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<td>Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048</td>
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<td>16. SECURITY CLASSIFICATION OF:</td>
<td>Unclassified Unclassified Unclassified</td>
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<td>18. NUMBER OF PAGES</td>
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<td>19a. NAME OF RESPONSIBLE PERSON</td>
<td>Leilani Richardson</td>
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<tr>
<td>19b. TELEPHONE NUMBER</td>
<td>(661) 275-5015</td>
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Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. 238.18
MEMORANDUM FOR PRR (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO)       27 May 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY990109
Drake et al., “New Energetic Salts for Monopropellants”

HEDM CONFERENCE

(Public Release)
New Energetic Salts for Monopropellants

June 9, 1999

U.S. Air Force High Energy Density Materials Meeting

Greg Drake, Adam Brand, Milton McKay, Ismail Ismail*, Tom Hawkins

Propulsion Directorate and *ERC, inc.
Air Force Research Laboratory, Edwards AFB, CA 93524

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited
Overview of Talk

I. Introduction
II. 2-Hydroxyethylhydrazine salts
III. Dimethyltriazaninium salts revisited
IV. A look at energetic nitrocyanamide salts
V. Summary, Conclusions, and Outlook
Hydrazine ($N_2H_4$) is currently the state of the art monopropellant

**Problems:** Extreme vapor and dermal toxicity  
Relatively high vapor pressure at ambient temperature (12 torr)  
Leads to very high handling and loading costs  
Density (1.0 g/cm$^3$) and performance aren’t that spectacular

Another candidate receiving renewed attention is hydrogen peroxide ($H_2O_2$)  
Notorious history of violent decomposition  
Incompatible with many materials especially organics and metals

**Objective:** To find safer, higher performing monopropellant materials for eventual replacement of hydrazine

At AFRL, we have been exploring energetic salts as possible new monopropellant materials. Several advantages including significantly higher densities and little or no vapor pressure at ambient conditions.
2-hydroxyethylhydrazine, [HO-CH₂-CH₂-NH-NH₂] extensively used in the agricultural field in the 60's and 70's as a flowering agent, especially in pineapple plants.


Liquid to low temperatures with no real freezing point to $-50^\circ$C

Very low vapor pressures at room temperature.

Could salts of this form new monopropellant ingredients?
2-hydroxyethylhydrazinium nitrate (HEHN) from the simple reaction of HEH with concentrated HNO$_3$

\[
\text{HO-CH}_2\text{-CH}_2\text{-NH-NH}_2 + \text{HNO}_3 \text{ (aq.)} \rightarrow [\text{HO-CH}_2\text{-CH}_2\text{-N}_2\text{H}_4^+] [\text{NO}_3^-]
\]

"HEHN"

viscous liquid at RT
great physical properties, f.p. = -50°C, density = 1.42 g/cm
\( \text{H}_\text{f} \text{ (calc.)} : -107 \text{ kcal/mol} \)
Impact sensitivity: 38 kg cm (5 negatives)
Friction: 9 kg (5 negatives)

≥ 1.3 explosive
patent applied for by A. Brand and T. Hawkins
HEH mononitroformate $[\text{HO-CH}_2-\text{CH}_2-\text{N}_2\text{H}_4^+][\text{C(NO}_2)_3^-]$  
"HEHNF"

$\text{HO-CH}_2-\text{CH}_2-\text{NH-NH}_2 + \text{H-C(NO}_2)_3 \rightarrow [\text{HO-CH}_2-\text{CH}_2-\text{NH-NH}_3^+][\text{C(NO}_2)_3^-]$

"HEHNF"

Viscous yellow oil with significant vapor pressure  
Decomposes slowly at RT (gasses), turns dark with bubbles  
Can be detonated with a strong hammer blow  
DSC studies large exotherm beginning at $75^\circ\text{C}$ with pan exploding
HEH monodinitramide \([\text{HO-CH}_2\text{-CH}_2\text{-N}_2\text{H}_4^+][\text{N(NO}_2\text{)}_2^-]\)

Carried out in a strong acid cation exchange resin, using MeOH as the solvent

\[
\text{HO-CH}_2\text{-CH}_2\text{-NH-NH}_2 + \text{“H-N(NO}_2\text{)}_2” \rightarrow [\text{HO-CH}_2\text{-CH}_2\text{-NH-NH}_3^+][\text{N(NO}_2\text{)}_2^-]
\]

“HEHDNA”

Straw-colored viscous liquid which discolors upon long exposures to light
DSC studies: revealed no decomposition below 150° C
Impact: 5 negatives at 5 kg cm
Friction: 5 negatives at 112 Newtons
Thermal stability at 75° C: decent, losing only 1.2% per day
Sample: HEHDNA 1:1 STRAW OIL
Size: 2.0000 mg
Method: PROPELLANTS
Comment: Rate 10°C/MIN, SEALED (CTD) AL PANS IN DRYBOX/ N2 FLOW

DSC
File: C:DRAKE.059
Operator: DRAKE
Run Date: 4-Jun-98 02:41

Heat Flow (W/g)

Temperature (°C)

147.80°C
HEH dinitramide at 75°C

- 0.55% H₂O
- 1.2% per day
HEH dinitrate \[ [\text{HO-CH}_2\text{-CH}_2\text{-NH}_2\text{NH}_3^+] \left[\text{NO}_3^\text{-}\right]_2 \]

\[ \text{HO-CH}_2\text{-CH}_2\text{-NH-NH}_2 + 2 \text{HNO}_3 \text{ (aq)} \rightarrow [\text{HO-CH}_2\text{-CH}_2\text{-N}_2\text{H}_5^{+2}] \left[\text{NO}_3^\text{-}\right]_2 \]

“HEHDN”

White crystalline solid, m.p. 61°C
Density (g/cm\(^3\)): 1.78 (calc.); 1.77 ±0.03 (expt.)
Impact sensitivity: 30 kg-cm
Friction: 12kg
DSC studies: Slow decomp. starting at 110°C
Thermal properties: very poor losing 40% in first 3hrs at 75°C
\( H_f \) (kcal/mol) = -107 (calc.)
HEH di perchlorate \([\text{HO-CH}_2\text{-CH}_2\text{-NH}_2\text{NH}_3^{+2}]\text{[ClO}_4^-]_2\)

\[
\text{HO-CH}_2\text{-CH}_2\text{-NH-NH}_2 + 2 \text{HClO}_4 \text{(aq)} \rightarrow \text{[HO-CH}_2\text{-CH}_2\text{-N}_2\text{H}_5^{+2}] \text{[ClO}_4^-]_2
\]

"HEHDP"

White solid, mp 110\(^\circ\)C
Density (g/cm\(^3\)) : 2.09 (ca\[\_\])
Impact sensitivity: \(< < 10 \text{ kg cm}\)
Friction : \(< < 1 \text{ kg}\)
Extremely sensitive to both friction and impact, destroyed testing cup and anvil. Friction completely destroyed ceramic plate on lowest setting.
DSC : surprisingly stable with no decomposition until 130\(^\circ\)C
\(H_f\) (kcal/mol) : -117 (ca\[\_\])
Thermal stability at 75\(^\circ\)C: > 1% per day
Performance Estimates of "HEHDN" and "HEHDP" versus some known explosive materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density (g/cm³)</th>
<th>Detonation Velocity (m/sec)</th>
<th>Heat of explosion (kcal/kg)</th>
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<tbody>
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<td>PETN</td>
<td>1.76</td>
<td>8400</td>
<td>1421</td>
</tr>
<tr>
<td>RDX</td>
<td>1.82</td>
<td>8750</td>
<td>1375</td>
</tr>
<tr>
<td>HMX</td>
<td>1.85</td>
<td>9100</td>
<td>1357</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>1.59</td>
<td>7600</td>
<td>1617</td>
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<tr>
<td>Lead azide</td>
<td>4.8</td>
<td>5300</td>
<td>367</td>
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<tr>
<td>Lead stypnate</td>
<td>3.0</td>
<td>5200</td>
<td>370</td>
</tr>
<tr>
<td>HEHDN</td>
<td>1.78</td>
<td>8370</td>
<td>1077</td>
</tr>
<tr>
<td>HEHDP</td>
<td>2.09</td>
<td>9150</td>
<td>1270</td>
</tr>
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</table>

HEHDN and HEHDP compare very well to known materials.
The Dimethyltriazanium cation \([\text{H}_2\text{N-}N\text{(CH}_3\text{)}_2\text{-NH}_2]^+\)

Stable catenated nitrogen chain of 3 nitrogen atoms
First prepared by Goesl in 1962 as the sulfate salt
in a straightforward reaction:

\[
\begin{align*}
4 \quad \begin{array}{c}
\text{N} \quad \text{NH}_2 \\
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array} & \quad + \quad 2 \quad \begin{array}{c}
\text{H}_2\text{N} \\
\text{O} \\
\text{SO}_3\text{H}
\end{array} \\
\downarrow & \\
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{H}_2\text{N} \\
\text{CH}_3
\end{array} & \quad \text{SO}_4 & \quad + \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{NH}_2 \\
\text{H}_3\text{C}
\end{array} \quad \text{SO}_4
\end{align*}
\]

Energetic salts are made in a straightforward manner, following the synthesis route used by a Rocketdyne chemist\textsuperscript{1}, and later by Soviet workers\textsuperscript{2}

Nitrate salt:
\[
\begin{array}{c}
\text{SO}_4^+ + \text{Ba(NO}_3)_2 \rightarrow 2 \text{NO}_3^- + \text{BaSO}_4 \\
\end{array}
\]

Perchlorate salt:
\[
\begin{array}{c}
\text{SO}_4^+ + \text{Ba(ClO}_4)_2 \rightarrow 2 \text{ClO}_4^- + \text{BaSO}_4 \\
\end{array}
\]

\textsuperscript{1} Grant, L. R. "Chemistry of Catenated Nitrogen Compounds" Rocketdyne Final Report April 1972, Contract # N0019-71-C-0374.

Dimethyltriazaninium nitrate

White crystalline solid
Melting point: 134°C
$H_f = -34.8$ kcal/mole (Russian work)*
DSC: large exotherm after melt
Impact sensitivity: 17 kgcm (5 negatives)
Friction sensitivity: 9 kg (89 newtons)
Thermal stability at 75°C: Very poor

Dimethyltriazaninium Perchlorate

White crystalline solid
Melting point: 185°C
\( H_f = -16.6 \text{ kcal/mole} \)
DSC: exothermic decomposition occurring right after melt
Impact sensitivity: Rather sensitive, 6 kg/cm
Friction sensitivity: \(< 0.5 \text{ kg}, \text{ detonates very easily with pressure} \)
Thermal stability at 75°C: very poor

she is loosing ~ 7.2% per day... bad bad girl
Dimethyltriazanium dinitramide synthesis

Metathesis:

\[ \text{Dimethyltriazanium dinitramide synthesis} \]

\[ \text{Metathesis:} \]

\[ \text{Dimethyltriazanium dinitramide synthesis} \]
Sample: DIMETHYLTRIAZANUM CHLORIDE
Size: 1.0000 mg
Method: GREG
Comment: SEALED COATED AL PANS UNDER N2/50 ML/MIN N2

---

Heat Flow (W/g)

Temperature (°C)

110.44°C
113.64°C
141.72°C
152.68°C
196.90°C
200.58°C

DSC V4.0B DuPont 2000
Dimethyltriazaninium dinitramide

White crystalline solid
Melting point: 32°C
DSC: Surprising liquid range with major exotherm at 145°C
Impact: xxx kgcm
Friction: xxx newtons
Thermal stability at 75°C: xxx
Sample: DMTDN CRYSTALS
Size: 1.7000 mg
Method: PROPELLANTS
Comment: 10°C/MIN, HERMETIC ALUM PANS, GN2 50ML/MIN, REPAVED IN GLOVE BOX

File: GD.009
Operator: GREG DRAKE
Run Date: 7-Mar-99 19:53

![DSC Graph]

- 31.21°C, 55.65 J/g
- 36.94°C
- 146.66°C, 178.3 J/g
- 149.90°C
Energetic salts of the nitrocyanamide anion

First isolated by McKay and coworkers\(^1\) in 1950 as one of the products in the synthesis of diazohydrocarbons

\[\text{R} - \text{C} = \text{C} - \text{N} = \text{N} - \text{NO}_2 + \text{KOH} \rightarrow \text{R} - \text{H} + \text{HC} = \text{C} - \text{N} = \text{N} - \text{H}_2\text{O} + \text{K}^+ \]

In 1958, Sam Harris reported the synthesis and characterization of a large family of nitrocyanamide salts as new primary explosives/initiators as possible replacements of mercury fulminate.

General reaction scheme:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{NH} \\
\text{N} & \quad \text{C} \quad \text{N} \quad \text{H} \\
\text{NO} & \quad \text{NO}_2 \\
\end{align*}
\]

1. \(\text{NaOH} / \text{O}^\circ\text{C}\)

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{N} \quad \text{N} \\
\end{align*}
\]

2. \(\text{HNO}_3 / \text{AgNO}_3\)

\[
\begin{align*}
\text{N} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{C} \quad \text{N} \\
\end{align*}
\]

Harris, S. *J. Amer. Chem. Soc.* 1958, 80, 2302.
Ammonium Nitrocyanamide, $[\text{NH}_4][\text{N(NO}_2\text{)(CN)}]$ 

\[
\text{Ag}^{+} \text{N} \text{C} \text{C} \text{N} \text{NO}_2^{-} + \text{NH}_4\text{Cl} \rightarrow \text{AgCl} + \text{NH}_4^{+} \text{N} \text{C} \text{C} \text{N} \text{NO}_2^{-}
\]

White powder
Melting point: $92^\circ \text{C}^*$
DSC: slow exotherm beginning at $160^\circ \text{C}$
Impact sensitivity: impact insensitive at highest setting
200 kg cm (4 kg at 50 cm)
Friction sensitivity: insensitive at highest setting
37.8 kg (371 Newtons)
Thermal stability at $75^\circ \text{C}$: not very good at 3.8% per day

Harris, S. J. Amer. Chem. Soc. 1958, 80, 2302.
Sample: NH₄N(NO₂)(CN)
Size: 1.3000 mg
Method: PROPELLANTS
Comment: 10°C/MIN, HER AL PANS, GN2 50 ML/MIN

DSC
File: A:DRAKE.030
Operator: JONES/DRAKE
Run Date: 10-Feb-98 07:24

Temperature (°C)

Heat Flow (W/g)

88.54°C  79.39 J/g
92.07°C
240.54°C
234.42°C  1046 J/g

DSC V4.0B DuPont 2000
Methoxy ammonium nitrocyanamide at 75°C

Weight (% weight)

Time, min

> 20% per day

051799.XLS
Guanidinium nitrocyanamide, $[\text{C(NH}_2\text{)}_3][\text{N(NO}_2\text{)}\text{(CN)}]$ 

$$\text{Ag}^+ \text{N}^+ \text{C} = \text{N}^+ \text{NO}_2^- + \text{C(NH}_2\text{)}_3\text{Cl} \rightarrow \text{AgCl} + \text{C(NH}_2\text{)}_3^+ \text{N}^+ \text{C} = \text{N} \text{NO}_2^-$$

White solid
Melting point: $131^\circ\text{C}$
DSC: melt with a large exotherm at $148^\circ\text{C}$
Impact sensitivity:
Friction sensitivity:
Thermal stability at $75^\circ\text{C}$: good passing at $0.64\%$ loss/24 hours
Guanidinium Nitrocyanamide at 75°C

W, % weight

liberation of solvent

0.68% per day

Time, min

GNC.XLS
Hydrazinium nitrocyanamide, \([\text{N}_2\text{H}_5][\text{N(NO}_2)(\text{CN})]\)

White, crystalline needles
Melting point: 89° C
DSC: complex decomposition with broad exotherms after melt
Impact sensitivity: 10 kg cm (5 negatives)
Friction sensitivity: 7.8 kg (77 newtons)
Thermal stability at 75° C: < 1% per day
Summary and Conclusions

2-hydroxyethylhydrazine makes an excellent starting material for a new set of energetic salts. The 1:1 salts of 2-hydroxyethylhydrazine have good physical properties, including good densities, liquids at ambient temperatures, and good thermal stabilities at elevated temperatures. These 1:1 salts pass the initial “tough” hurdles required for new candidates and look promising as replacements for hydrazine. The 1:2 salts are impact and friction sensitive, but they may have a future in high explosives work.

Dimethyltriazanium salts were reinvestigated and put through several tests. Although energetic, they have poor thermal stability at elevated temperatures and probably will not make good propellant ingredients.

Simple nitrocyranamide salts are energetic materials, which will require more work. Our initial work with small energetic cations (NH$_4$, N$_2$H$_5$, CH$_3$ONH$_3$), show that these salts are not very stable at elevated temperatures. But, larger cations, such as the guanidinium salt, appear to be more thermally stable, and more work will be put into investigating larger cation based salts.
Acknowledgements

United States Air Force (Funding)

Dr. Suresh Suri

Dr. Pat Carrick

Dr. Jeff Sheehy and Dr. Jerry Boatz

Dr. Steve Rodgers

Dr. Karl Christe and Dr. Bill Wilson

Mr. Paul Jones