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14. ABSTRACT

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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (TI) (STINFO) 04 Dec 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-231**
Hawkins, T., "Advanced Propellants"

Visit by Swedish Diplomats to AFRL **(Statement A)**
(AFRL/Edwards, 05 Dec 2000)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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Comments:____

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PHILIP A. KESSEL Date
Technical Advisor
Propulsion Science and Advanced Concepts Division

ADVANCED PROPELLANTS

5 December 2000

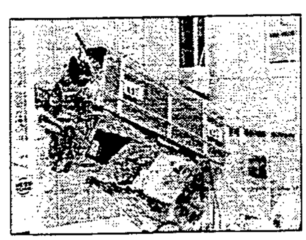
Dr. Tom Hawkins
Sr Research Chemist
Air Force Research Laboratory

Problem

- Low Performance of SOTA Propellant
  - Low D*Isp
- Increased Operations Costs:
  - Carcinogenic Vapor (Respiratory Route)
  - Dermal Toxicity
  - Strong Reducing Agent
  - Flammable (LEL = 4.7%, UEL = 100%)
- On-Orbit Propulsion Systems Affected

System	Mission
FltSatCom	Military Comm
STARDUST	Deep Space Probe
INTELSAT	Commercial Comm
HEAO-B	X-Ray Astronomy

- Hundreds of Satellites Use Hydrazine for RCS & ACS



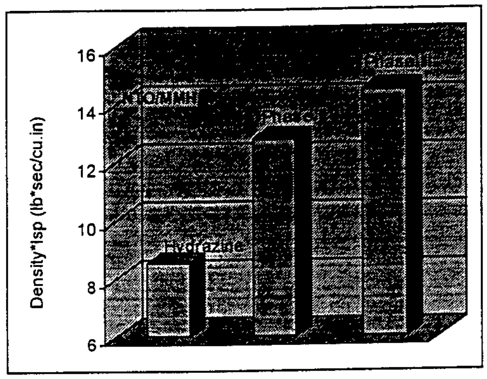
Monopropellant Performance Objectives

- Increase Density Isp of New Monopropellants for IHPRPT Demonstration:

  50% by 2005

  >70% by 2010

- New Monopropellants to Have Reduced Toxicity- Allowing Operations w/o SCAPE-suited Crews



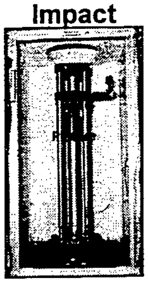
USAF is Lead for IHPRPT Monopropellant Development

Desirable Monopropellant Properties

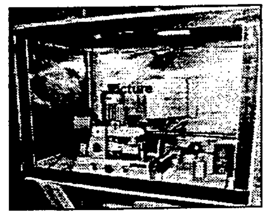
Characteristic	Objective
Density Isp [300 psi-vac; exp=50]	>70 % (Over SOTA)
Vapor Toxicity	Does Not Require SCBA
Carbon Content	No Solid Carbon Forms in Theoretical Exhaust
Melting Point	< 2°C
Detonability [NOL Card Gap]	Class 1.3; (Prefer 24 Cards Maximum (E_{50}))
Impact Sensitivity [Drop Weight]	20 kg-cm Minimum (E_{50})
Adiabatic Compression [U-Tube Test]	No Explosive Decomposition (Pressure Ratio of 35)
Thermal Stability	< 2% by wt. Decomposition for 48 hrs at 75 °C
Critical Diameter	No Propagation in Lines of < 0.75 inch Diameter

Ingredient/Propellant Testing

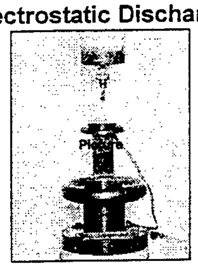
Impact



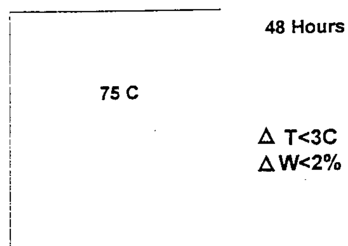
Friction



Electrostatic Discharge



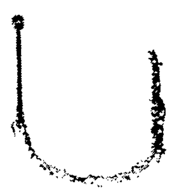
Thermal



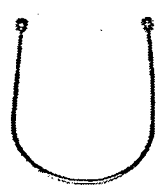
Adiabatic Compressibility

- Designed/Constructed Apparatus in FY00

- Propellant Sensitive to Rapid Compression



- <u>Desired Result</u>: Insensitive to Rapid Compression



Propellant Testing
Shock to Detonation Tests

- All current solid rocket propellants are divided into two hazard classifications (1.1 or 1.3)
- Two tests are used to distinguish between classes 1.1 and 1.3.

Detonation Test

Blasting Cap
Propellant Cube
Lead Cylinder

Dented 1/8" or more is class 1.1

Card Gap Test

Blasting Cap
Explosive Charge
Cards
Propellant
3/8" Steel Plate
Wood Stand

70 (0.7") Cards or more is class 1.1

R&D Strategy For Reduced Toxicity Monopropellants

Technical Challenges

- High Toxicity and Vapor Pressure of N_2H_4 Creates High Costs
- Performance Limited by Low Energy Density (8.4 $lb_f s/in^3$)
  - Need 14.4 $lb_f s/in^3$ by 2010
- Highly Ionic Solutions Tend to Have High Melting Points

Approaches

- Use Ionic Compounds with Extremely Low Vapor Pressures and Structures of Reduced Toxicity versus Hydrazine
- Target Energetic Structures Which Confer High Isp
  - High N Content Cations
  - Anions (e.g., $C(NO_2)_3^-$, NO_3^-, $N(NO_2)_2^-$)
- Employ Miscible and Low Melt Point Components

SAB B2650.ppt

PHASE II Monopropellant

ACCOMPLISHMENT	SIGNIFICANCE
Synthesis/Delivery of 12 high-N salt compounds for additional toxicological screening at AFRL/HEST	•Additional toxicity data on new propellants/compounds •Supports development of QSAR for new propellant molecules' toxicity
Evaluated monopropellant (Swedish Space Corp)	•Has Phase II performance •High solution miscibility temperature with hazardous solid residue
Produced liquid salt-type propellant for successful thruster test	•Catalytic ignition verified •Spurs hardware development •Patent issues being worked

SAB B2650.ppt

Monopropellant Properties

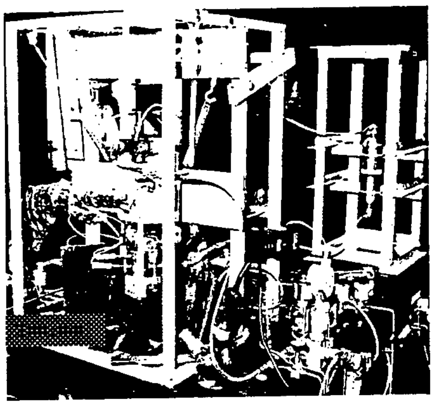
Properties	AFN1	AFN2	Hydrazine
Density, g/cc	1.43	1.46	1.01
Viscosity, cp	8.6	23.1	0.97
Chamber Temp. (Theoretical), K	2070	2083	883
Carbon Content of Exhaust; (b)	none	none	none
Impact Sensitivity*, kg-cm (5 negatives)	>200	60	>200
Friction Sensitivity, N (5 negatives)	318	300	>371
NOL Card Gap (at 69 Cards)	negative	negative	negative
Thermal Stability, %wt loss/48hr,75°C	< 2.0	< 2.0	(< 0.1)
Melt Point, C	5 (c)	<-22	1

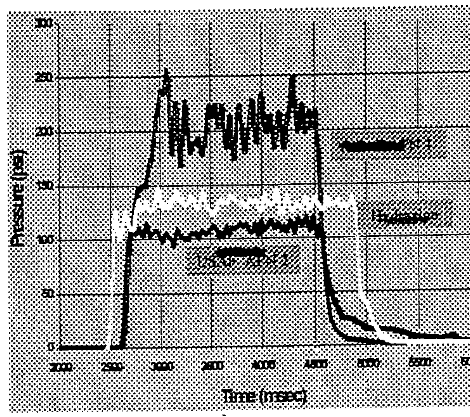
a: Theoretical, calculated with 300psi chamber pressure, exhaust to vacuum, 50/1 expansion
b: as soot or solid carbon (by theoretical computation)
c: by DSC; melt transition was broad, melt peak reported
*: For reference, n-propylnitrate had an impact sensitivity of 8 kg-cm

AFN-Based Propellants Display Acceptable Safety/Sensitivity Properties For Continued Development

Monopropellant Thruster Testing

Monopropellant Thrust Stand





AFRL Fabricated Thruster and Initiated Testing

Catalyst Material Development

Contract Program Objectives

- SELECT CANDIDATE HIGH TEMPERATURE MATERIALS SUITABLE FOR CATALYTIC COMBUSTION OF AFRL MONOPROPELLANT
- MANUFACTURE AND SCREEN CATALYST/THERMAL BED SAMPLES
- EVALUATE PERFORMANCE OF DOWNSELECTED CATALYSTS IN THRUSTER FIRINGS WITH AFRL MONOPROPELLANT

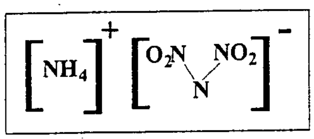
Monolithic Catalyst Bed

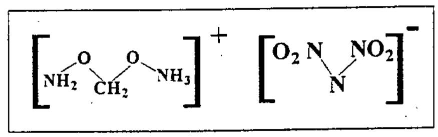
AFRL Collaboration Activity in FY01

- EVALUATES CATALYST MATERIALS
- SUPPLIES PROPELLANT/COMPOUNDS FOR CATALYST EVALUATION

PHASE III MONOPROPELLANT Ingredient R&D

- Synthesizing/Evaluating dinitramide-based salts
- Many such salts (or salt-based monopropellants) exhibit 'challenging' safety properties
  - Performed evaluations with ADN and MBO salts





Methylene bisoxamine $H_2C(\text{-}ONH_2)_2$

Dr. C.S. McDowell et.al. original work published as U.S.patents in 1973, in which the detailed synthesis of MBO selected salts

$CH_3CN + CH_3CH_2\text{-}OH \longrightarrow CH_3C(=NH{\cdot}HCl)OCH_2CH_3$

$CH_3C(=NH{\cdot}HCl)OCH_2CH_3 + H_2N\text{-}OH{\cdot}HCl \longrightarrow CH_3C(=N\text{-}OH)OCH_2CH_3 + NH_4Cl$

$2\ CH_3C(=N\text{-}O^- K^+)OCH_2CH_3 + CH_2Br_2 \longrightarrow [CH_3C(O\text{-}CH_2CH_3)=N\text{-}O]_2\text{-}CH_2 + 2\ KBr$

$[CH_3C(O\text{-}CH_2CH_3)=N\text{-}O]_2\text{-}CH_2 + 2\ HCl(aq) \longrightarrow H_2C(O\text{-}NH_3)_2Cl_2$

$H_2C(O\text{-}NH_3)_2Cl_2 + 2\ KOH \longrightarrow H_2C(O\text{-}NH_2)_2$

MBO bis(dinitramide)
$[H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2$

- Russians apparently synthesized through one or two routes:

- Metathesis with silver salts:

$AgN(NO_2)_2 + H_2C(O\text{-}NH_3)_2Cl_2 \longrightarrow [H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2 + 2\,AgCl$

- Or, ion exhange:

$H_2C(O\text{-}NH_2)_2 + 2\text{ "H-N}(NO_2)_2\text{"} \longrightarrow [H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2$

- Reported (1995) as a colorless oil with a melting point of 20° C.

Dinitramide Salts of MBO

USAF production via cation exchange / neutralization

$H_2C(O\text{-}NH_2)_2 + 2\text{ "H-N}(NO_2)_2\text{"} \longrightarrow [H_2\text{-}C(O\text{-}NH_3)_2][N(NO_2)_2]_2$

<u>Bis-dinitramide Salt:</u>

Appearance: White crystals

M.P. 95° C

Impact: < 5 kg-cm (detonated with a light hammer blow)

DSC Exotherm: 103 °C

<u>Mono-dinitramide Salt:</u>

Appearance: White crystals

M.P. 96° C

Impact: 12 kg-cm (very friction sensitive)

DSC Exotherm: 119 °C

High Performance Monopropellants
-Summary-

- Continue work in monopropellant development & characterization
  - Promising, new approaches
    - Incorporating high energy density molecules
    - Encouraging initial propellant properties
    - Performance potential meets/exceeds bipropellant
      - Simpler, lighter propulsion system
  - Critical work remains
    - Stability, material compatibility, rheology
    - Propellant ignition , high temperature catalyst/materials
      - Teamed with industry

Work with Industry for Successful Technology Demonstration