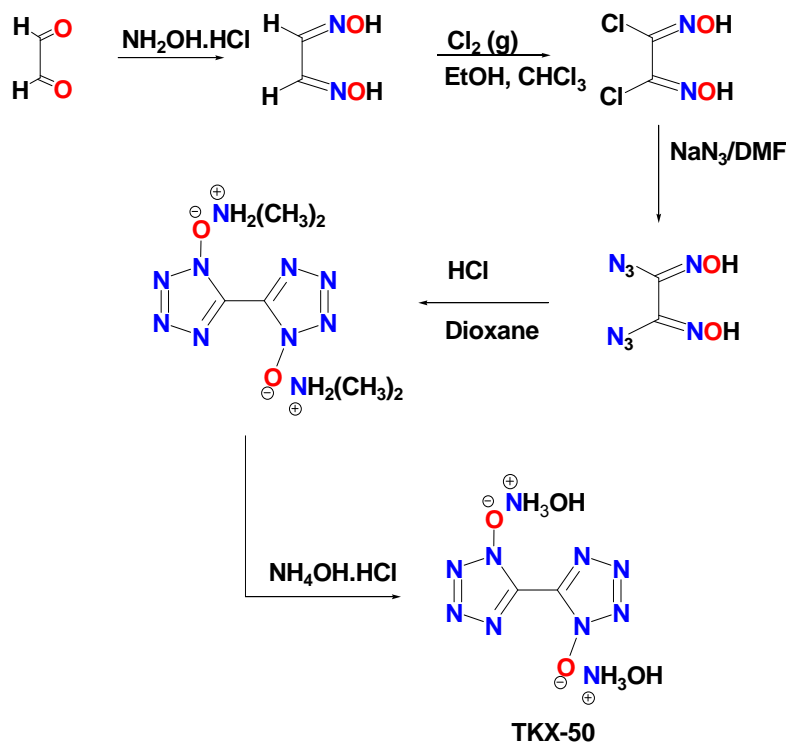
**Introduction**

TKX-50 (Table 1, Scheme 1) was selected for evaluation as a promising new energetic ingredient under the JIMTP Directed Study. It has a crystal density of 1.877 g/cc @ 25 C (measured, Xray). It was first synthesized by the Klapötke group who reported that the molecule is "easily prepared and exceedingly powerful, but also possesses the required thermal insensitivity, low toxicity, and safety of handling to replace the most commonly used military explosive, RDX (1,3,5-trinitro-1,3,5-triazacyclohexane)" (ref 1). As the DoD moves forward with the scale-up and formulation of TKX-50, it is natural to consider new synthetic routes as well as characterize the performance of this new

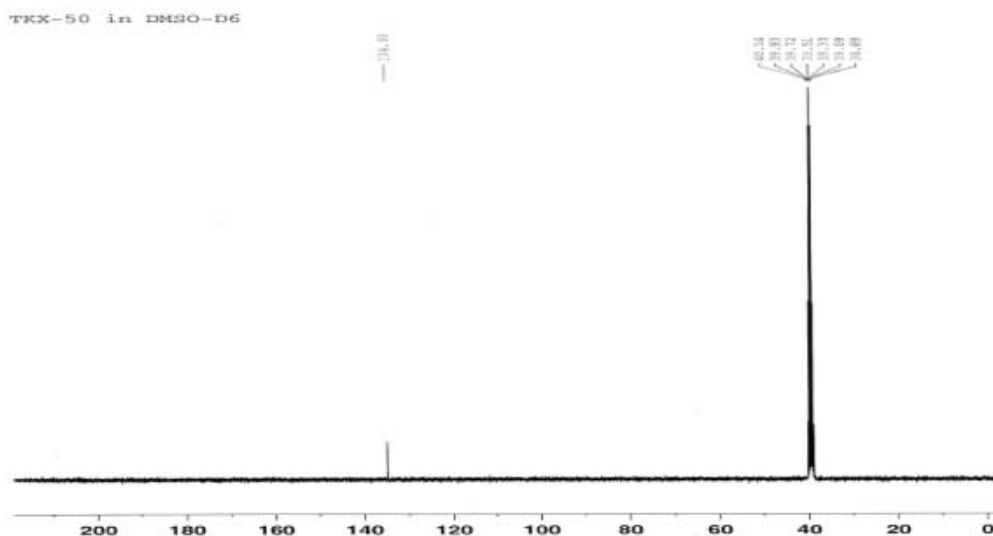
compound. This paper will discuss the synthesis route used by ARDEC to produce over three pounds of TKX-50 for solubility, safety testing, and chemical compatibility of this compound with other materials that it will come in contact with while processing.

### Synthesis

The U.S. Army Research Development and Engineering Center (ARDEC) established the viability of the developed process for TKX-50 (Scheme 1) on a 75.0 gram scale. The process is reproducible and produced TKX-50 in a consistent manner. Carbon Nuclear Magnetic Resonance ( $^{13}\text{C}$  NMR) as shown in Figure 1 provided verification of the purity of the TKX-50 produced. Small scale experiments were performed with an objective to further improve the process.



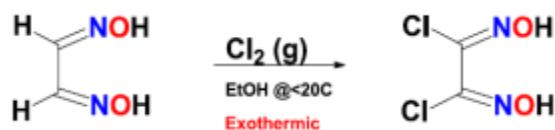
**Scheme 1.** Synthesis of dihydroxylammonium 5,5-bistetrazolate-1,1'-diolate (TKX-50) from glyoxime



**Figure 1.**  $^{13}\text{C}$  NMR spectrum of TKX-50 reveals one peak at 135 ppm in  $d_6$ -DMSO

### DCG Preparation

In preparation for testing and evaluation of TKX-50, ARDEC conducted the synthesis of dichloroglyoxime from glyoxime (Scheme 2 and Figure 2). Gaseous elemental chlorine is passed through a solution of glyoxime in ethanol (EtOH) at between -40 and -30 degrees C. Accurate control of the feed rate of the chlorine is critical to control both reaction temperature as well as the total amount of chlorine added (stoichiometry). Over-addition of chlorine (above ~10% excess) can cause the condensation of excess chlorine in the cold solvent which can then result in sudden gasification of the chlorine and the exothermic decomposition of unidentified intermediates upon warming the reaction flask to room-temperature. The use of a corrosion-proof rotameter allows for the establishment of a controlled, measured feed rate. 1-L and 3-L chlorination experiments set-ups were established. The overall yield per batch was 150-160 grams in the three liter reactor. The process is reproducible and consistently yielded DCG in good yields. The 3-L process was repeated multiple times in order to produce a total of 1.5kg DCG from glyoxime. The DCG was purified by slurring in water and filtering product prior to subsequent synthesis steps.



**Scheme 2.** Chlorination of Glyoxime



**Figure 2.** DCG process lab setup

### TKX-50 Preparation

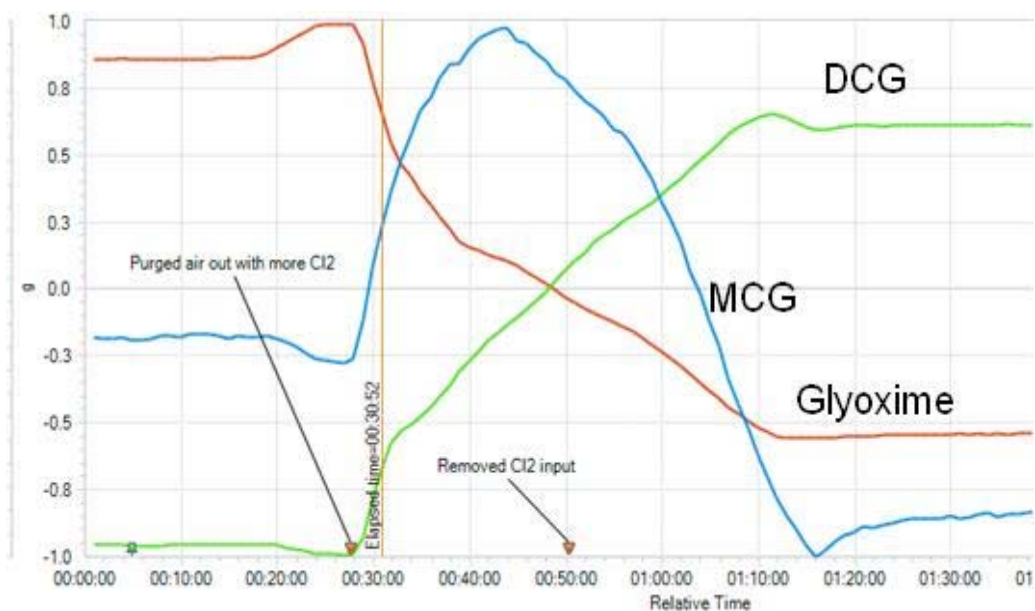
Purified DCG was dissolved in DMF at ambient temperatures. The solution was cooled to 10 degrees C so that sodium azide could be added iteratively maintaining the reaction temperature below 15 degrees C. A solution of HCl in dioxane was then added drop wise while maintaining the reaction temperature below 15 degrees C. The resulting suspension was stirred for several days at room temperature. The majority of the solvents and high boiling byproducts were removed by rotary evaporation and the paste-like products were re-dissolved in boiling water to which a solution of hydroxylamine hydrochloride was added. Crystalline TKX-50 was collected by vacuum filtration, washed, and required no further purification. Syntheses were carried out at the 3-L scale yielding 100-110 grams of TKX-50 per batch in repetition until 3 lbs were produced.

### Easymax Experiments

A Mettler-Toledo Easy Max unit (Figure 3) was used to better understand the chemistry involved in the synthesis of TKX-50 from glyoxime. The EasyMax unit has several useful features including excellent stirring and thermal control, an in-situ IR probe and the ability to continuously monitor the reaction chemistry (by IR) and heat flow in real time. First, the chlorination of glyoxime in ethanol was monitored by FT-IR using the ConcertIR software. The rapid consumption of glyoxime upon the introduction of chlorine is accompanied by the initial formation and subsequent disappearance of the monochloroglyoxime species followed by formation of the dichloroglyoxime product (Figure 4).



**Figure 3.** Mettler Toledo Easymax

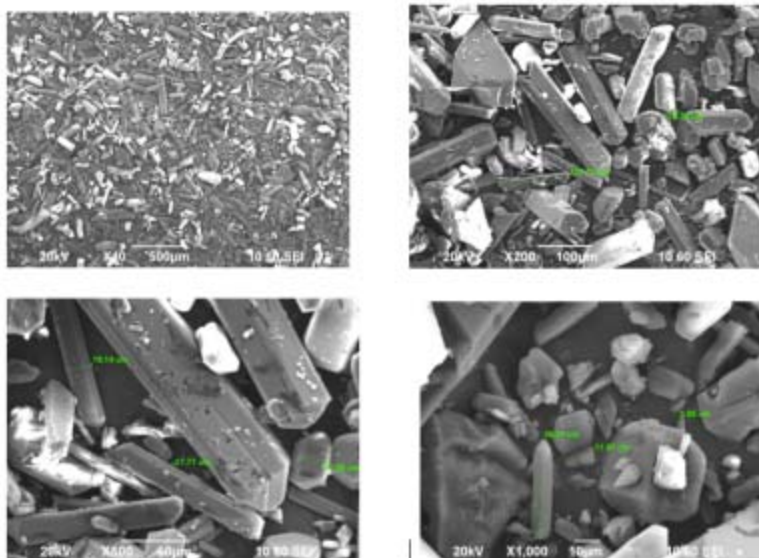


**Figure 4.** The formation of dichloroglyoxime from glyoxime proceeds through the monochlorinated species as evidenced by ConcertIR analysis of the in-situ FT-IR data

## Experimental

### Scanning Electron Microscopy (SEM)

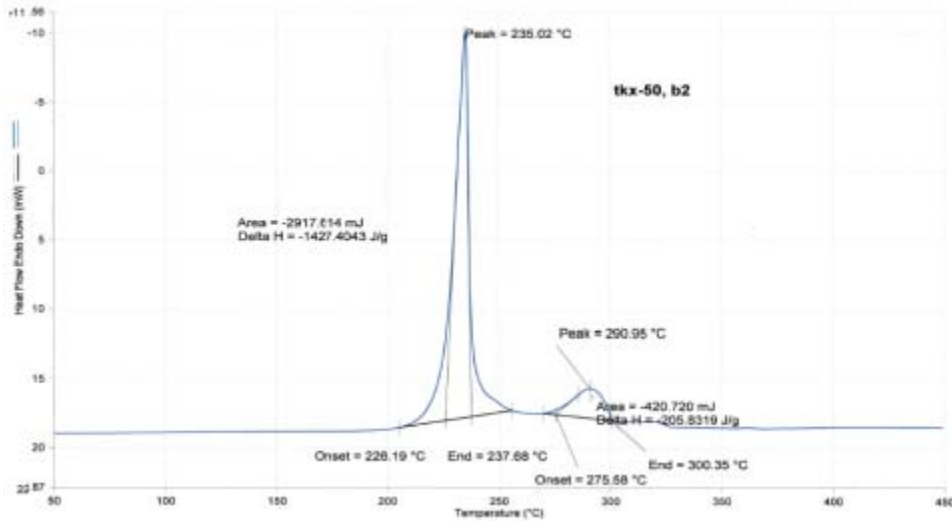
SEM images were obtained using a JEOL JCM 5700 tungsten filament scanning electron microscope using palladium/gold-coated samples in high vacuum mode as shown in Figure 5.



**Figure 5.** SEM images of TKX-50

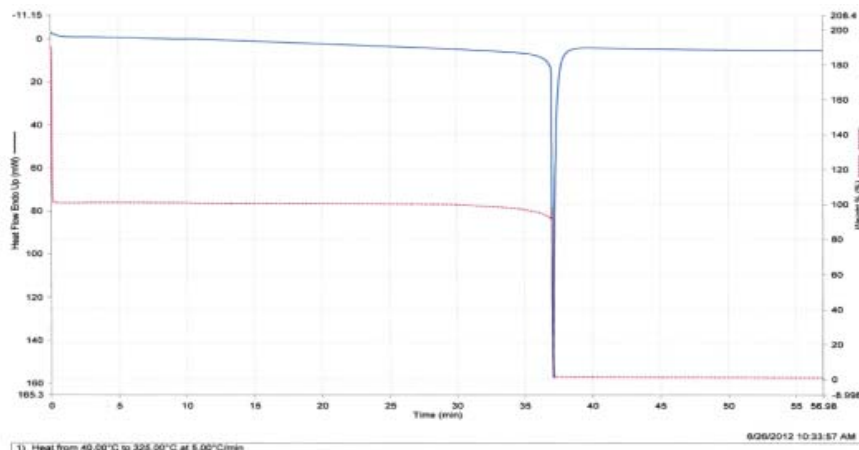
### Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA)

The DSC was performed according to AOP-7, US 202.01.020 (MIL-STD-1751A (1072)) or STANAG 4515 where 20 mg TKX-50 was subjected to a heating rate of 10 °C/min until decomposition of the sample occurred. The sample endotherm(s), exotherm(s), onset temperature(s), and peak temperature(s) are recorded. TKX-50 exhibited an exotherm onset at 226 °C, and an exotherm peak temperature at 235 °C as shown in Figure 6. By comparison, RDX exhibited an exotherm onset at 210 °C, and an exotherm peak temperature at 241 °C.



**Figure 6.** DSC Scan of TKX-50

The Thermogravimetric Analyzer (TGA) and Differential Thermal Analysis (DTA) provides insight to a materials' decomposition and atmospheric reactions. The TGA was performed on TKX-50 in accordance with STANAG 4515. The TKX-50 sample was heated at a rate of 5°C/min. The results show that there was a greater than 85% weight loss at the end of the decomposition, meaning no anomalies were detected (impurities, excess moisture) as shown in Figure 7.



**Figure 7.** TGA Scan of TKX-50



### Vacuum Thermal Stability (VTS) Testing

Vacuum Thermal stability testing was performed in accordance to STANAG 4556 ED.1 (Explosives: Vacuum Stability Test). This standard testing procedure measures the stability of an explosive at an elevated temperature under vacuum. The candidate explosive and materials are tested alone as control subjects. The explosive is then mixed with each individual material and tested. The reactivity (compatibility) is then determined by comparing the gas evolved by the candidate explosive control, the material control, and the mixture. The materials were tested for 40 hours at 100 °C. The criteria used are summarized in Table 1. VTS results for TKX-50 with common energetics and binders are shown in Table 2. ARL also conducted compatibility testing via GC-MS (ref 2, 3). Their results matched up well with the VTS testing at ARDEC.

**Table 1. Compatibility Criteria for VTS Tests**

Gas Generation (mL)	Degree of Reactivity
0.0-3.0	Compatible
3.0-5.0	Marginally Compatible
>5.0	Incompatible

**Table 2. TKX-50 VTS Compatibility Summary**

ml gas of 1:1 mix	Reactivity of mix (ml)	Result
TKX-50	0.067	pass
TKX-50 & CUO(II)	0.62	pass
TKX-50 & Steel shavings	Negligible	pass
TKX-50 & Al powder	0.13	pass
TKX-50 & R8002	2.4	pass
TKX-50 & BDNPA/F	0.94	pass
TKX-50 & Chlorez wax	negligible	pass
TKX-50 & Viton	negligible	pass
TKX-50 & DNAN	negligible	pass
TKX-50 & TNT	negligible	pass
TKX-50 & DEMN	9.84	fail
TKX-50 & NTO	negligible	pass
TKX-50 & HMX	negligible	pass
TKX-50 & PrNQ	1.2	pass

### Solubility

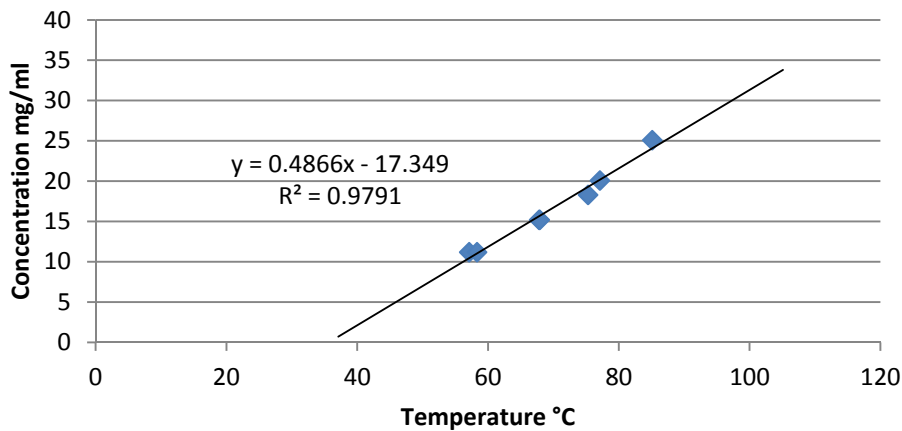
Solubility is an important factor for formulation efforts. The objective was to characterize the solubility of TKX-50 in water over a given range of temperatures. Solubility curve determinations were run on an Avantium Crystal16. In each experiment solute is weighed into a small clear/colorless HPLC vials equipped with a small magnetic stir bar. A known volume of solvent is added with a pipetman. An array of samples is constructed with a range of solution concentrations. The solubility point of each vial solution was determined by identifying a clear point. The clear point is defined as the temperature at which the turbidity of the solution decreases upon heating and the solution becomes transparent (all crystalline material has dissolved into the solvent). Graphing the concentration of the solution versus the clear point temperature yields the

solubility curve and trend line equation. TKX-50 becomes more soluble in water and a water:MEK at 3:1 by volume as the temperature increases as shown in Table 3 and Figure 8. TKX-50 solubility in Ethyl Acetate was less than 5 mg/ml.

**Table 3. TKX-50 Solubility in Water Results**

Clear Point Temperature	Concentration
°C	mg/ml
57.1	11.2
58.3	11.2
67.8	15.2
67.9	15.2
75.3	18.3
77.1	20.1
85.1	25.1

### TKX-50 in Solubility in Water



**Figure 8. TKX-50 Solubility Curve in Water**

### SENSITIVITY TESTS

#### Electrostatic Sensitivity (ESD)

The test procedure is described in reference 1, AOP-7, 201.03.001, “Electrostatic Discharge Sensitivity Test” as shown in Figure 19. This test determines the energy threshold required to ignite explosives by electrostatic stimuli of varying intensities. The TKX-50 did not react in 20 trials at 0.09 Joule. TKX-50 passes this test as does most of the secondary explosives as shown in Table 4.

#### Impact Sensitivity Test

The ERL, Type 12 impact tester, utilizing a 2 ½ kg drop weight, was used to determine the impact sensitivity of the sample as shown in Figure 20. The drop height corresponding to the 50% probability of initiation is used to measure impact



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sensitivity. The ERL, Type 12 Impact Test Method is described in STANAG 4489 Ed.1 “Explosives, Impact Sensitivity Tests”. All impact tests were conducted using 180A garnet sandpaper and the test procedures given in AOP-7, 201.01.001. Bruceton method of statistical analysis was used to determine the 50% point of 45.5 cm for TKX-50.

**Friction Sensitivity Test**

The Large BAM Friction Test Method is described in AOP-7, 201.02.006, “BAM Friction Test”. A sample of TKX-50 was placed on the porcelain plate. The porcelain pin was lowered onto the sample and a weight was placed on the arm to produce the desired load. The tester was activated and the porcelain plate was reciprocated once to and fro. The results are observed as either a reaction (i.e. flash, smoke, and/or audible report) or no reaction. Testing is begun at the maximum load of the apparatus (360 N) or lower if experience warrants it. If a reaction occurs in ten trials, the load is reduced until no reactions are observed in ten trials. TKX-50 did not react in 10 trials at 120 N.

**Table 4. TKX-50 Safety Test Results Compared to RDX and HMX**

Molecule	ERL Impact (cm)	BAM Friction (N)	ABL ESD (J)
TKX-50	45.5	Reacted @ 128N, Did not React in 10 trials @ 120N	Reacted @ 0.128J; Did not React in 20 trials @ 0.09J
RDX (Class I)	33.5	Reacted @ 216N, Did not React in 10 trials at 192N	Reacted @ 0.063J; Did not React in 20 trials @ 0.051J
RDX (Class V)	30.5	Reacted @ 324N, Did not React in 10 trials at 288N	Reacted @ 0.051J; Did not React in 20 trials @ 0.040J
FEM HMX	27.1	Reacted @ 168N, Did not React in 10 trials @ 160N	Reacted @ 0.040J; Did not React in 20 trials @ 0.031J

**Theoretical Calculations**

Cheetah 6.0 and Jaguar 10 were utilized for determining the performance of TKX-50 and comparing it to baseline formulations such as PBXN-5, PBXN-9, Composition A5 and PAX-46 as shown in Table 5. Professor Leonard Stiel from Polytechnic University assisted the team by conducting computations of TKX-50 for equation of state using Jaguar 10 as shown in table 6.

**Table 5. Cheetah 6.0 Cheetah Calculations using EXP6.3 Library**

Formulation	Density (g/cc) [98%TMD]	Detonation Velocity (Km/s)	CJ Pressure (Gpa)	Gurney
PBXN-5 (Baseline)	1.86	8.75	35.32	3.11
Comp A5 (Baseline)	1.75	8.25	30.73	2.95
PBXN-9 (Baseline)	1.72	8.43	29.52	2.90
PAX-46 (Baseline)	1.77	8.47	31.25	3.07
TKX-50	1.83	9.5	37.5	3.02
95% TKX-50, 5% Viton A	1.83	9.23	35.62	2.96
98% TKX-50, 2% Stearic Acid Wax	1.79	9.19	33.63	2.9

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**Table 6.** Jaguar 10 Calculations for Energetic Materials

Explosive	Formula	Density	$\Delta H_f$	Det Vel	C-J P	CJ T	Gurn Vel(3)	Gurn Vel(7)	E0
		$\text{g/cm}^3$	$\text{kJ/mol}$	$\text{km/s}$	$\text{GPa}$	$\text{K}$	$\text{km/s}$	$\text{km/s}$	$\text{kJ/cm}^3$
TKX-50	C <sub>2</sub> H <sub>8</sub> N <sub>10</sub> O <sub>4</sub>	1.877	193	9.83	42.1	2433	2.66	2.9	-9.72
TNT	C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>6</sub>	1.654	-63	6.89	19.8	3092	2.20	2.43	-7.11
RDX	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	1.816	70	8.76	34.8	3708	2.73	3.01	-10.88
HMX	C <sub>4</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>	1.905	75	9.09	38.7	3514	2.76	3.04	-11.38

**Conclusions**

TKX-50 was tested for compatibility with variety of polymers, plasticizers, metals and metal oxides was investigated using a traditional vacuum thermal test and a new desorption-gas chromatography test. TKX-50 exhibits outstanding compatibility across the range of materials investigated.

The team was successful in producing over three pounds of TKX-50 over the course of a year. ARDEC developed a reproducible process for the purification of DCG. The team developed a scaled-up synthesis of TKX-50 from DCG. There are still more pathways that need to be evaluated for a better synthetic route to avoid the use of Chlorine gas. Future work needs to establish one-pot procedure of TKX-50 in DMF (initial experiments at gram scale one pot synthesis look encouraging for scale up).

**References**

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2. R. Pesce-Rodriguez and K. Spangler, Development and Application of a New Gas Chromatography-mass Spectrometry (GC-MS) Compatibility Screening Method for Energetics, ARL-TR-6429, April 2013.
3. R. Pesce-Rodriguez, E. Klier, H. Grau, P. Samuels. Compatibility of TKX-50. ARL-TR-7043. August 2014.