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<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> Foundation of International Symposium on Special Topics in Chemical Propulsion c/o Prof. Kenneth Kuo 140 Research Building East, Bigler Road University Park, PA 16802	<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>
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<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Office of Naval Research 875 North Randolph Street Arlington, VA 22203-1995	<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>
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Approved for Public Release; distribution is Unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**  
In order to promote technical communication and to encourage further advancements of new energetic materials and chemical propulsion, the International Advisory Committee for the Foundation of International Symposium on Special Topics in Chemical Propulsion conducted the International Symposium on Special Topics in Chemical Propulsion (8-ISICP) in Cape Town, South Africa from November 2-6, 2009. During the 4-day technical program, 79 papers were presented (including 9 Invited Papers) on 18 different topic areas: 1) Nano Technology and Innovative Methods in New Energetic Material Development; 2) Synthesis and Characterization; 3) Formulation, Processing, and Manufacturing; 4) Insensitive Munitions; 5) Hazard Reduction and Safety Aspects; 6) Theoretical Modeling and Numerical Simulation Techniques; 7) Performance Evaluation; 8) Aging, Stability, and Compatibility; 9) Recycling, Disposal, and Environmental Aspects; 10) Test Methods and Diagnostic Techniques; 11) Ignition and Initiation Processes; 12) Detonation and/or Deflagration Processes; 13) Thermobarics and Thermites; 14) Innovative Rocket Propulsion Techniques; 15) Rocket Thermal Protection Materials; 16) Environmentally-Friendly "Green" Propellants; 17) Commercial Applications; and 18) Advanced Propulsion Systems. In addition, 12 posters were presented during a special session. The authors of technical papers were encouraged to submit their final manuscripts to the International Journal of Energetic Materials & Chemical Propulsion for publication by Begell House.

**15. SUBJECT TERMS**  
International Symposium, energetic materials, chemical propulsion, nano technology, synthesis, characterization, formulation, processing, manufacturing, hazard reduction, safety, insensitive munitions, theoretical modeling, numerical simulation, performance, aging, stability, recycling, environmental aspects, diagnostic techniques, ignition and initiation, detonation, deflagration, thermobarics, thermites; thermal protection materials; green propellants; 8-ISICP

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# 8-ISICP

Eighth International Symposium on Special Topics  
in Chemical Propulsion

## ADVANCEMENTS IN ENERGETIC MATERIALS & CHEMICAL PROPULSION

November 2-6, 2009  
Cape Town, South Africa

### Program and Book of Abstracts

Symposium Organizers:

**Prof. Kenneth K. Kuo**  
The Pennsylvania State University  
USA

**Prof. Hansie Knoetze**  
University of Stellenbosch  
South Africa

**Dr. Deon van Zyl**  
Rheinmetall Denel Munition  
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## List of International Advisory Committee (IAC) Members for 8-ISICP

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Prof. S. Krishnan <sup>6,8,9</sup>	India		
Dr. Naminosuke Kubota <sup>6,5</sup>	Japan		
Prof. Kenneth K. Kuo <sup>9,8,6</sup>	USA		

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**Topic Areas**

- (1) Reaction Kinetics of Energetic Materials (Solid, Liquid, Hybrid, and Gel Propellants)
- (2) Environmental Considerations in Combustion of Energetic Materials
- (3) Commercial Applications of Energetic Materials (Airbags, Gas Generators, etc.)
- (4) Recycling of Energetic Materials
- (5) Safety and Hazards Considerations in Combustion of Energetic Materials
- (6) Ignition and Combustion of Propellants for Space and Rocket Propulsion
- (7) Pyrolysis and Combustion Processes of New Ingredients
- (8) Theoretical Modeling and Numerical Simulation of Combustion Processes of Energetic Materials
- (9) Combustion Diagnostic Techniques
- (10) Thermal Insulation and High-Temperature Material Ablation Processes

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**Defense Threat Reduction Agency**



**Office of Naval Research,  
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**European Office of  
Aerospace and Development**



**The Pennsylvania State  
University**



**University of  
Stellenbosch**

**"We wish to thank the following organizations for their contribution to the success of this conference:**

**Office of Naval Research, US Navy**

**US Army Research Office**

**European Office of Aerospace Research and Development, Air Force Office of Scientific Research, United States Air Force Research Laboratory <<http://www.london.af.mil>>."**

**Rheinmetall Denel Munitions and Rheinmetall Defence**

**US Defence Threat Deduction Agency**

**The Pennsylvania State University**

**University of Stellenbosch**

# General Information

## **Badges**

Your identification badges must be worn at all times in order to have access to symposium sessions.

## **Dress code**

Business Casual for all events.

## **Official Language**

The official language of the conference is English.

## **Oral Presentations**

Authors of oral presentations are requested to arrive at the assigned session room 20 minutes prior to the start of the session in order to meet the session chairperson and prepare for presentation.

Visual equipment in session rooms are Data Projector and PC (Microsoft Office 2007, Microsoft Vista and Microsoft Powerpoint). Bring your presentation file in USB memory stick or CD and install the file in the PC. Apple Mac is not available.

## **Poster Presentations**

Poster papers will be displayed in Meeting Room 2.65 – 2.66 on Wednesday 4 Nov. from 8:30 till 17:00. The room will be available from 8:00 for mounting and exhibiting purposes.

## **Contacts and Opening Hours**

### **Registration Desk: Jasminium Restaurant**

You can pick up your name badge and symposium documents at our registration desk on site during the following hours:

Monday 2 Nov. 15:00 – 18:00

### **Sight-seeing Tour Desk**

In Jasminium restaurant Monday 2 Nov. 15:00 – 18:00

### **General Information Desk**

Meeting Room 2.64

Tuesday 3 Nov. – Thursday 5 Nov. 8:00 – 17:00

## **Social Events**

### **Welcome reception: Clivia Restaurant**

Delegates, students and registered accompanying persons are invited to attend the Welcome Reception at the Clivia Restaurant.

Monday 2 Nov. 18:00 – 20:00

### **Coffee and Tea Breaks**

Tuesday to Thursday at 10:15 to 10:30 and 15:25 to 15:45 in Terrace Room.

### **Lunch**

Will be served from Tuesday to Thursday for delegates in Jasminium restaurant from 12:40 to 14:00.

### **Gala Dinner**

Thursday 5 Nov. at Moyo Restaurant (African Theme) on Spier Wine Estate near Stellenbosch (about 45 km from Cape Town) for delegates and registered accompanying persons. Buses will depart from the main entrance of the Conference Centre (CTICC) at 18:15.

### **Tour and Excursion**

Friday 6 Nov. – 7:30 – 18:00

Buses will depart from the Conference Centre (CTICC).

A tour around the Cape Peninsula including a visit to Cape Point, the Winelands near Stellenbosch with lunch at the Neethlingshof Wine Estate ending with a visit to the Cheetah Outreach as well as the Eagle Encounters at the Spier Estate.

**Medical Care**

Medical care is available in a Medi-Clinic private consulting room from 8:00 – 17:00 every day on Ground Floor of Conference Centre.

**Lockers**

Available on Ground floor of Conference Centre for your own account.

**Parking**

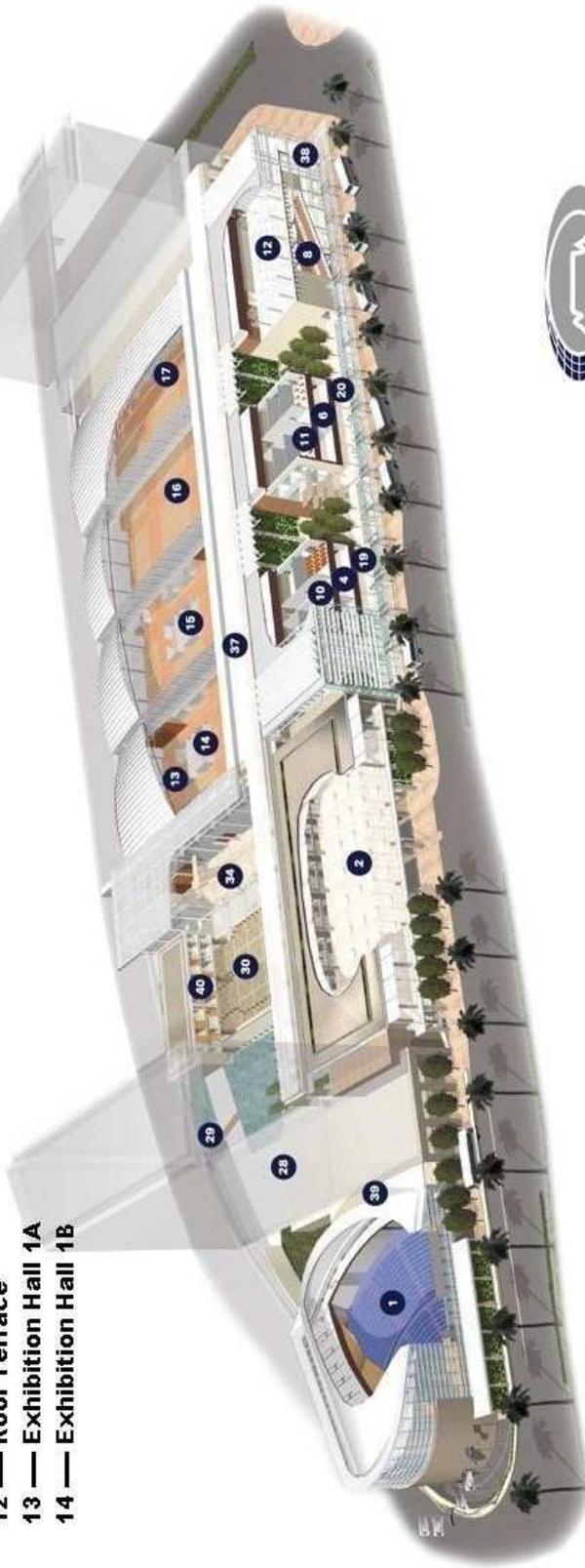
Parking available for delegates at the Conference Centre. Free parking tickets will be available daily at the General Information Desk.

**Safety and Security**

Cape Town is an international city and a very popular international tourist destination. As such, the city authorities have put a host of safety and security measure in place to ensure the well-being of its visitors. The CTICC also has a highly visible 24-hour security presence to ensure the peace of mind of all its visitors. Of course, as an international city, it is advisable for a visitor to Cape Town, and any other international city, to be aware of his or her security at all times and to consider common-sense personal safety precautions.

## Floor plan – Conference Centre

- |                          |                                  |  |
|--------------------------|----------------------------------|--|
| 1 — Auditorium I         | 15 — Exhibition Hall 2           | 30 — Convention Square & Main Entrance       |
| 2 — Ballroom East / West | 16 — Exhibition Hall 3           | 34 — Main Foyer, Lounge & Business Centre    |
| 4 — Room 1.40            | 17 — Exhibition Hall 4           | 37 — Gallery Walkway                         |
| 6 — Room 1.60            | 19 — Jasmine Restaurant          | 38 — Marimba 200 seat Al La Carte Restaurant |
| 10 — Room 2.40           | 20 — Strelitzia Restaurant       | 39 — Auditorium I Foyer                      |
| 11 — Room 2.60           | 28 — Arabella Sheraton Hotel     | 40 — Management Offices                      |
| 8 — Auditorium II        | 29 — Canal Head & Ferry Terminal |  |
| 12 — Roof Terrace        |                                  |  |
| 13 — Exhibition Hall 1A  |                                  |  |
| 14 — Exhibition Hall 1B  |                                  |  |

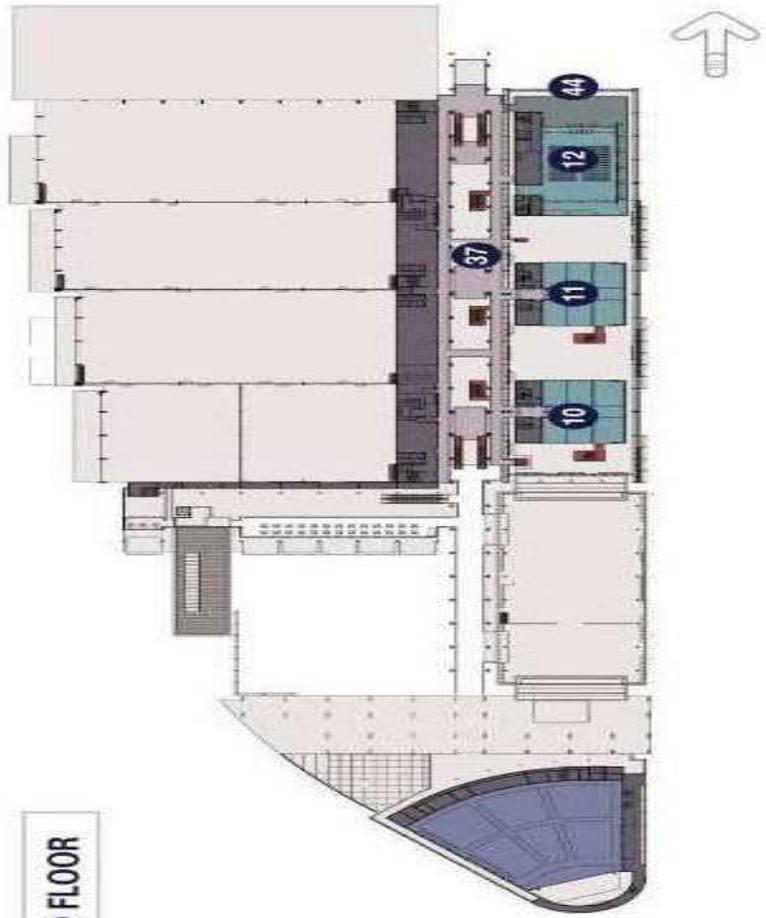


**CAPE TOWN**  
INTERNATIONAL CONVENTION CENTRE

## Ground Floor – Conference Centre



## Second Floor



### SECOND FLOOR

- 10-11 Meeting Rooms
- 12 Roof Terrace Room
- 37 The Gallery
- 44 Roof Terrace

# Practical Information

## VENUE

Cape Town International Conference Centre (CTICC)  
 Convention Square, 1 Lower Long Street, Cape Town 8001  
 South Africa

Phone: +27 21 410 5000

Fax: +27 21 410 5001

e-mail: [info@cticc.co.za](mailto:info@cticc.co.za)

Website: [www.capetownconvention.com](http://www.capetownconvention.com)



# HOTELS

## CIRCA

5 min. walk form Conference Centre

**15 Anton Anreith Square**

**Cape Town**

**Tel: +27(0)21-410 4000**

**Fax: +27(0)86-616 0714**

**E-mail: [anjad@urbanhiphotels.com](mailto:anjad@urbanhiphotels.com)**



# ICON

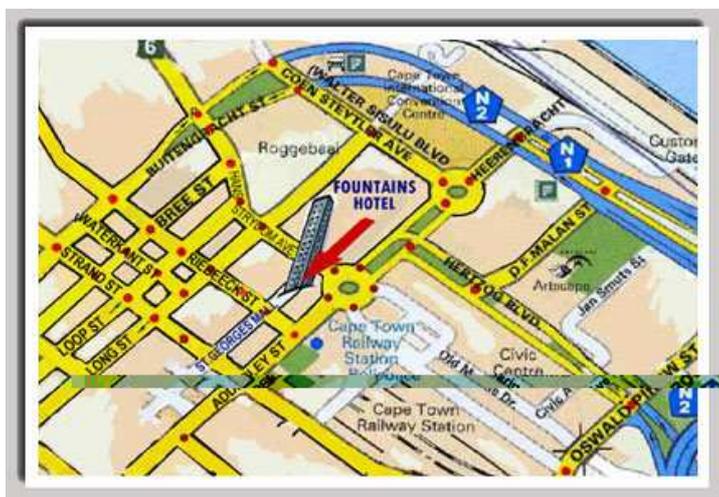
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Foreshore  
Cape Town**

**Tel:** +27(0)21-421 4434  
**Fax:** +27 (0)21-86 608 7226  
**E-mail:** [cornes@urbanhiphotels.com](mailto:cornes@urbanhiphotels.com)



## FOUNTAINS HOTEL

**1 St Georges Mall**  
**Tel: +27 (0) 21 - 443 1100**  
**Fax: +27 (0) 21 - 425 6070**  
**E-mail: [reserve@fountainhotel.co.za](mailto:reserve@fountainhotel.co.za)**



## WESTIN GRAND



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**Cape Town**  
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**E-mail: [westin.grand.capetown@arabellastarwood.co.za](mailto:westin.grand.capetown@arabellastarwood.co.za)**

## **City Transportation**

There is much to see around Cape Town, from the spectacular Atlantic coastline, to the coastal villages of False Bay, the beautiful wine route and the rugged west coast. The peninsula spreads out over a vast area - the distance from Simon's Town in the south, to Bloubergstrand in the north is close to 100 km. A car is probably essential for getting to the less accessible areas.

### **By Car**

A valid driver's licence and minimum age of 21 or 25 are generally required in order to hire a car. All the major car rental companies have branches in Cape Town. Most will drop off and collect rental vehicles at your hotel. Car rentals are also available at the airport. For more information on rental cars ask at the reception desk of your hotel.

### **Public Transport**

Public transport is available with a scheduled bus service covering some areas, and the city is linked by a comprehensive suburban rail network to the outlying suburbs. However, public transport in South Africa is not always dependable. Do not use it if you are alone or if you are uncertain of where you are going.

### **Taxi Cabs**

Taxi cabs are another option, and are specially recommended at night. Although you can't hail a taxi New York-style on the streets of Cape Town, they can be hired at taxi ranks or ordered by phone through one of the many taxi companies. Not cheap, but definitely the safest bet, the average charge is about R4.50 per km.

### **Shuttle Services**

Numerous tour and transport companies offer shuttle services to and from the airport, as well as to other destinations around the city. Although this means less responsibility than would be the case with a hired car, there is slightly less flexibility, but at least you won't have to be concerned with navigating your way around the city.

### **On Foot**

In the city centre you'll find walking a most pleasant way to get around, roaming the many curio and antique markets, or strolling through the city's oak-lined Company Gardens, en route to the National Gallery or Natural History Museum, are popular with both visitors and residents. For those with energy, or whose schedules are not too hectic, Cape Town is best explored on foot, preferably during daytime.

## Time Difference

South Africa does not crossover any time zones and does not incorporate summer time. The time difference between South Africa and major world cities is given below.

Europe	North America	Asia, Near & Middle East
Athens: 0h	Chicago: - 8h	Beijing: + 6h
Frankfurt: - 1h	Los Angeles: - 10h	Hong Kong: + 6h
London: - 2h	New York: - 7h	Jerusalem: 0h
Moscow: + 2h	San Francisco: - 10h	Seoul: +7h
Paris: - 1h	Toronto: - 7h	Taipei: + 6h
Rome: - 1h	Washington DC: - 7h	

**Example:** London is 2 hours behind South Africa. When South Africa is 12:00 on November 3, London will be 10:00 on November 3.

## Money

### Currency

Rand (ZAR; symbol R) = 100 cents. Notes are in denominations of R200, 100, 50, 20 and 10. Coins are in denominations of R5, 2 and 1, and 50, 20, 10 and 5 cents.

### Currency Exchange

Money can be changed at banks, bureaux de change and some hotels. Proof of identity may be requested; therefore, it is advisable to carry a passport. Visitors are restricted to bringing in and taking out a maximum of R5 000 in cash.

### Credit/Debit Cards and ATMs

MasterCard and Visa are preferred. American Express and Diners Club are also widely accepted. ATM's are available all over the towns and cities including shopping malls and petrol stations, and accept all international debit and credit cards. Almost all hotels, shops and restaurants, and even national parks and game reserves, accept credit cards. Credit and debit cards are not always accepted at petrol stations, however, especially outside the big cities.

### Traveller's Cheques

Traveller's cheques are accepted by most banks, hotels, and some tourist-orientated shops and restaurants. To avoid additional exchange rate charges, travellers are advised to take traveller's cheques in Pounds Sterling or US Dollars.

## **Currency Restrictions**

Restrictions apply.

## **Banking Hours**

Normal banking hours are: Mon-Fri 09:00-15:30, Sat 08:30-11:00.

## **Exchange Rate Indicators**

1.00 GBP = 12.33 ZAR

1.00 USD = 7.73 ZAR

1.00 EUR = 11.31 ZAR

Currency conversion rates as of 6 October 2009

## **Tips**

Good service is usually rewarded with a tip of about 10% in restaurants – some restaurants add it automatically. Check your bill whether it has been added or not.

## **Business Hours**

There are no fixed business hours in South Africa. Most shops will be open between 9:00 and 17:00, but in certain shopping malls the shops stay open until 21:00. Most government offices are open between 9:00 and 16:30 on weekdays and closed on weekends. ATM's are open 24h per day, 7 days a week. Most gasoline stations have convenience stores that are open 24h.

## **Communication**

South Africa has 11 official languages – with Zulu, isiXhosa and Afrikaans the predominant first languages. However, most people in South Africa can speak and understand English and English is the language usually used in business. In some tourist shops the staff would be able to serve you in German.

Public pay phones are available, but they are becoming less prominent with the increasing spread of mobile phones. Some of them work with coins but most work with telephone cards (available at post offices, Telkom offices and some vending machines).

Mobile phones of most other countries will be compatible with the South African system. Local mobile phones can be rented at airports.

Internet connections are available at internet cafes and most hotels offer internet connections.

## Emergencies

During normal conference hours there is medical care available at the Medi-Clinic room on the bottom floor. For all other cases the following numbers could be helpful:

### Cell Phone Customer Care

Cell C - 084	021 935 7000
MTN - 083 & 073	021 401 7200
Vodacom - 082 & 072	080 011 1234

### Directory inquiries

Local numbers	1023
International numbers	1903

### Emergency numbers

Any Emergency - from Telkom landline	107
Any Emergency - from Cell phone	112
Ambulance	10177
Automobile Association Rescue	080 001 0101
Fire - Residential & Mountain	021 535 1100
Flying Squad - Police	10111
Lifeline	021 461 1111
Mountain Rescue	021 948 9900
Tourist Assistance - Police	021 418 2852
Cape Town International Airport	021 937 1200

### Hospitals

Chris Barnard Memorial Hospital	021 480 6111
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## Voltage

Electricity in South Africa is 230 Volts, alternating at 50 cycles per second. If you travel to South Africa with a device that does not accept 230 Volts at 50 Hertz, you will need a voltage converter. Some hotels have a special 110V outlet for razors. You will probably also need an electrical plug adapter.

**THE EIGHTEEN (18) DIFFERENT AREAS COVERED IN THIS SYMPOSIUM AND THE INTERNATIONAL JOURNAL OF ENERGETIC MATERIALS AND CHEMICAL PROPULSION (IJEMCP):**

1. Nano Technology and Innovative Methods in New Energetic Material Development;
2. Synthesis & Characterization of Energetic Materials;
3. Formulation, Processing, and Manufacturing of Energetic Materials;
4. Insensitive Munitions;
5. Hazard Reduction and Safety Aspects;
6. Theoretical Modeling and Numerical Simulation Techniques for Propellants, Combustion, and Chemical Propulsion Topics;
7. Performance Evaluation of Propellants, Pyrotechnics, and Explosives;
8. Aging, Stability, and Compatibility;
9. Recycling, Disposal, and Environmental Aspects;
10. Test Methods and Diagnostic Techniques in Chemical Propulsion and/or Combustion of Energetic Materials;
11. Ignition and Initiation Processes;
12. Detonation and/or Deflagration Processes;
13. Thermobarics and Thermites;
14. Innovative Rocket Propulsion Techniques;
15. Rocket Thermal Protection Materials;
16. Environmentally-Friendly "Green" Propellants;
17. Commercial Applications of Energetic Materials; and
18. Advanced Propulsion Systems (e.g., Pulse Detonation Engines, Hybrid Rockets, Gel Propellants, Micro Propulsion, Ramjets, Scramjets, etc.).

# **Eighth International Symposium on Special Topics in Chemical Propulsion (8-ISICP)**

## **TECHNICAL PROGRAM** **“Advancements in Energetic Materials & Chemical Propulsion”**

**November 2-6, 2009**

### **Cape Town International Convention Centre (CTICC)**

Convention Square, 1 Lower Long Street, Cape Town, 8001, South Africa

Phone: 27-21-410-5000, Fax: 27-21-410-5001

<b>Monday, November 2, 2009</b>	
15:00 18:00	<b>On-Site Registration &amp; Check-In</b>  <b>Clivia Conservatory &amp; Jasminium Restaurant</b>
18:00 20:00	<b>Welcome Reception</b>  <b>Clivia Conservatory &amp; Jasminium Restaurant</b>

Tuesday Morning, November 3, 2009			
8:30	<b>Roof Terrace Room</b>	<b>SYMPOSIUM OPENING – Prof. Kenneth K. Kuo, Prof. Hansie Knoetze, and Dr. Deon van Zyl</b>	
8:50 9:35	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b>	<b>Prof. Charles Kappenstein of the University of Poitiers, France</b> <b>“Propulsion and Catalysis - Historical Survey, up-to-date Overview and Current Challenges” (Log #181)</b> <i>Session Chair: Prof. Kenneth K. Kuo</i>	
	<b>Roof Terrace Room (Session 1)</b>	<b>Room 2.61-2.63 (Session 2)</b>	<b>Room 2.65-2.66 (Session 3)</b>
	<b>Nano-Technology &amp; Innovative Methods in Energetic Material Development</b> <b>Topic 1</b> <i>Co-Chairs: Prof. C. Kappenstein &amp; Dr. B. Tappan</i>	<b>Ignition and Initiation Processes</b> <b>Topic 11</b> <i>Co-Chairs: Drs. P. Nel &amp; A. Atwood</i>	<b>Theoretical Modeling &amp; Numerical Simulation for Chemical Propulsion Topics</b> <b>Topic 6</b> <i>Co-Chairs: Prof. M.C. Lin &amp; Dr. J.E. Boyer</i>
9:35 9:55	<b>Development of Metallic Nanoparticles Based Energetic Materials: A Review</b> (Log #130) <i>P. Joulain, V. An, and H. El-Rabii</i>	<b>Design of a Modular Test Chamber for the Analysis of Flame Spreading Rates, Black Powder Jet Penetration, and Vent-Hole Geometry into a Granular Bed</b> (Log #173) <i>A. Colletti, E. Boyer, K.K. Kuo, and R. Acharya</i>	<b>A Creation of Propellant Combustion Models by Means of Data Mining Tools</b> (Log #118) <i>V.S. Abrukov, K.K. Riskov, and V.A. Shushkanov</i>
9:55 10:15	<b>Nano-RDX Synthesis by RESS Process and Sensitivity Characterization</b> (Log #149) <i>A. Cortopassi, T. Wawiernia, J. Essel, P. Ferrara, K.K. Kuo, and R.M. Doherty</i>	<b>Radiative Ignition of Solid Propellants</b> (Log #151) <i>F. Cauty, Y. Fabignon, and C. Eradès</i>	<b>Mathematical Modeling of Alpha-Iron Coated Pyrophoric Substrates</b> (Log #188) <i>J.A. Puszynski, Z. Doorenbos, D. Kapoor, and C. Haines</i>
10:15	<b>Roof Terrace Foyer</b>	<b>COFFEE BREAK</b>	
10:35 11:20	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b>	<b>Prof. Thomas Klapötke of the Ludwig-Maximilians-University of Munich, Germany</b> <b>“High-Nitrogen and High-Oxygen Explosives as Possible Replacements for RDX” (Log #102)</b> <i>Session Chair: Prof. Hansie Knoetze</i>	
	<b>Roof Terrace Room (Session 4)</b>	<b>Room 2.61-2.63 (Session 5)</b>	<b>Room 2.65-2.66 (Session 6)</b>
	<b>Nano-Technology &amp; Innovative Methods in Energetic Material Development</b> <b>Topic 1</b> <i>Co-Chairs: Drs. R. Caro &amp; D. Chavez</i>	<b>Ignition and Initiation Processes</b> <b>Topic 11</b> <i>Co-Chairs: Drs. A. Peretz &amp; A. Atwood</i>	<b>Theoretical Modeling &amp; Numerical Simulation for Chemical Propulsion Topics</b> <b>Topic 6</b> <i>Co-Chairs: Profs. J.A. Puszynski &amp; R.A. Yetter</i>
11:20 11:40	<b>Improved Munitions Development by Novel Techniques</b> (Log #209) <i>J.H.G. Scholtes, W.P.C. de Klerk, C.A. van Driel, and M. Zebregs</i>	<b>Improvement of a Turbine Engine Start by an External Oxygen-Rich Gas Generator</b> (Log #109) <i>A. Peretz, S. Khosid, and A.H. Gross</i>	<b>Dynamical Simulation of Burnt Zone of Metallized Composite Propellants</b> (Log #162) <i>S. Rashkovskiy</i>
11:40 12:00	<b>Synthesis and Characterization of Coated Energetic Materials Using a RESS System</b> (Log #137) <i>J. Essel, A. Cortopassi, and K.K. Kuo</i>	<b>Convective Burning Studies of Pyrotechnic Powders</b> (Log #145) <i>A.I. Atwood, P.O. Curran, K. P. Ford, J.F. Moxnes, and G. Odegardstuen</i>	<b>Modeling of Self-Ignition, Structure and Velocity of Free Propagation Flame of Hydrogen Azide</b> (Log #166) <i>O.P. Korobeinichev, N.V. Budachov, A.A. Paletsky, T.A. Bolshova, and V.D. Knyazev</i>
12:00 12:20	<b>Application of Nanometer Materials for Propellants, Pyrotechnics and Explosives</b> (Log #178) <i>F. Li, X. Guo, W. Jiang, L. Liu, Z. Ma, and W. Chen</i>	<b>Suppression of Dust Explosions by Means of Active Super Fast Explosion Suppression System of 5 Litres Volume</b> (Log #180) <i>M. Gieras, M. Kaluzny, and R. Klemens</i>	<b>Factors affecting Combustion Behaviour of Metal Powder in Fuel Rich Propellants of Ramjet Rockets : A Fresh Look</b> (Log #119) <i>H. Shekhar and H. Singh</i>
12:20 12:40	<b>Mutual Influence of Nanometal Additives on Heat Release Rate in Condensed Systems</b> (Log #110) <i>V.F. Komarov, G. V. Sakovich, A.B. Vorozhtsov, A.G. Vakutin, M. V. Komarova</i>	<b>Internal Ballistic Simulation of a 40mm Round</b> (Log #194) <i>J. Kriel, C. Muller, V. Schabort, and J. Goosen</i>	
12:40	<b>Clivia Conservatory &amp; Jasminium Restaurant</b>	<b>LUNCH</b>	

Tuesday Afternoon, November 3, 2009			
14:00 14:45	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b> Prof. Valery Sinditskii of the Mendeleev University of Chemical Technology, Russia “Combustion of Energetic Materials Governed by the Reactions in the Condensed Phase” (Log #106)		<i>Session Chair: Prof. Kenneth K. Kuo</i>
14:45	<b>Roof Terrace Room (Session 7)</b>	<b>Room 2.61-2.63 (Session 8)</b>	<b>Room 2.65-2.66 (Session 9)</b>
	<b>Nano-Technology &amp; Innovative Methods in Energetic Material Development <u>Topic 1</u></b> <i>Co-Chairs: Profs. V. Sinditskii &amp; L. DeLuca</i>	<b>Performance Evaluation of Propellants <u>Topic 7</u></b> <i>Co-Chairs: Profs. T. Klapötke &amp; A. Gany</i>	<b>Theoretical Modeling &amp; Numerical Simulation of Nozzle Erosion <u>Topic 6</u></b> <i>Co-Chairs: Dr. C Bedford &amp; Prof H. Knoetze</i>
14:45 15:05	<b>High-Nitrogen-Metal Complexes As Burning-Rate Modifiers For The Aluminum-Water Propellant System (Log #215)</b> <i>B.C. Tappan and B.A. Mason</i>	<b>Thermal Decomposition Behaviour of Ammonium Nitrate and Carbon Mixtures (Log #168)</b> <i>A. Miyake and Y. Izato</i>	<b>Effect of Reaction Kinetic Schemes on Graphite Rocket Nozzle Erosion Rates (Log #142)</b> <i>R. Acharya and K.K. Kuo</i>
15:05 15:25	<b>Combustion of Bimodal Al and Ice Mixtures (Log #216)</b> <i>T.L. Connell, Jr., G.A. Risha, R.A. Yetter, S.F. Son, and V. Yang</i>	<b>Combustion Characteristics of HAN Solutions (Log #169)</b> <i>T. Katsumi, R. Matsuda, T. Inoue, H. Ogawa, N. Tsuboi, and K. Hori</i>	<b>Coupling of Transient Heating and Induced Stresses Computations in Graphite Nozzle Materials (Log #150)</b> <i>R. Acharya, B. Evans, J. Pitt, F. Costanzo, and K.K. Kuo</i>
15:25	<b>Roof Terrace Foyer</b> <b>COFFEE BREAK</b>		
15:45	<b>Roof Terrace Room (Session 10)</b>	<b>Room 2.61-2.63 (Session 11)</b>	<b>Room 2.65-2.66 (Session 12)</b>
	<b>Synthesis &amp; Characterization of Energetic Materials <u>Topic 2</u></b> <i>Co-Chairs: Prof. L. DeLuca &amp; Mr B. Kosowski</i>	<b>Performance Evaluation of Propellants <u>Topic 7</u></b> <i>Co-Chairs: Profs. T. Klapötke &amp; A. Gany</i>	<b>Theoretical Modeling &amp; Numerical Simulation for Chemical Propulsion Topics <u>Topic 6</u></b> <i>Co-Chairs: Dr. C. Bedford &amp; Prof H. Knoetze</i>
15:45 16:05	<b>Compatibility of Ammonium Dinitramide (ADN) with Polymeric Binders Studied by Thermoanalytical Methods (Log #175)</b> <i>G. Santhosh and H.G. Ang</i>	<b>Reduced Agglomeration Resulting from Nickel Coating of Aluminum Particles in Solid Propellants (Log #160)</b> <i>Y. Yavor, V. Rosenband, and A. Gany</i>	<b>First-Principles Study of Water Effect on the Sublimation of Ammonium Perchlorate (Log #174)</b> <i>R. Zhu and M.C. Lin</i>
16:05 16:25	<b>Boron-rich Fuels for Gas Generators and Propellants (Log #208)</b> <i>R.J. Pontes Lima, C. Dubois, O. Mader, R. Stowe, and S. Ringuette</i>	<b>Ballistics of Metallized Solid Rocket Propellants (Log #200)</b> <i>L.T. DeLuca, E. Marchesi, M. Spreafico, A. Bandera, F. Maggi and B.M. Kosowski</i>	<b>Numerical Calculations Predicting Solid Propellant Ingredient Interactions (Log #131)</b> <i>M. Gross and M. Beckstead</i>
16:25 16:45	<b>Characterization and Comparison of Two HTPE Pre-polymers (Log #172)</b> <i>R. Caro and J.M. Bellerby</i>	<b>On the Influence of Microstructure of Heterogeneous Explosive Materials on Their Detonation Behaviour (Log #203)</b> <i>S.A. Kolesnikov, A.V. Ananin, V.M. Mochalova, A.V. Utkin</i>	<b>Mechanical Properties of Composite Propellants and Effect of Propellant Stretch on Its Burn Rate (Log #163)</b> <i>S. Rashkovskiy, A.V. Fedorychev, Y.M. Milyokhin and A.N. Klyuchnikov</i>
16:45 17:05	<b>Controlled Synthesis of Nitrogen-Doped Carbon Nanotubes for Nanoscale Ems (Log #129)</b> <i>H. Liu, H. Abou-Rachid, Y. Zhang, Y. Zhong, M. Ionescu, R. Li, A.X. Sun, and L. Lussier</i>	<b>The Influence of Spherical Granular Propellants on the Combustion Properties of High-Burning-Rate Propellant (Log #179)</b> <i>X. Guo, F. Li, W. Jiang, and L. Zhao</i>	<b>Excitation of Hydrodynamic Micro-Structures During Energetic Materials Unsteady Combustion and Phenomenon of Waves of Negative Erosion (Log #120)</b> <i>A. Lukin</i>
17:05 17:25		<b>Temperature Insensitive Propulsion System (TIPS®) based on SCDB® Propellant and new CCC Design of Cartridge 120mmx570 DM63 (Log #123)</b> <i>K. Kratzsch and A. Huber</i>	

Wednesday Morning, November 4, 2009			
8:30 9:15	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b> <b>Dr. Fred Blomshield of the Naval Air Warfare Center, China Lake, California</b> "Pressure Coupled Response of Solid Propellants" (Log #184)		<i>Session Chair: Dr. R.H. Woodward Waesche</i>
	<b>Roof Terrace Room (Session 13)</b> <b>Synthesis &amp; Characterization of Energetic Materials</b> <b>Topic 2</b> <i>Co-Chairs: Dr. G. Ampleman &amp; Prof. O.P. Korobeinichev</i>	<b>Room 2.61-2.63 (Session 14)</b> <b>Performance Evaluation of Propellants Burning Under Pressure Oscillations</b> <b>Topic 7</b> <i>Co-Chairs: Drs. F. Blomshield &amp; L. Galfetti</i>	<b>Room 2.65-2.66</b>
9:15 9:35	<b>Synthesis and Combustion Characteristics of Novel High Nitrogen Materials</b> (Log #214) <i>D.E. Chavez and B.C. Tappan</i>	<b>Mechanisms and Methods of Suppression of Combustion Instability</b> (Log #219) <i>R.H.W. Waesche</i>	Poster Preparation
9:35 9:55	<b>Reductive Debenzylation of 2,4,6,8,10,12-hexaazaisowurtzitane</b> (Log #126) <i>S.V. Sysolyatin, A.I. Kalashnikov, G.V. Sakovich, I.A. Surmacheva, V.N. Surmachev, and V.V. Malykhin</i>	<b>Improving the Method for Determination of an Admittance Function from Pulsed Tubular Grain Motor Tests</b> (Log #198) <i>W. Rousseau and H. Knoetze</i>	
9:55 10:15		<b>Burning Behaviour of Nitramine Gun Propellants Influenced by Pressure Oscillations</b> (Log #167) <i>G. Pauly and R. Scheibel</i>	
10:15	<b>Roof Terrace Foyer</b> <b>COFFEE BREAK</b>		
10:35 11:20	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b> <b>Prof. Bo Janzon of SECRA Security Research, Sweden</b> "Recent Advances in Energetic Materials in Sweden, Especially at the FOI" (Log #135)		<i>Session Chair: Prof. Kenneth K. Kuo</i>
	<b>Roof Terrace Room (Session 15)</b> <b>Recycling, Disposal, and Environmental Aspects</b> <b>Topic 9</b> <i>Co-Chairs: Prof. B. Janzon &amp; Dr. G. Ampleman</i>	<b>Room 2.61-2.63 (Session 16)</b> <b>Performance Evaluation of Explosives</b> <b>Topic 7</b> <i>Co-Chairs: Drs. F. Blomshield &amp; E.L. Baker</i>	<b>Room 2.65-2.66</b>
11:20 11:40	<b>Less Sensitive and "Green" Propellant</b> (Log #213) <i>C.F. Wiehahn</i>	<b>Combined Effects Aluminized Explosives</b> (Log #114) <i>S. Nicolich, L.I. Stiel, W. Balas, C. Capellos, and J. Pincay</i>	Poster Preparation
11:40 12:00	<b>Fate and Behavior of Propellant Residues in Water of the Unsaturated Zone under an Anti-Tank Firing Position</b> (Log #183) <i>R. Martel, A. Bellavance Godin, G. Ampleman, S. Thiboutot, and L. Trépanier</i>	<b>Development, Optimization and Application of Combined Effects Explosives</b> (Log #112) <i>W. Balas, E.L. Baker, J. Pincay, S. Nicolich, and L.I. Stiel</i>	
12:00 12:20		<b>Formic Acid Investigation for the Prediction of High Explosive Detonation Properties and Performance</b> (Log #132) <i>E.L. Baker, L.I. Stiel, C. Cappellos, B.M. Rice, S.W. Bunte, and E.F.C. Byrd</i>	
12:40	<b>Clivia Conservatory &amp; Jasminium Restaurant</b> <b>LUNCH</b>		
Wednesday Afternoon, November 4, 2009			

14:00	<b>8-ISICP Invited Plenary Lecture</b>	<i>Session Chair: Prof. Hansie Knoetze</i>
14:45	<b><u>Roof Terrace Room</u></b>	<b>Dr. Guy Ampleman of Defense Research and Development Valcartier, Canada</b> <b>“Development of a New Generation of Insensitive Explosives and Gun Propellants” (Log #105)</b>
	<b><u>Roof Terrace Room</u></b>	<b>Poster Snapshot Session</b> <i>Co-Chairs: Prof. H. Knoetze &amp; Dr. D. van Zyl</i>
14:45	Each Poster Presenter have 2 minutes to make a brief presentation to highlight his/her paper. There will be no time allowed for questions. Questions can be asked to the Poster Presenters during the Poster Session. The poster snapshot presentations will be made in the same chronological order as indicated in the list of poster presentations on pages 30 & 31.	
15:45		
15:45	<b><u>Roof Terrace Foyer</u></b>	<b>COFFEE BREAK</b>
16:05		
	<b><u>Room 265-266</u></b>	<b>Poster Session</b> <i>Co-Chairs: Prof. H. Knoetze &amp; Dr. D. van Zyl</i>
16:05	See list of poster presentations on pages 8 & 9	
17:00		
18:30	<b>Bus departs from CTICC for Chairman’s Dinner</b>	
19:00	<b>Chairman’s Dinner at On the Rocks Restaurant, Bloubergstrand</b>	

Thursday Morning, November 5, 2009			
8:30 9:15	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b>		<i>Session Chair: Prof. Kenneth K. Kuo</i>
<b>Prof. Brian Cantwell of Stanford University, Palo Alto, California</b> <b>“Modern Developments in Hybrid Propulsion” (Log #182)</b>			
	<b>Roof Terrace Room (Session 17)</b>	<b>Room 2.61-2.63 (Session 18)</b>	<b>Room 2.65-2.66 (Session 19)</b>
	<b>Hybrid Rocket Propulsion Techniques <u>Topic 14</u></b> <i>Co-Chairs:</i> <i>Prof. B. Cantwell &amp; Dr. J.E. Boyer</i>	<b>Rocket Thermal Protection Materials <u>Topic 15</u></b> <i>Co-Chairs:</i> <i>Dr. D. van Zyl &amp; Mr. F. Cauty</i>	<b>Test Methods &amp; Diagnostic Techniques in Chemical Propulsion &amp; Energetic Materials <u>Topic 10</u></b> <i>Co-Chairs: Drs. F. Mostert &amp; Prof. M.R. Zachariah</i>
9:15 9:35	<b>Fuel Regression Rate Behavior in Swirling-Oxidizer-Flow-Type Hybrid Rocket Engines (Log #143)</b> <i>S. Yuasa, M. Sakamoto, C. Sezaki, T. Sakurai, N. Shiraishi, and T. Shimada</i>	<b>Determination of Total Surface Heat Flux to Thermal Protection Materials in Solid Rocket Motors via Inverse Heat Conduction Analysis (Log #156)</b> <i>H. Martin, K.K. Kuo, R. Houim, and M. Degges</i>	<b>Munition Health Monitoring – Principles and Evaluation of Ammunition Stress Data Gathered under Operational Conditions (Log #122)</b> <i>K. Kratzsch</i>
9:35 9:55	<b>Investigation of Paraffin-Based Fuels in Hybrid Combustors (Log #158)</b> <i>A. Weinstein and A. Gany</i>	<b>A Novel Radiative Heat Flux Measurement Technique for Combustion Products Flowing in Solid Rocket Motors (Log #157)</b> <i>H. Martin, K.K. Kuo, R. Houim, and M. Degges</i>	<b>Lidar Detection of Explosives Vapors Using Excimer Laser (Log #127)</b> <i>S. Bobrovnikov, E. Gorlov, G. Sakovich, and A. Vorozhtsov</i>
9:55 10:15	<b>Hybrid Rocket using GAP as a Solid Fuel (Log #164)</b> <i>K. Hori, Y. Nomura, K. Fujisato, T. Yagishita, K. Hasegawa, K. Kobayashi, M. Nishioka, Y. Wada and M. Kimura</i>	<b>A Study on the Fabrication Process, the Heat Transfer and Ablation Analysis for Solid Rocket Motor Nozzle Thermal Liners (Log #161)</b> <i>J. Kim, J. Lee, T. Rho, W. Lee, H. Suh, and Y. Rhee</i>	<b>Regression Rates and CCPs Measurement of Metallized Solid Fuels (Log #201)</b> <i>L. Galfetti, L. DeLuca, L. Merotto, M. Boiocchi, and C. Paravan</i>
10:15	<b>Roof Terrace Foyer</b>	<b>COFFEE BREAK</b>	
10:35 11:20	<b>8-ISICP Invited Plenary Lecture</b> <b>Roof Terrace Room</b>		<i>Session Chair: Prof. Hansie Knoetze</i>
<b>Dr. Frederik Mostert of the Council for Scientific and Industrial Research, South Africa</b> <b>“Detonics and Ballistics in South Africa : A Past, Present and Future Perspective” (Log #140)</b>			
	<b>Roof Terrace Room (Session 20)</b>	<b>Room 2.61-2.63 (Session 21)</b>	<b>Room 2.65-2.66 (Session 22)</b>
	<b>Formulation, Processing, and Manufacturing of Energetic Materials <u>Topic 3</u></b> <i>Co-Chairs: Profs. P. Vashishta &amp; F. Li</i>	<b>Insensitive Munitions <u>Topic 4</u></b> <i>Co-Chairs:</i> <i>Dr. E.L. Baker &amp; Dr. R. Bouma</i>	<b>Thermobarics and Thermites <u>Topic 13</u></b> <i>Co-Chairs:</i> <i>Dr. F. Mostert &amp; Prof. A. Gany</i>
11:20 11:40	<b>Analysis of Thermoplastic Propellants Based on Novel Binder System (Log #159)</b> <i>V. Bozic and I. Krakovsky</i>	<b>Explosive Venting Technology for Cook-Off Response Mitigation (Log #111)</b> <i>E.L. Baker, T. Madsen, S. DeFisher, D. Suarez, N. Al-Shehab, A. Wilson and B. Fuchs</i>	<b>Probing Reaction Dynamics in Nanothermites (Log #125)</b> <i>L. Zhou, N. Piekiet, S. Chowdhury, and M.R. Zachariah</i>
11:40 12:00	<b>A New Class of Bonding Agents for High Energy Propellants (Log #190)</b> <i>B.M. Kosowski, J. Consaga, and A. Condo</i>	<b>Formulation &amp; Development of an Explosive that Allows Conventional 155mm Projectiles to Achieve IM Status (Log 108)</b> <i>S. Singh, P. Samuels, A. Di Stasio, B. Fishburn, &amp; P. Vinh</i>	<b>Formation of Nanothermite Structures Using Various Support Substrates and Binder Materials (Log #187)</b> <i>J.A. Puszynski, C.J. Bulian, and J.J. Swiatkiewicz</i>
12:00 12:20	<b>Control of Main Characteristics of Composite Propellants Based on Ammonium Nitrate by Nano-sized Metal Powders (Log #134)</b> <i>A. Zharkov, G. Sakovich, A. Vorozhtsov, B. Pevchenko, V. Popok, and N. Popok</i>	<b>Booster Candidates for IM Application at Rheinmetall Denel Munition (RDM) (Log #189)</b> <i>C.E. du Toit</i>	<b>Thermoelectric Pulse Power Generation Using Self-Sustaining Gasless Nanoreactant Systems (Log #192)</b> <i>J.A. Puszynski, R. Shende, and M.M. Bichay</i>
12:20 12:40		<b>Mitigation Techniques for Reduced Rocket Motor Vulnerability against External Thermal Stimuli (Log #210)</b> <i>Benjamin T. Smit</i>	<b>High-Reactivity Aluminum Powders (Log #141)</b> <i>V. Rosenband and A. Gany</i>
12:40	<b>Clivia Conservatory &amp; Jasminium Restaurant</b>		<b>LUNCH</b>

Thursday Afternoon, November 5, 2009			
14:00	<b>8-ISICP Invited Plenary Lecture</b>		<i>Session Chair: Prof. Richard A. Yetter</i>
14:45	<b>Roof Terrace Room</b> Prof. Priya Vashishta of the University of Southern California "Fast Reaction Mechanism of an Al/Al <sub>2</sub> O <sub>3</sub> Nanoparticle in Oxygen" (Log #221)		
	<b>Roof Terrace Room (Session 23)</b>	<b>Room 2.61-2.63 (Session 24)</b>	<b>Room 265-266</b>
	<b>Advanced Propulsion Systems &amp; Thermites</b> <b>Topic 18 &amp; 13</b> <i>Co-Chairs:</i> <i>Prof. K. Hori &amp; Dr. F. Mostert</i>	<b>Rocket Nozzles</b> <b>Topic 15</b> <i>Co-Chairs:</i> <i>Profs. R.A. Yetter &amp; M.C. Lin</i>	
14:45 15:05	<b>Experimental Investigation of Metallized Solid Fuel Ramjet Combustor</b> (Log #144) <i>S. Saraf and A. Gany</i>	<b>Phase Transformation of Graphite at High Surface Temperatures</b> (Log #138) <i>J. Essel, R. Acharya, J. Sabourin, B. Zhang, K.K. Kuo, and R.A. Yetter</i>	
15:05 15:25	<b>Thermal Reactivity of Al/Fe Core-Shell Composite</b> (Log #177) <i>W. Jiang, F. Li, Y. Wang, X. Guo, Z. Cheng, and X. Zhang</i>	<b>Characterization of Nozzle Erosion Behavior under Rocket Motor Operating Conditions</b> (Log #133) <i>B. Evans, K.K. Kuo, E. Boyd, and A. Cortopassi</i>	
15:25 15:45	<b>Roof Terrace Foyer</b> <b>COFFEE BREAK</b>		
15:45 16:45	<b>Room 261-263</b> <b>Chairman's Meeting</b>		
16:45 17:25	<b>Roof Terrace Room</b> <b>Future Symposium Site Selection &amp; Best Paper Awards</b>		
18h15	<b>Buses depart from CTICC for Symposium Dinner</b>		
19:00 22:00	<b>Symposium Dinner at African Themed Restaurant Moyo at Spier</b>		

**Poster Presentations [November 4, 2009 ]**  
**Snapshot presentations in Roof Terrace Room: 14:45-15:45**  
**Poster Presentation in Room 2.65-2.66: 16:05 – 17:00**  
***Co-Chairs: Dr. Deon van Zyl & Prof. Hansie Knoetze***

1. *A.V. Vorontsov, A.S. Besov, N.A. Krivova, V.N. Parmon, A.B. Vorozhtsov, and V. Komarov, “Fast Adsorptive-Photocatalytic Air Decontamination from Chemical Agents with Nanosize Aerosols Generated by Combustion or Explosion,”* (Log #103) – Area 1
2. *Deon Steyn, “Extruded Thermoplastic Elastomer Composite Propellant for IR Decoy Flare Applications,”* (Log #193) – Area 3
3. *Bernard C. Halls, “Munitions Safety Information Analysis Center,”* (Log #104) – Area 4
4. *Anthony Ralph Di Stasio, Sanjeev Singh, Philip Samuels, and Victor Stepanov, “Nano-energetics for Insensitive Booster Explosives,”* (Log #107) – Area 4
5. *Sanjeev Singh, Philip Samuels, Anthony Di Stasio, Barry Fishburn, and Paul Vinh, “Formulation and Development of an Explosive that Allows Conventional 155mm Projectiles to Achieve IM Status,”* (Log #108) – Area 4
6. *Omar Abbassi, Sanjeev Singh, Philip Samuels, and Anthony Di Stasio, “IM Comp A5 Replacement,”* (Log #116) – Area 4
7. *Amy Chau, Sanjeev Singh, Philip Samuels, and Anthony Di Stasio, “IM H6 Replacement,”* (Log #117) – Area 4
8. *Melinda Diedericks, “STANAG 4170 Qualification of Insensitive PBX Formulations,”* (Log #185) – Area 4
9. *Deon van Zyl, “Insensitive Composite Propellants Based on a HTPE Binder System,”* (Log #191) – Area 4
10. *Khalifa Al-Kaabi and Albert J. van Reenen, “Control Radical Polymerization Techniques for Synthesis of Energetic Thermoplastic Elastomers,”* (Log #197) – Area 4
11. *Rodrigo R. Rapozo, “Semi-Analytical Model for Subsonic Tailpipe flow: Considerations on SRM Performance”,* (Log #206) Area 6
12. *Izak M. Snyman, “The Scaling of Peak Over-Pressure of Small Spherical Charges,”* (Log #202) – Area 7

13. *Gregory Young, Grant A. Risha, and Richard A. Yetter*, “**Combustion of ALANE-Based Solid Fuels,**” (Log #217) – Area 7
14. *Alexander V. Ananin, Sergey A. Koldunov, Victor V. Garanin, Vasily A. Sosikov and Sergey I. Torunov*, “**Shock Wave Sensitivity of Nitromethane Mixtures With Non-Explosives Liquids,**” (Log #218) – Area 7
15. *Vladimir A. Arkhipov, Sergey S. Bondarchuk, Alexander G. Korotkikh, Gennadiy V. Sakovich, and Alexander B. Vorozhtsov*, “**The Comparative Analysis of Nonstationary Burning Rate of Solid Propellants,**” (Log #124) – Area 10
16. *Katsuya Hasegawa and Keiichi Hori*, “**An Infrared and X-ray Diagnostic Study on the Combustion of Solid Propellants,**” (Log #139) – Area 10
17. *Sergey A. Koldunov and Alexander V. Ananin*, “**Detonation Characteristics of Nitromethane Diluted with Non-Explosive Liquids,**” (Log #199) – Area 12
18. *Saburo Yuasa, Takashi Sakurai, Koki Kitgawa, and Toshiaki Sakurzawa* “**LOX Vaporization Techniques for Swirling-Oxidizers-Flow-Type Hybrid Rocket Engines,**” (Log#153) –Area 14
19. *Luiz Eduardo Nunes de Almeida and Koshun Iha*, “**Characterization of Carbon Fiber Reinforced Composites Used in Rocket Motors,**” (Log #212) - Area 15

## Technical Tour & Social Excursion

Friday, November 6, 2009	
7:30	<b>Bus Departure from Conference Center</b>
7:30	<b>Tour of Cape Peninsula &amp; Cape of Good Hope Nature Reserve (including Cape Point)</b>
13:00	
13:00	<b>Wine &amp; Food Pairing Lunch</b>
15:00	<b>Neethlingshof Wine Estate</b>
15:00	<b>Visit to Cheetah Outreach &amp; Eagle Encounters</b>
17:00	<b>Spier Wine Estate</b>

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<i>Session Chair: Prof. Hansie Knoetze</i>	
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<b>Prof. Priya Vashishta</b> of the University of Southern California	

# PROPULSION AND CATALYSIS - HISTORICAL SURVEY, UP-TO-DATE OVERVIEW AND CURRENT CHALLENGES

Charles J. Kappenstein, Yann Batonneau, Rachid Brahmi, and Laurence Pirault-Roy  
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## ABSTRACT

### *Introduction: short historical survey*

The use of catalysis in the field of propulsion began just before WWII in Germany with the catalytic decomposition of 80-85 wt-% hydrogen peroxide  $H_2O_2$  through liquid injection of permanganate salts: He-176 plane; V1 catapult; V2 turbo-pump gas generator. Hydrogen peroxide was also used for torpedo and submarine propulsion with diesel oil. After WWII, the UK Black Knight rocket program associated kerosene with  $H_2O_2$  and silver screen catalyst bed.

### *Catalytic decomposition of hydrazine*

The beginning of the space programs lead to the replacement of  $H_2O_2$  by more stable hydrazine using Ir/ $Al_2O_3$  catalysts, in order to control the orbit and orientation of launched satellites. The catalysts contain between 30 and 40 wt-% iridium, with the iridium size in the range of 2 to 5 nm. On iridium, the catalytic decomposition proceeds through two successive reactions:



The first step depends only on the number of the surface iridium atoms, whereas the second step is a structure sensitive reaction depending on the size of the iridium crystallites.

### *Replacement of hydrazine by new less toxic or green monopropellants*

The toxicity of pure hydrazine leads to the search for less toxic monopropellants. The most currently studied substitutes are energetic aqueous ionic mixtures containing an oxidizer and a fuel. The proposed oxidizers are HAN (hydroxylammonium nitrate  $[NH_3OH][NO_3]$ ) or ADN (ammonium dinitramide  $[NH_4][N(NO_2)_2]$ ). Different fuels are associated with these oxidizers: molecular fuels (glycine, glycerol, urea, methanol, etc.) or ionic fuels. The current challenge is to develop a catalyst that is active at low temperatures and is able to sustain the high temperatures of the product gases. One important result from numerous studies on the decomposition of these ionic oxidizers is the formation of major nitrogen and nitric acid during the catalytic or thermal ignition, in agreement with enthalpy driven reactions.

Other candidates have also been proposed:

- Highly concentrated hydrogen peroxide (90-98 wt-%) and,
- Nitrous oxide  $N_2O(g)$ , with the challenge to find an active catalyst, which is stable up to 1600°C.

### *Current objectives, prospective applications, and challenges*

- Hybrid engines: to improve the impulse, the hot oxygen formed during the catalytic decomposition of an oxidizer can be used to burn a solid fuel.
- Hypergolic bipropellants: the direct mixture of an oxidizer (e.g.,  $H_2O_2$ ) and a liquid fuel (like kerosene) can be made hypergolic, by adding an adequate catalyst to the fuel.
- Air breathing pulse detonating engines (PDE): the catalytic transformation of the current fuels can increase the detonability of the air-hydrocarbon mixtures.
- Catalytic ignition of cryogenic  $H_2-O_2$  mixtures.
- Catalyst as burn rate modifier for solid propulsion.

# High-Nitrogen and High-Oxygen Explosives as Possible Replacements for RDX

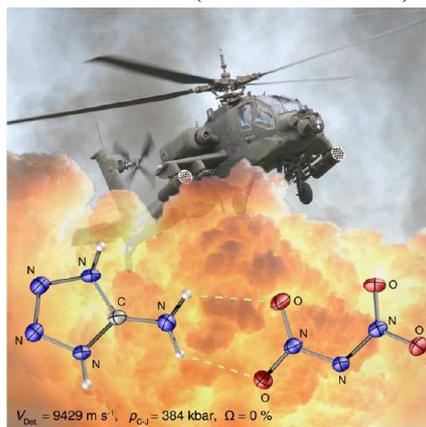
Thomas M. Klapötke, Michael Göbel, and Jörg Stierstorfer  
 LMU, Dept. Chemistry and Biochemistry, Munich, Germany

## abstract

Conventional energetic materials currently in use at army training ranges negatively impact the environment when released through Unexploded Explosive Ordnance (UXO), low-order, and high-order detonations. This, in turn, requires costly, long-term range remediation and clean-up efforts. The development of replacement materials that are environmentally benign and also meet or exceed performance and vulnerability requirements will ensure that army operational ranges and munitions production facilities will remain available and sustainable in support of transformation and objective forces. Toward this end, a combined experimental and theoretical effort has been implemented, with a focus on developing novel high-nitrogen and high-oxygen-containing energetic materials as environmentally acceptable replacements for RDX, which is a leading contaminant of training ranges.

We have considered different possibilities for the processing of high-nitrogen compounds. While all nitrogen species would be ideal materials due to their high energy content and extremely favorable gaseous byproducts (with a large percentage of  $N_2$ ), there are only very few candidates that have been (identified?) and characterized. In addition, some candidates have significant stability problems. Some high nitrogen molecules which do not include oxidizing groups show promise as candidates for propellant charges and for high explosives, but these molecules do not release enough energy to act as a suitable replacement for those explosives. However, the combination of high-nitrogen compounds with strongly oxidizing groups should be advantageous in delivering the explosive energy required. Because nitrogen-rich compounds suffer from stability issues, we have attempted to design systems that take advantage of  $\pi$  aromatic delocalization. These could include five-membered cyclic molecules that contain three, four or five nitrogens (triazoles, tetrazoles and pentazoles, respectively). Triazoles often do not possess enough intrinsic energy to be suitable candidates for high explosives, and pentazole derivatives are usually far too sensitive and unstable for any application. The tetrazole compounds offer a good compromise between high nitrogen content and reasonable kinetic stability. Moreover, six-membered tetrazine compounds have also been included in the study.

The most promising neutral candidates that we have synthesized for potential replacement of RDX are anhydrous bistetrazolylamine (H2BTA) and N3,N6-bis(2,2,2-trinitroethyl)-1,2,3,4-tetrazine-3,6-diamine (BTAT) whereas the two most promising ionic compounds are triaminoguanidinium dinitramide (TAG-DN) and triaminoguanidinium 1-methyl-5-nitriminotetrazolate (TAG-1-MeAtNO<sub>2</sub>).



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1. Triaminoguanidinium Dinitramide - Improved Synthesis, Single Crystal X-ray Structure and Detonation Parameters, T. M. Klapötke, J. Stierstorfer, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4340 - 4346.
2. N-Rich Salts of 1-Methyl-5-nitriminotetrazolate – An Auspicious Class of Thermal Stable Energetic Materials T. M. Klapötke, J. Stierstorfer, A. U. Wallek, *Chem. Mater.* **2008**, *20*, 4519 - 4530.
3. Bistetrazolylamines - Synthesis and Characterization, T. M. Klapötke, J. Stierstorfer, *J. Chem. Soc., J. Materials Chemistry* **2008**, *18*, 5248 - 5258.
4. Development and Testing of Energetic Materials: The Concept of High Densities Based on the Trinitroethyl Functionality, M. Göbel, T. M. Klapötke, *Adv. Funct. Mat.*, **2009**, *19*, 347-365.

## **COMBUSTION OF ENERGETIC MATERIALS GOVERNED BY THE REACTIONS IN THE CONDENSED PHASE**

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and Sergey Filatov

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### **ABSTRACT**

Combustion of energetic materials (EM) with leading reactions in the condensed phase is being considered in this study. It is assumed that the leading role belongs to the condensed phase not only for the case that the heat flux from the gas phase to the burning surface is negligibly small, but also for the case that a substantial heat flux comes from the gas phase. Based on numerous thermocouple-aided experimental studies on the combustion of different EMs, it has been shown that a material in the condensed phase can be heated up to its boiling point or, in the case of salts, to their dissociation temperatures. This circumstance provides the possibility to resort to known temperature dependences of vapor pressures along with experimental data on surface temperatures to describe the temperature-pressure relation in a broad range of pressure intervals and, thus, significantly reduce a possible error.

In contrast to the gas-phase model, the condensed-phase model has an energy limitation. Since in condensed-phase model the burning rate increases at the expense of surface temperature increase with pressure, there can be a situation when the heat effect of EM decomposition is no longer sufficient for warming-up substance to the surface temperature. This induces instability of combustion.

Experimental data on the burning rates and surface temperatures have been shown to allow for the derivation of unique kinetic information about decomposition of energetic materials at high temperatures, provided the burning of these materials follows a condensed-phase combustion model. The knowledge of kinetic parameters of combustion leading reactions and the dependency of surface temperature on pressure, in turn, allows for the simulation of burning EM in a wide range of initial temperatures and pressures.

Combustion of AP, AN, ADN, HNF, HMX, RDX, bicycle-HMX, CL-20, DAAzF, and NTO is considered in the work, and the resulting kinetic parameters of the leading reactions of these EMs will be presented.

## PRESSURE COUPLED RESPONSE OF SOLID PROPELLANTS

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### ABSTRACT

Combustion instability in solid rocket motors has been a technical issue in the development of rocket motors since modern rocket motors were first developed in the late 1940's and 50's. Roughly 80-90 percent of solid rocket motor development programs experienced some form of combustion instability during development. These problems ranged from minor issues (causing no effect on the propulsion system) to major obstacles (leading to motor failure). Combustion instability manifests itself as thrust oscillations which can impact and couple with other motor components including: electronic guidance systems, thrust vector control, and structural components. Combustion instability can cause unpredictable and unacceptable changes to the motors ballistic pressure-time history. A motor's stability is determined by the various acoustic gains and losses in the system. Losses include nozzle damping, particle damping, vortex shedding, structural damping, and other types of acoustic flow loss. Driving factors include: pressure coupling, velocity coupling, and distributed combustion driving. The most dominant driving mechanism is the pressure coupling. It is the coupling between acoustic pressure oscillations at the surface of a burning solid propellant with the combustion processes of the propellant. It is defined as follows:

$$R_p = \frac{\hat{r}/\bar{r}}{\hat{P}/\bar{P}}$$

In this equation,  $\hat{r}$  and  $\hat{P}$  represent the oscillatory burning rate and chamber pressure, respectively, and  $\bar{r}$  and  $\bar{P}$  represent their mean values. For example, a value of 2 for  $R_p$  would mean for a given pressure oscillation, the burning rate will double. The higher the  $R_p$  value, the more likely a propellant will drive pressure oscillations. The pressure coupled response function,  $R_p$ , is a function of frequency, pressure, and propellant formulation. The pressure coupled response is the key input to motor stability prediction programs for predicting the likelihood and anticipated degree of a given motor's instability. Measurements of the response function are often used to evaluate new propellant ingredients such as new binders and oxidizers; to parametrically examine formulation changes such as aluminum particle size variations; and to look at the effect of propellant additives on the response. The most common way to measure the pressure coupled response is the T-Burner. A photograph of China Lake's T-burner is shown in Figure 1. The T-Burner Technique has been used to successfully measure the response function of propellants since the late 1950's. The T-Burner shown in Figure 1 was built in the mid-1980's. It is capable of measuring the response function up to 4000 psi over a frequency range of 300 to 3000 Hz.



Figure 1: Photograph of China Lake's T-Burner

In today's dollars the cost of using the T-Burner to understand the pressure coupled response of a propellant can easily cost \$100K or more, depending upon the pressures required and formulation. Often, during motor development, guesses must be made to approximate the response function. These guesses can often be incorrect due the vast differences among formulations. Burning rates, particle sizes, oxidizer types, reduced smoke, minimum smoke, metalized, inert binder, energetic binder, and other propellant property dependences can all affect the pressure coupled response. This paper will summarize the vast amount of pressure coupled response data that has been measured over the years. The objective of this paper will be to organize response data in one place and to draw general conclusions about the pressure coupled response for various families of propellants. Numerous pressure coupled response curves as functions of pressure and frequency will be included. This paper will also include a review of response measurement techniques and data analysis, with particular attention to the pulsed during burn after burn technique used at China Lake. It is hoped that this document will aid in estimating response functions for future propellants. It is further hoped that this work will enable conclusions to be drawn on the functionality of solid propellant variables and allow general trends to be postulated.

## RECENT ADVANCES IN ENERGETIC MATERIALS IN SWEDEN, ESPECIALLY AT THE FOI

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<sup>2</sup>FOI, Defence and Security Systems Div., Tumba, Sweden, and Nanyang Technical University, Singapore

### ABSTRACT

During the 20th Century few breakthroughs occurred in energetic materials. Most current explosive substances, like TNT, RDX and PETN, were synthesised already in the 19th century. HNB (hexanitrobenzene) was judged only twenty years ago by the Los Alamos National Lab to be the theoretically best explosive conceivable. HNIW (CL-20) later proved to be 20 % better than HMX and 6 % better than HNB.

Early in the 1990's successful FOA synthesis of HNIW enabled Sweden to purchase this material from the United States. In 1995, an effective synthesis process for ammonium dinitramide (ADN) was found. ADN gives a much lower signature in rockets than AP, enables higher performance and has low environmental impact. ADN is produced by the Eurenco Co. ADN-GAP propellant will be tested in 2010 in a 5" rocket configuration. ADN has excess of oxygen and can enhance the performance of traditional explosives. A water and glycerol solution of ADN forms an interesting green monopropellant, marketed by the Swedish company ECAPS for applications in space vehicle thrusters.

Aluminium is a highly energetic additive to propellants and High Blast Explosives. Nanometric aluminium inherently becomes coated with a layer of alumina, comprising up to 25 % of the total weight, and is expensive. The same problem affects larger-sized Al grains or flakes, which prevents them from burning. A method to activate the surface of grains gave better performance and faster combustion with 100 micron grains than with 5 nm untreated ones. Aluminium grain with ADN as a matrix forms an affordable cast explosive with world-record underwater blast performance.

FOX-7 (FOX = "FOI explosive", Diaminodinitroethene) - a high explosive with lower sensitivity than TNT and similar performance as RDX - can be pressed with wax or polymer. It is an ideal material for IM boosters and can be used in high performance (tank) gun propellants. FOX-12 (GUDN, Guanlyurea dinitramide) has properties similar to NC, is very insensitive and inherently more thermally stable and is easily manufactured. It is marketed by the Eurenco Co. and has applications in automotive airbags, gun propellant (as a replacement for NC), and for melt-cast low sensitivity explosives (with TNT, called "Guntol").

An FOI effort to synthesise new HEDMs (High Energy Density Materials) started with tetrahedral N<sub>4</sub>, sponsored by the U.S. DARPA. This non-natural substance was modelled by numerical quantum mechanics, and promises to have 3-4 times the energy of HMX, a detonation velocity of 15000 m/s, and a C-J pressure of 1.4 GPa. Synthesis was attempted by unconventional means: laser, microwaves and -particles. So far, the existence of this molecule has not been verified and efforts continue. Other nitrogen clusters, such as N<sub>8</sub> or polymeric N<sub>x</sub>, promise even higher yields, up to 10-20 times that of HMX. Even this does not seem to be a limit for the power of new explosives.

The ion N<sub>5</sub><sup>-</sup> (pentazole) was successfully made by laser synthesis. With the N<sub>5</sub><sup>+</sup> counter-ion, synthesised by the U.S. AFRL, it could form a very energetic all-nitrogen molecule. Other positive counter-ions can be used. Synthesis of N<sub>5</sub><sup>-</sup> is currently being scaled up and now applies wet chemistry methodology.

Work on new high-energy oxidisers is ongoing, with a concentration on N-oxy compounds. This area appears to have excellent potential.

The step in energy density from HMX to N<sub>4</sub> is much greater than the change from black powder to high explosives, like Picric Acid or TNT, which occurred in the 1870's. That change most certainly caused a complete revolution in warfare methods and weapons technology. If such new HEDMs can be realised, they may create a need for completely new warhead and propulsion technologies.

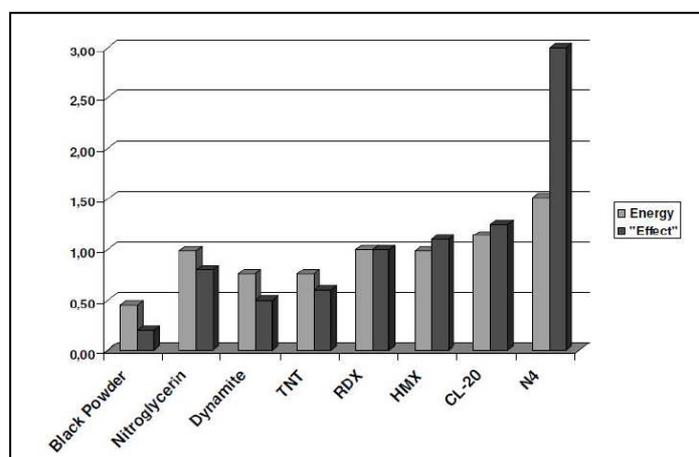


Figure 1: Performance of explosives at 220 % expansion, typical for metal acceleration in a shaped charge

## **DEVELOPMENT OF A NEW GENERATION OF INSENSITIVE EXPLOSIVES AND GUN PROPELLANTS**

Guy Ampleman

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### **ABSTRACT**

For the last few decades, DRDC Valcartier has been involved in the synthesis of energetic thermoplastic elastomers (ETPEs) based on linear Glycidyl Azide Polymer (GAP). A new generation of energetic polyester homopolymers was also developed and their polymerizations yielded energetic thermoplastic elastomers containing ester groups that could be degraded. Some ETPEs were also synthesized based on poly-nitratomethylmethyl-oxetane (PolyNIMMO) and polyglycidyl nitrate (Polyglyn). These energetic homopolymers were used as macromonomers and were reacted with 4,4'-methylenebis (phenylisocyanate) to yield copolyurethane thermoplastic elastomers. These ETPEs are physically cross linked rubbery materials that can be solubilized, recycled and then provide the basis for a new generation of insensitive explosives and High Energy Low Vulnerability Ammunition (HELOVA) gun propellants. The mechanical properties of these ETPEs were adjusted to serve as binders for the introduction into formulations of propellants and explosives and to produce the formulations with insensitive character. An insensitive explosive named XRT for eXperimental Rubbery TNT was developed and led directly to the development of a new insensitive recyclable green explosive (GIM). In addition, the ETPEs were introduced into gun propellant formulations to yield HELOVA, and the latest developments yielded green HELOVA gun propellants with improved energy. Furthermore, our understanding of the environmental impacts of explosives during live fire-training led us to the development of a green weapon that will contain both green explosives and gun propellants. A major project named RIGHTTRAC for Revolutionary Insensitive Green and Healthier Training Technology with Reduced Adverse Contamination was initiated last year and will produce a green weapon based on these concepts. Since ETPEs are recyclable, they will allow for easier disposal and reuse of the new formulations at the end of their life cycle. This paper will describe the syntheses of these ETPEs, the strategies that yielded the XRT and GIM explosives and the HELOVA gun propellants, the results describing their properties and insensitive characters and the RIGHTTRAC project that will include the concept and incorporation of the green explosives and gun propellants.

## MODERN DEVELOPMENTS IN HYBRID PROPULSION

Brian Cantwell

*Stanford University, Palo Alto, CA, USA*

### ABSTRACT

The hybrid propulsion concept has been around for more than seventy-five years. The idea is to store the oxidizer as a liquid and the fuel as a solid, producing a design that is immune to chemical explosion. The fuel is contained within the combustion chamber in the form of a cylinder with one or more channels, called ports, hollowed out along its axis. Combustion takes place between vaporized oxidizer flowing through the ports, and fuel evaporating from the solid surface. While the hybrid rockets enjoy many safety and environmental advantages over conventional systems, large hybrid rockets have not been commercially viable. The reason is that traditional systems use polymeric fuels that evaporate too slowly making it difficult to produce the high thrust needed for most applications. To compensate, the surface area for burning must be increased, and as the scale of a hybrid rocket increases, the number of required ports also increases, leading to poor volumetric loading and poor fuel structural characteristics. Recent research at Stanford University has led to the identification of a class of paraffin-based fuels that burn at surface regression rates several times higher than those of conventional hybrid fuels. These new fuels form a thin, hydrodynamically unstable liquid layer on the melting surface of the fuel grains. Entrainment of droplets from the liquid-gas interface can substantially increase the rate of fuel mass transfer, leading to much higher surface regression rates than those achieved with conventional polymeric fuels. This permits the design of a high volumetric loading single-port hybrid rocket system with a density impulse comparable to a conventional hydrocarbon fueled liquid rocket propulsion system. Since the start of this work, more than 500 tests have been carried out using a variety of oxidizers, including LOX, GOX and Nitrous Oxide. The analysis and performance of these fast burning systems will be discussed along with comparisons with conventional solid and liquid rocket propulsion systems.

## **DETONICS AND BALLISTICS IN SOUTH AFRICA: A PAST, PRESENT, AND FUTURE PERSPECTIVE**

Frederik Johannes Mostert  
*CSIR, South Africa*

### **ABSTRACT**

The application of science in the field of energetic materials (relating to ballistics) in South Africa evolved mainly from the technical isolation of the country during the last three decades of the 20th century. Although there was an established energetic material industry that primarily serviced the mining industry before this time, virtually all military equipment was procured externally before this period. Expertise in detonics (the science of detonation and related phenomena) and sub-disciplines of ballistics relating to energetic materials was sparse with only a small group of researchers working in the field prior to 1970. During the 1970s and early 1980s a dedicated government investment effort was initiated in an attempt to ensure self-sufficiency of supply to the defense forces. During this time pockets of scientists were established in various parastatal companies to develop and apply expertise in detonics and ballistics to the defense needs of the RSA.

Owing to the unique requirements of the South African defense force and the unique characteristics of the African battle-space environment, certain R&D innovations were initiated in the detonics and ballistic sphere during this period. Some notable examples relating to the field of energetic materials that will be discussed are counter-mine technology, various elements of rocket and missile technology and insensitive munitions technology. In most of these fields science was applied semi-empirically with a large emphasis on experimental testing.

The political changes in the country after 1994 brought a sharp decline in general defense spending and rapid changes to the defense science community. With international isolation removed the need for self-sufficiency was eliminated. A number of parastatals were privatized as independent companies with, recently, international shareholding in some cases. These changes present new challenges to R&D groups now residing in the “semi-commercial” field.

The participation of the South African National Defense Force in peacekeeping missions in Africa is predicted to continue for the foreseeable future. The lessons learned from other international peacekeeping forces in foreign countries, has a direct bearing on future research in the detonics and ballistics field in South Africa.

This paper pays tribute to the various contributions of scientists and engineers in the detonics and (energetic material related) ballistics field in South Africa over the past few decades. The thrust of the research in various current groups will be highlighted and some predictions will be made on the direction of future work.

# FAST REACTION MECHANISM OF AN AL/AL<sub>2</sub>O<sub>3</sub> NANOPARTICLE IN OXYGEN

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## ABSTRACT

Atomistic mechanisms of the oxidation of a Core (Aluminum)-Shell (Alumina) nanoparticle (ANP) are investigated using multimillion-atom molecular dynamics simulations. We find a thermal-to-mechanochemical transition of oxidation mechanism at elevated temperatures. The transition from thermal diffusion to mechanically enhanced diffusion to ballistic transport of atoms is accompanied by a change of intermediate reaction products from aluminum-rich to oxygen-rich clusters. Higher initial temperature of the Al core causes catastrophic fracture of the alumina shell during the expansion of the ANP, which provides direct oxidation pathways for core Al atoms, resulting in faster oxidation reaction and thus faster energy release.

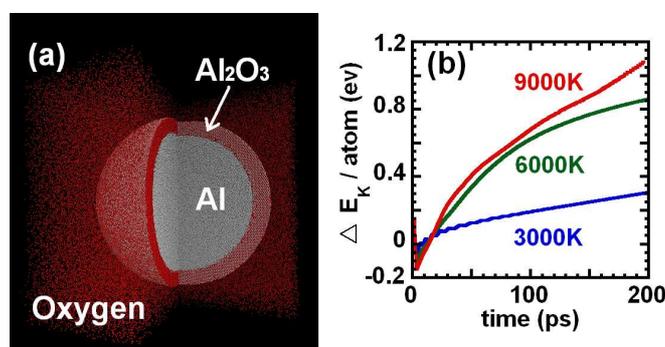
Nanoscale energetic materials have recently attracted much attention due to their high heat of combustion and fast energy release rates. An example is metastable intermolecular composite (MIC)—a subclass of thermites consisting of a mixture of metal and oxidizer particles of nanometer sizes. Burning of traditional thermites consisting of micrometer-size particles is well described by mass diffusion of oxygen through the oxide shell of the metal particle to the metal core. In contrast, MIC has increased reactivity by orders of magnitude [1–6], which cannot be explained by the simple diffusion-based oxidization mechanism.

To explain the observed fast reactivity of various MICs (*e.g.* Al+MoO<sub>3</sub> and Al+Fe<sub>2</sub>O<sub>3</sub> nanocomposites), a melt-dispersion mechanism has been proposed by considering the spallation of the oxide shell due to the high pressure of the molten metal core when the nanoparticle is heated [4]. In laser flash-heating experiments of ALEX particles by Dlott's group [7, 8], a linear relationship was found between the reaction propagation distance and laser energy, which was explained with a hydrodynamic model instead of the thermal explosion model. However, no single theory explains all observed behaviors of nanoparticle combustion. As mentioned above, mechanical breakdown of the nanoparticle's shell has been suggested to play an important role in the initiation of MIC [4, 9, 10], but atomistic processes underlying this mechanism are yet to be understood. Yip, Abraham and their collaborators have studied material damages at atomic level using molecular dynamics (MD) simulations [11, 12]. In this paper, we have investigated the atomistic mechanisms of chemical reactions in a Core(Al)-Shell(Al<sub>2</sub>O<sub>3</sub>) aluminum nanoparticle (ANP) embedded in an oxygen environment using MD simulations.

When the Al core is preheated to higher temperatures, the reaction mechanism is found to transition from diffusion to mechanically enhanced diffusion to ballistic mass transport of atoms. Change of reaction mechanisms from defect-induced diffusional processes to non-diffusional processes of mechanochemical effects is also proposed for reactions in powder mixtures when changed from shock-assisted reactions to shock-induced reactions [13]. In our simulations, we found that for systems with higher Al core temperatures, abrupt mechanical breakdown of the alumina shell at the nanoscale plays an important role in enhancing the diffusion of atoms and transforming the mechanism from thermal to mechanochemical regimes.

All the simulations reported here have a single 48-nm ANP which has a 4-nm alumina shell, and the ANP is embedded in oxygen. A total of 11,018,467 atoms—including 1,928,931 core Al, shell atoms (1,152,528 Al and 1,727,292 O), and 6,210,716 environmental oxygen surrounding the nanoparticle—are contained in a cubic box with edge length of 226.419 nm. Size of the MD box is sufficiently large not to impose boundary effects. A snapshot of the initial configuration is shown in Fig. 1(a).

In laser flash-heating experiments of ALEX particles by Dlott *et al.* [7, 8], the wavelength of laser beam is selected in the near IR regime (~1.06 μm), which is absorbed only by the metal core leaving the oxide shell unheated. Similarly, at the start of our simulations, the Al core is heated, while the shell is maintained at room temperature. To study the effect of the initial core temperature, we heat the core of the ANP to 3000, 6000 and 9000 K, which will be referred to as C3, C6 and C9 systems, respectively. These systems are then thermalized for 2 ps while keeping the alumina shell atoms fixed. To obtain a uniformly heated core, Langevin dynamics is run at the desired temperature for the core atoms for an additional picosecond. After this preparation, the constraints on the shell atoms are removed and the nanoparticle undergoes thermal expansion for 200 ps within the micro-canonical ensemble.



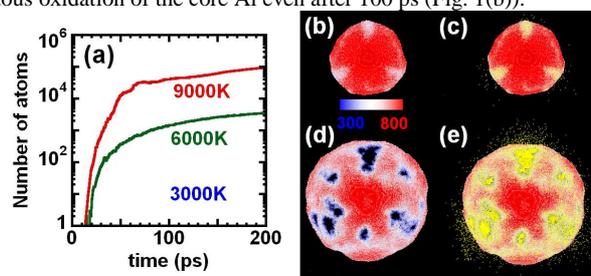
**FIG. 1.** (a) Initial setup of the system consisting of a single Core-Shell nano-particle embedded in oxygen. Most of the oxygen atoms surrounding the nano-particle are not shown for clarity. To show the inside, a quarter of the nano-particle has been removed. (b) Increase of kinetic energy per Al atom in the process of oxidation for the C3 (3000K), C6 (6000K) and C9 (9000K) systems.

The modeling of Al<sub>2</sub>O<sub>3</sub> is based on an inter-atomic potential that incorporates ionic and covalent effects through a combination of two- and three-body terms [14, 15]. For the aluminum core atoms, we use an embedded atom method (EAM) potential [16]. Lu *et al.* have used concurrent multi-scale method to study chemical reactions in metal [17]. In our case, the oxidation reactions of Al atoms happen ubiquitously, thus modeled by a bond-order based coupling scheme [18].

To compare the different energy release rates in the three systems, time variation of the average kinetic energy per atom is shown in Fig. 1(b). We observe that among the three systems, higher initial core temperature releases more energy up to 200 ps. This correspondence between higher initial heat in the Al core and faster reaction of the nano-particle is consistent with experiments by Dlott *et al.* [19, 20]. In their experiments, the energy release rate was inferred from the consumption rate of oxidizers by ALEX fuel. They also found that the energy release is a two-stage process, consisting of initial reaction of Al fuel with the surrounding oxidizer and subsequent slower consumption of oxidizer in between Al nanoparticles. Our simulation results in Fig. 1(b) reveal similar two-stage energy release characteristics. In all three systems, after the initial rapid drop of the kinetic energy due to the expansion of the shell, the kinetic energy of each atom increases rapidly at first and at a slower rate subsequently. Figure 1(b) also shows that the energy release rate for the C3 is much lower. The energy release rates of C6 and C9 are similar in the first 100 ps, but subsequently it slows down for C6 whereas it continues to increase in C9.

Oxidation reaction is accompanied by migration of atoms. By dividing each system into core, shell and outside regions, migration of atoms into each region is quantified. Here, the shell is identified as the largest covalently bonded aluminum-oxide cluster, and the other two regions are defined based on relative positions to the shell region. We find large number of atoms moving from and to the shell region in each system. Higher initial core temperature causes more atom-migration events, leading to faster change of shell stoichiometry.

Figure 2 (a) is a semi-log plot of the number of core Al atoms jetting into the oxygen environment. The C3 system shows no direct transport of core Al to oxygen environment because of the intact shell surrounding the core. For C6, the number of core Al atoms that cross the shell is on the order of hundred, signifying limited direct oxidation reactions between core Al and oxygen. This number is small because the expansion of the shell driven by the pressure of the core is not large enough to generate pores in the shell. Instead, there are low-density regions in the shell (Fig. 2 (b)), through which core Al jet out (Fig. 2(c)). These low-density regions close up again in the subsequent shrinking phase and prohibit further jetting out of core Al into the environment. In C9, the number of core Al that jet into oxygen environment is orders-of-magnitude larger than that in C6 (Fig. 2(a)) due to the opening of large pores in the shell (Fig. 2(d)) that provides pathways for the core Al to directly pass through the shell (Fig. 2(e)). The large number of ballistically transported core Al into the environment results in the fastest energy release rate for C9, and permanent opening of pores in the shell of C9 ensures continuous oxidation of the core Al even after 100 ps (Fig. 1(b)).



**FIG. 2.** (a) Semi-log plot of the number of Al core atoms jetting into oxygen environment in the C3, C6 and C9 systems. (b) and (d) are snapshots of shell morphology in C6 and C9, respectively, at 100ps with colors representing the number density (in unit of # of atoms/nm<sup>3</sup>) in the shell as shown by the color bar. (c) and (e) are snapshots of the shell morphology superimposed with jetting-out core aluminum atoms (in yellow) for C6 and C9, respectively. Environmental oxygen is not shown for clarity of presentation.

Experimentally, the burning of an Al nanoparticle has been found to last several nanoseconds [20] before the most stable products Al<sub>2</sub>O<sub>3</sub> are formed. Simulations of the oxidation of Al clusters [21] and experiments [20, 22] of the laser ablation of Al films have all shown the production of AlO before the formation of the final product Al<sub>2</sub>O<sub>3</sub>.

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- 24 Details are included in section 3 in the supplementary document.

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# DEVELOPMENT OF METALLIC NANOPARTICLES BASED ENERGETIC MATERIALS: A REVIEW

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## ABSTRACT

This review is devoted to the state of the art in the field of applications of energetic metallic nano-sized particles. For the last decade this area has been developing very fast in the world. The use of metallic nano-particles provides new opportunities to ameliorate significant characteristics of energetic formulations. When studying the behavior of metallic nano-particles in solid combustion systems, there are several aspects to be affected: the chemistry of the interaction between solid and gases, multi-level kinetics of the oxidation process of each ingredient, features of heat and mass transfer at a micro and nano-scales, homogeneity of the formulation, and agglomeration/aggregation processes in condensed products. The quality of the metallic nano-particles used is likewise a key point of the domain. It is linked to the degree of disparity, particle size distribution and the type of a protective shell on nano-particles. Another problem to be solved is homogeneity of the body of an energetic material with incorporated nano-particles. We will then survey the research works pertaining to the development in this area, as well as some preliminary results and our perceptions of new approaches to promote these researches in the near future.

There are a few major motives of using metallic nano-particles in energetic materials instead of normal-sized particles. It is presumed that the extraordinary properties of metallic nano-particles can ameliorate the performance of traditional energetic formulations. Firstly, nano-particles possess a larger specific surface area which stipulates their higher reactivity in comparison with that of conventional (micron and submicron-sized) particles. Undoubtedly, nano-sized aluminum is the most interesting metal because it is a light material and characterized by the high enthalpy of its reaction with oxygen.

It is well known that when adding an aluminum powder into a propellant formulation, the burning rates of rocket solid propellants increase. At the same time, it was previously found that the burning rate of a 20% nano-aluminum admixture in an HTPB-based propellant can be increased by 70%, whereas for the same added percentage of conventional aluminum powder, the burning rate is much lower. Another example was also reported. The effect of partially replacing the conventional aluminum powder with an electro-explosive aluminum nano-powder (Alex) in a propellant formulation on the burning rate and temperature sensitivity was observed. They found that the addition of Alex particles to the propellant formulation substantially enhances the burning rate, and also the temperature sensitivity of the aluminized propellant.

Generally, we can emphasize the following principal motives for using metal nano-particles as additives to energetic materials:

- their higher reactivity;
- increased oxidation and combustion rates in comparison with conventional particles;
- low temperatures of oxidation onset and ignition;
- low degree of agglomeration in condensed combustion products of energetic materials.

We make an attempt to analyze results obtained by various research teams concerning the search for the optimal use of the aforesaid properties of nano-particles. At the end we reach the following conclusions:

- The elaboration of new protective and functional coatings on the particles still remain one of the most important points in improvement of formulation performances. This problem consists of two principal aspects: amelioration of the coating protective properties and reducing the agglomeration degree during combustion.
- The binder nature plays a special role in solving the problem of agglomeration. Even though the use of polypropylene glycol demonstrated a significant decrease in the amount of unburned aluminum and an increase in the aluminum oxide among the combustion products, the search for more eco-friendly ingredients remains relevant.
- The modern quality standards require the replacement of toxic ingredients in energetic formulations by eco-friendly materials which do not comprise, for example, lead-based compounds or ammonium perchlorate.
- A technique for the study of nano-aluminum thin layers (embedded or non-embedded in a polymer binder-fuel) with an oxidizing gas counter-flow allows the experimental modeling under terrestrial conditions of the state of weak convection flows under reduced gravity.

## NANO-RDX SYNTHESIS BY RESS PROCESS AND SENSITIVITY CHARACTERIZATION

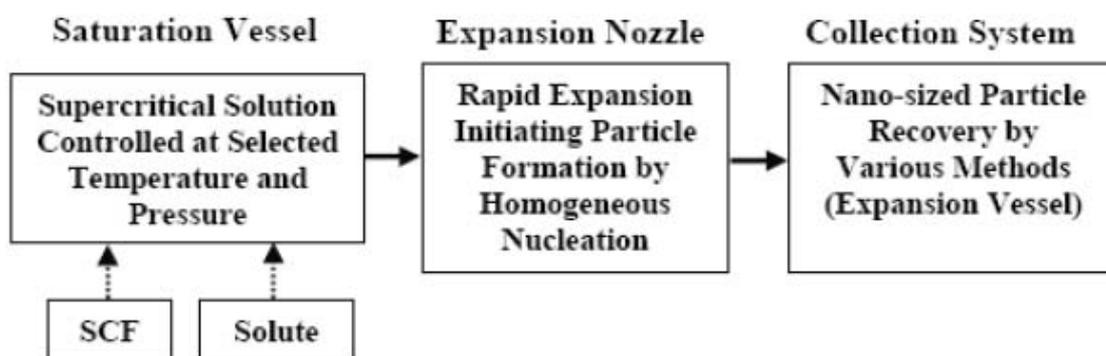
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### ABSTRACT

In order to develop insensitive munitions, it is advantageous to synthesize nano-sized energetic crystalline particles such as RDX. In this investigation, the method utilized to produce these nano-scale energetic particles is the rapid expansion of a supercritical solution (RESS) process (see Figure 1) with carbon dioxide as the solvent. The high-pressure RESS process is capable of generating the supersaturation of the supercritical solution required for the formation of nano-sized particles, initiated by homogeneous nucleation. Using varied operating conditions (pressure and temperature) and different nozzle throat diameters of the expansion nozzles, the dependency of particle size on these parameters has been determined. RDX particles ranging from 65 to 105 nm have been obtained from this RESS process using a controlled pre-expansion pressure up to 120 MPa (17,500 psi) and a controlled pre-expansion temperature up to 363 K. Collection efficiency of the synthesized particles was greatly enhanced by the formation of dry ice in the collection system. The synthesized particles have been analyzed using a field emission scanning electron microscope (FE-SEM) to deduce surface characteristics and particle size distributions. Sensitivity of the synthesized nano-scale RDX to impact, friction, and electro-static discharge (ESD) has been evaluated using standardized testing devices at NSWC-IHDIV and compared to the military grade RDX powders. It was found that there was a noticeable decrease in the impact sensitivity of the synthesized nano-RDX particles, while the sensitivity to ESD and friction remained similar.



**Figure 1: RESS Process**

# **DESIGN OF A MODULAR TEST CHAMBER FOR THE ANALYSIS OF FLAME SPREADING RATES, BLACK POWDER JET PENETRATION, AND VENT-HOLE GEOMETRY INTO A GRANULAR BED**

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## **ABSTRACT**

Understanding the detailed ignition, flame spreading, and combustion processes inside of a granular solid propellant bed is vital for accurate internal ballistic modeling and development of many weapon systems, including mortars and small- and medium-caliber gun systems. Although there have been recent studies on loading density<sup>1</sup> and one-dimensional flame spreading<sup>2</sup>, there has been little experimental work on flame propagation in three dimensions or the enhancement of heat transfer rates to the ball propellant from the condensed phase products in the black-powder igniter jet. This information is especially pertinent because recent numerical models<sup>3</sup> have been required to use one-dimensional approximations for jet penetration or assumptions for the two-phase flow heat transfer characteristics<sup>4</sup>. Particularly, the degree and phase of the black-powder product jet penetration into the granular bed, flame spreading rates, and the effects of vent-hole geometry on those factors have not been well developed.

To characterize these items and to develop correlations for modeling, a modular test rig was developed and fabricated. This device is capable of using a wide variety of granular propellants. Sharing a common ignition system in the head end section, two test configurations were developed; one to investigate radial and a second for axial flame spreading. Operation of the ignition train begins with a swinging pendulum that strikes a percussion primer with energy and velocity typical of a real system. A flame jet generated by the primer ignites a black powder pellet. Flow of the black-powder igniter products is then controlled through a vent-hole before entering the granular propellant bed. The geometry of the propellant bed is set by a modular test section attached to the head end, while the jet configuration is set by a modular vent-hole section. Contact of the pendulum hammer head with the firing pin is measured by an ultra-low current digital continuity circuit which allows for measurement and comparison of ignition delays. Both setups have been fitted with quartz windows, transparent in the near IR, over thin borosilicate sacrificial windows in front of the area of interest. Use of these materials provides continuous strength to the chamber, which is otherwise provided by the stainless steel body, and allows passage of visible light and infrared radiation. Chamber diagnostics also include dynamic piezoelectric pressure transducers to help characterize the black powder and granular bed combustion.

For characterization of igniter jet penetration into the granular bed, materials with characteristics similar to the live ball propellant have been utilized. One material is a fuel-rich propellant simulant chosen based on similar particle size, physical, thermal, chemical properties. Inert glass beads similar in diameter to the ball propellant are also used. To investigate the condensed phase deposition onto granular propellants or simulants, the live bed is replaced with simulants, and after firing, physical analysis of the propellant simulants recovered from various locations in the bed indicate the extent of penetration of condensed phase black powder products into the granular propellant bed as a function of jet properties.

Presence of condensed phase products (using potassium as a marker) is detected through use of energy dispersive X-ray spectroscopy.

Through the use of two different types of high-speed photodetectors that are sensitive to either the visible or infrared spectrum, the position of the hot gas and burning surface flame fronts can be distinguished to allow flame-spreading rates to be calculated<sup>5</sup>. Figure 1 shows the igniter jet and the burning granular bed. A series of high-speed images have also been collected which show the jet penetration and flame spreading processes.

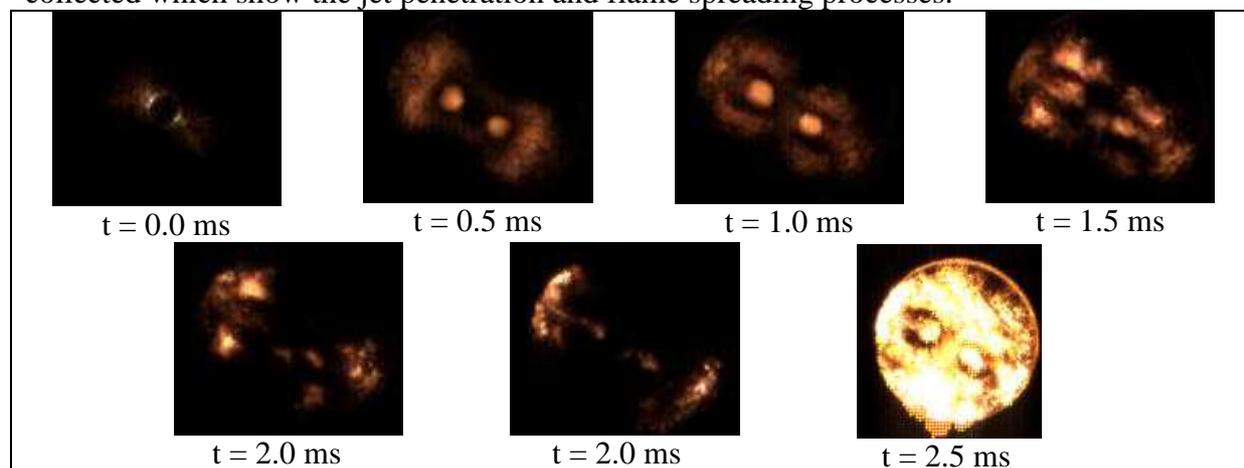


Figure 1: Video footage of burning granular propellant at 2000 frames per second.

Note: times are relative to first frame visible light.

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## **RADIATIVE IGNITION OF SOLID PROPELLANTS**

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### **ABSTRACT**

Ignition sensitivity of any energetic material or solid propellant is always investigated; this allows for checking and/or determining the Arrhenius' degradation law and the thermal properties of these materials. The classical relationship of ignition delay time versus heat flux, plotted in Log-Log coordinates, shows a linear slope in a large flux range and is dependent upon the tested energetic material.

We were interested in solid propellant time to ignition determination by two aspects. Firstly, we determined experimentally the sensitivity to ignition of composite propellants using a CO<sub>2</sub> laser beam instead of the classical convective heat generator used at ONERA for many decades. The setup and the associated measurement systems are described in details in the paper. High speed video images and surface luminance temperature evolutions, from optical-fiber pyrometers, were determined showing the inert heating of the sample, then the starting of the binder degradation and, once a first AP grain was ignited ("first light"), the quick raising of the temperature up to the stationary combustion level.

These experimental results were compared to a 1D numerical simulation model. The solid propellant thermal and reaction parameters were determined from the literature values of the ingredients (AP, HTPB and Al) and their mixture ratio. The relationships were adapted to each parameter following the commonly used rules. Thermal diffusivity and emissivity factor of the solid propellant were checked with the experimental data. These evaluated data are commented and some adjustment was made aiming at validating the experimental quantity evolution. The model gives the surface temperature evolution and the burning rate variation from 0 to the stationary value. The definition of the time to ignition can be related to the "first light" via images and to the temperature drastic variation at the ignition from pyrometer luminance signals.

We comment on the different ignition delay times corresponding to criteria and the physical process of the AP propellant grain ignition. The first AP grain large enough to propagate heat to others grains around it, and close enough to the surface stands as the starting element of the ignition process. The experimental and numerical results showed that the pre-exponential factor of the Arrhenius' law governs the delay time and the ignition surface temperature level. The time to ignition delay is linked to the propellant properties but also to the surface roughness or surface local mixture ratio: a kind of "skin" function.

# A CREATION OF PROPELLANT COMBUSTION MODELS BY MEANS OF DATA MINING TOOLS

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## ABSTRACT

There is a great deal of experimental data about combustion characteristics of various propellants. A question is how can we generalize them? It is obvious that burning characteristics are associated with a composition of combustible mixtures and the types of mixture ingredients; chamber pressure; initial temperature; and heat of combustion, etc. A question is how we can create generalization models for these dependencies? In our work, we present the results of Data Mining (DM) usage for a creation of such models in a case of propellant burning. The DM is an integrated, contemporary software tool for data preprocessing, processing, analyzing, and visualization. The DM involves such kinds of tools as various data preprocessing tools, correlation analysis, decision trees, artificial neural networks (ANN), self-organization maps, etc. ANN have a leading role from the point of view of a creation of multifactor calculation models, which allow for the determination of burning characteristics subject to the changes of internal and external parameters. Other tools of DM have the auxiliary role for data preprocessing, processing, and data choosing for a creation of ANN calculation models. At the present time, we have three ANN calculation models.

1. The models "Temperature Profile vs. Burning Rate" (the first versions of it(them) had been presented at 7-ISICP symposium in 2007). They allow for the determination of a temperature profile of the thermal wave in a burning propellant as a function of pressure, burning rate, and a portion of the heat released near the burning surface of the propellant (or adiabatic temperature in flame). The scheme of a construction of the ANN model was as follows. The different sets of experimental values of pressure, burning rate, a portion of the heat released near the burning surface of the propellant (or adiabatic temperature in flame), and coordinates in burning waves taken from a scientific literature were installed on the input layer of ANN. The corresponding values of temperature were installed on the output layer of ANN. By means of an appropriate training tool (the well known method of "back propagation of errors"), the ANN model was constructed. This model describes the "black box," which connects different variables. The "black box" obtained can be used in experimental investigation for the prediction (determination) of a temperature profile as follows. By inputting the values of pressure, burning rate, a portion of the heat released near the burning surface of the propellant (or adiabatic temperature in flame), and coordinates to the input layer of the "black box", the corresponding values of temperature can be obtained readily from the output layer of the "black box".

2. The models "Burning Rate vs. Operating Conditions and Mixture". This "black box" model consists of the relationship between value of burning rate on the one hand, and quantities of ammonium nitrate (AN), ammonium perchlorate (AP), AP particle diameter, and pressure on the other hand. This model allows for the prediction of a burning rate value of the propellant. The data for the models created were obtained by Dr. Makota Kohga et al. (2007).

3. The model "Mixture vs. Operating Condition and Burning Rate". This "black box" model consists of relationships between quantities of AP and AP particle diameter on the one hand, and a value of burning rate, a quantity of AN, and a value of pressure on the other hand. This model allows for the prediction of a mixture of propellant that we have to use for attaining the desired burning rate. The data for the models created were obtained by Dr. Makota Kohga et al. Our presentation will involve the demonstration of Data Mining tools work on the basis of our data, above mentioned data, data of Dr. A.I. Atwood et al. (1999) dealing with burning rate of solid propellant ingredients. We believe that Data Mining will be beneficial by expanding the experimental results that have been obtained.

## MATHEMATICAL MODELING OF ALPHA-IRON COATED PYROPHORIC SUBSTRATES

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### ABSTRACT

A mathematical model describing a combustion process in air inside a porous layer consisting of pyrophoric alpha-iron is proposed. The main focus of this research study has been on the investigation of pyrophoric iron layers deposited on various substrates. The effect of the layer's properties such as porosity, specific surface area, particle-size distribution of iron nanoparticles, overall layer's thickness, and various solid inert supports on combustion characteristics has been investigated. It is very important in several military applications to maintain high temperature profile within such layers for several seconds. Transient temperature profiles can be affected not only by the layer/supporting structure properties, but also by external conditions which include, oxygen and water vapor partial pressures, initial material temperature, and the heat-transfer conditions at interfaces.

The presentation will focus on fundamental aspects of mass and heat transfer with a simultaneous heterogeneous reaction inside of a pyrophoric layer. The most important parameters required for a quantitative analysis of a transient combustion process are those related to heterogeneous reaction kinetics between oxygen or water vapor and pyrophoric iron. These modeling studies are supported by experimental investigation of non-catalytic reaction kinetics between iron nanoparticles and oxygen. These reaction kinetic studies have been conducted using TGA/DSC instrument. The effect of iron particle size on the rate of chemical reaction with oxygen has been investigated as well. Comparison of transient combustion characteristics obtained from the proposed model and those experimentally determined will be discussed.

## IMPROVED MUNITIONS DEVELOPMENT BY NOVEL TECHNIQUES

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### ABSTRACT

The requirements that military operations place on munitions are becoming more challenging every year. Munitions must meet the IM requirements, be inexpensive, have at least a comparable performance, or in some cases have even better performance (e.g. extended range munitions, shaped charge impact), give a decreased barrel erosion and a temperature independent performance, have a multi purpose mode, scalable functionality for MOUT intervention, but should function reliably to decrease the number of UXO's and have a long lifetime. Such a list of requirements has become an enormous challenge using conventional techniques and novel techniques are necessary to make things happen.

One of the main tasks of TNO is to search for new and innovative techniques to overcome these kind of hurdles. In the search of understanding the functioning of munitions and IM-mechanisms that lead to a certain response in munitions, TNO has developed several techniques that can be used for the development of new improved munitions.

For the production of insensitive munitions, crystallisation techniques have been developed to produce so-called Reduced Sensitivity (RS) crystals (RDX, HMX, CL20, HNF, etc.) that form the bases for insensitive energetic compounds. TNO is capable of producing crystals from nano- and submicron-scale, up to even millimeter scale, with the proper crystal morphology (no defects like twinning or cracks, etc.) and hardly any inclusions. With respect to production techniques, a methodology has been developed to make the twin-screw extrusion apparatus suitable for safe and continuous production of high solids loading energetic compounds. Co-extrusion of propellants shows good potential for the production of a gun propellant for extended range shells. Also techniques have been developed to produce the so-called temperature-independent propellants; enabling the projectiles to perform in a constant manner in extreme weather conditions and increasing the precision. Also micro- and mini-igniters have been developed to make challenges like scalability, aimable warheads, multi-purpose munitions with high reliability possible. For lifetime assessment of gun propellants, a methodology has been developed based on heat flow calorimeter (HFC). Monitoring the performance changes of propellant is one of the other advantages of this technique. With the majority of these techniques, computer simulations are used to support the technique or to assist and enable its implementation in a system.

These novel techniques can help to address these challenges and make most of the requirements a reality in new munitions. An overview of the new techniques will be given in this presentation.

# SYNTHESIS AND CHARACTERIZATION OF COATED ENERGETIC MATERIALS USING A RESS SYSTEM

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## ABSTRACT

Coating energetic materials with other types of energetic materials has many potential benefits. One of these advantages is that a hard to ignite material can be coated with an easily ignitable material (for example RDX on aluminum). This makes it possible for a surface reaction to ignite the core energetic material. In the same manner, coatings can potentially make other energetic materials less sensitive by placing a less sensitive energetic shell over a more sensitive energetic material. Another advantage of coating energetic materials is to make them compatible with other propellant ingredients during the processing and curing stages. While these coatings are desirable, they can be difficult to attain in practice. Methods such as dripping dissolved solution over another material or vapor deposition have their drawbacks. Dripping dissolved solutions over energetic particles rarely yields uniform coatings. Vapor deposition can be hard or impossible if one of the two energetic materials has a low decomposition temperature.

One promising option for coating energetic materials involves a process called the rapid expansion of a supercritical solution (RESS). The RESS process involves dissolving energetic materials in a supercritical fluid and expanding the solution through a nozzle to create a high degree of supersaturation. The high degree of supersaturation will then cause the energetic solute in the supercritical solution to precipitate onto the surfaces of energetic particles serving as nucleation sites. This phenomenon is called heterogeneous nucleation. A major advantage of the RESS coating process by heterogeneous nucleation is that it can be performed at relatively low temperatures, since CO<sub>2</sub> has a critical temperature of around 31°C. This avoids the risk of decomposing the energetic materials during the coating process. Another advantage to the process is that heterogeneous nucleation is a rapid chemical process which can occur uniformly over the entire nucleation sites.

The ultra-high pressure RESS experimental setup was previously developed and reported by Cortopassi et al.<sup>1</sup> This system supplies supercritical solutions under controlled temperatures and pressures for rapid expansion through a sapphire nozzle. For the coating process, a particle entrainment vessel has been fabricated and placed in the upstream location to the expansion nozzle. This vessel serves to supply energetic particles as nucleation sites for coating when the stream of particle-laden supercritical solution is rapidly expanded through the nozzle. This expansion process allows the solute to precipitate onto the particles by heterogeneous nucleation. After the particles are coated, the cold jet at high speeds is totally contained in an expansion tube to facilitate the formation of dry ice. The dry ice adds substantial weight to the coated particles, which allows them to settle by gravitational force in the collection container. It is important for the container to be electrically conductive and grounded due to the high electro-static discharge (ESD) sensitivity of many energetic materials. There are two possible energetic materials that will be coated with RDX. The quality of the coatings will be observed through transmission electron microscopy (TEM). With a developed coating system, several parameters will be examined to optimize the quality of the coatings. These include: the number density of particles to be coated, the pre-expansion temperature and pressure of the supercritical solution, and the nozzle throat size for the supercritical solution to flow through.

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## **APPLICATION OF NANOMETER MATERIALS FOR PROPELLANTS, PYROTECHNICS, AND EXPLOSIVES**

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### **ABSTRACT**

The application of nanometer materials for propellants, pyrotechnics, and explosives has been summarized. The effects of nanometer materials on the energy and combustion performance of solid propellants are itemized, which include nanometer metal materials, metallic nanocomposites, nanometer metal oxides, nanometer rare earth materials, nanometer oxidizers, carbon nano-tubes (CNTs), and nanometer explosives. The combustion performance of pyrotechnics-added nanometer metal materials, nanometer metal oxides, and nanometer initiators are reported. In addition, the application of nanometer materials for explosives has been covered. Finally, the developmental trends and applied prospects of nanometer materials in these fields are put forward.

**Keywords:** *Nanometer materials; Propellants; Pyrotechnics; Explosives*

## THE MUTUAL INFLUENCE OF NANOMETAL ADDITIVES ON HEAT RELEASE RATE IN ENERGETIC CONDENSED SYSTEMS

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### ABSTRACT

The reactivity of nano-sized powders of Al, Ti, Cu, Zn and an alloy of Fe/Ni/Cu in the process of oxidation by decomposition products of tetrazole polymer plasticized with a mixture of nitroesters with nitroamines is studied from the rate and total heat release in the temperature range from 100 to 1200 °C at a heating rate of 50 °C/min. It is established that the oxidation rate of metal powders is defined by their chemical nature. Aluminum is the least reactive but most effective from the thermodynamic aspect. A possibility of earlier time and temperature introduction of aluminum into the process of oxidation by using additives of other more reactive metals is established, which can serve as a means of controlling the process of explosion and combustion of energetic condensed systems.

The processes of explosion and combustion of energetic condensed systems (ECSs) are supported by heat release in the condensed phase and oxidation of metal additives introduced into the ECS composition. The reactivity of metals is determined by their chemical nature. In the case of a determinative role of heat release rate, the balance of cumulative heat could be non coincident with thermodynamic characteristics of the metals, and systems containing two metals could be superior in this parameter to any of those separately. This paper is dedicated to experimental verification of such approach.

### *Experimental*

A composition of energetic condensed systems is comprised of an oxidizer or explosive, as well as an organic fuel or a metallic ingredient. As to an organic fuel, the preference is given to energy-rich plasticized polymers. According to specifications for creating ECSs, a metal additive is introduced into the polymeric matrix wherein the process of its oxidation by explosion or combustion begins.

The experiments were conducted on a thermoanalyzer *TGA/SDTA 851* (manufactured by METTLER TOLEDO) in an open bowl, in an atmosphere of air, at a heating rate of 50 °C/min and in the temperature range from 100 upto 1200°C. While conducting the experiments, there were recorded normalized changes in the weight of the sample, as well as heat release. This allowed us to characterize the process in terms of: total heat release ( $\Sigma Q$ ) in the whole temperature range, average heat release rate ( $\bar{V}_Q$ ), maximum heat release rate ( $V_Q^{\max}$ ) in the region of the most intensive fourth peak of heat release (Figure 1), and the approximate temperature  $T_{0s}$  at the start of the intensive interaction between metal and decay products along the curved bend reflecting an increase in the sample weight.

A tetrazole polymer plasticized with a mixture of nitroesters and nitroamines was chosen as a subject of the study and into which the metal powder in amount of 33 mass % was introduced, corresponding approximately to 10% of its content in the energetic condensed system. The nano-sized metal powders were obtained by electro-explosion of wire. The nano-sized

powders are an agglomeration that is susceptible and cannot be distributed in the polymeric matrix to the initial state. As for agglomerates, they will be oxidized as a single particle. Therefore, a mixture of the polymer with metal was characterized by the size distribution of the agglomerates; Table 1 shows the results. Data on the content of impurities of other metals in them are also presented. An alloy with 66% of Fe, 33% of Ni, and 1% of Cu obtained also by electro-explosion of wire was used as one of the metal additives. For comparison, powder of commercial aluminum of ASD-4 grade was also utilized.

Table 1: Characteristics of distribution of metal powders in polymeric matrix.

Metal	Content of impurities	Size of particles in matrix, $\mu\text{m}$	
		Range	Maximum
ASD-4	no	1.0–20.0	
Al	no	0.4–1.8	1.0
Ti	no	0.2–1.4	0.6
Fe	no	0.1–1.0	0.2
Ni	1.3% of Fe	0.4–1.5	0.9
Cu	no	0.4–1.5	1.0
Zn	0.26% of Fe	0.5–1.8	1.1
alloy		0.4–1.6	0.8

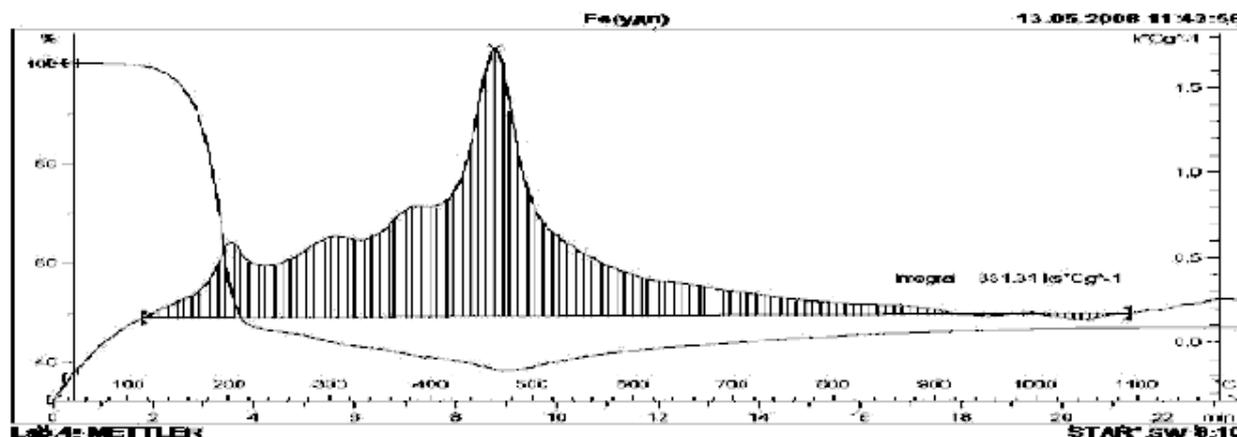


Figure 1: Diagram of the change in weight and heat release of the mixture of polymeric matrix with nano-sized powder of alloy in time.

The characteristic feature of decomposition of the polymeric matrix without metal additives is the constant presence of five peaks in the diagram; the latter of which is low-intensive. In separate cases, the introduction of metals leads to the disappearance of the fifth peak. The absence of the fifth peak is subject in greater extent to a certain batch of metal powder, except for ASD-4 powder in the presence of which the fifth peak is constant for various tested batches. The experimental results are shown in Tables 2–3, and illustrations are in Figure 2.

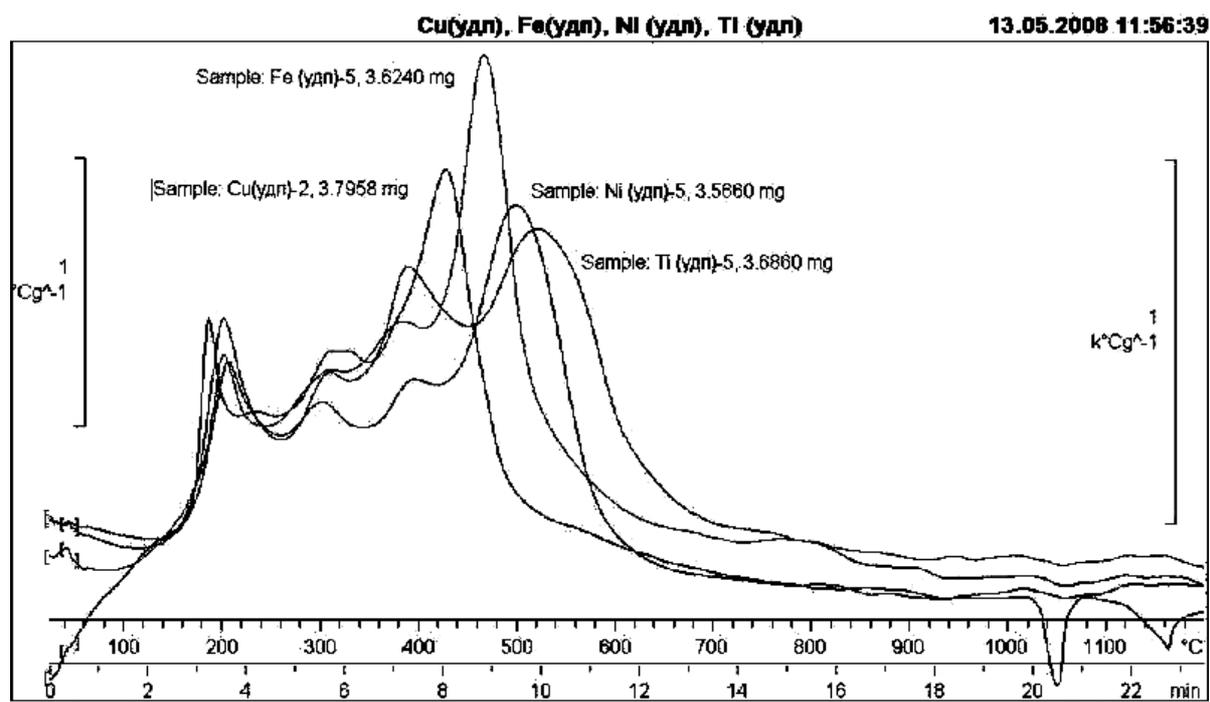


Figure 2: Diagram of the change in heat release in mixtures of polymeric matrix with ultra-dispersed powders of Cu, Fe, Ni and Ti.

Table 2: Characteristics of the process of interaction between metals and polymeric matrix decay products.

Metal	$\sum Q$ , cal/g	$\bar{V}_e$ , cal·g/s	$V_e^{\max}$ , cal·g/s	$T_{os}$ , °C
without metal	940	0.764	2.44	
ASD-4	929	0.754	1.51	760
Al	1410	1.146	3.08	700
Ti	1970	1.602	4.75	460–480
Fe	1346	1.095	3.67	460
Ni	1425	1.159	4.69	480
Cu	1400	1.138	5.78	470–480
Zn	810	0.659	3.75	480
alloy	1560	1.268	5.89	470

Table 3: Position of heat release peaks on the temperature scale.

Metal	Temperature of peak, °C				
	1	2	3	4	5
without metal	213	302	398	703	862
ASD-4	208	302	404	630–680	1150
Al	208	300	398	635	absent
Ti	204	307	396	546	absent
Fe	204	302	383	540	absent
Ni	207	306	398	531	absent
Cu	190	307	358	494	absent
Zn	210	303	410	570	absent

The obtained results are indicative of a large difference in heat release rate for metals of various natures. A series of efficiency increases in the heat release rate does not coincide with the thermodynamic series of heat of their oxidation. For example, it is a kinetic parameter of the oxidation process and characterizes the initial stage of development of the thermal processes in energetic condensed systems. Then, an additive of kinetically favorable metal can serve as an initiator of thermodynamically more effective metal, for instance aluminum, in the process of oxidation.

To check such an approach with respect to a composition containing 33% of aluminum; 4% of aluminum was subsequently replaced by one of the metals tested. The experimental results are shown in Tables 4 and 5.

Table 4: Characteristics of the process of interaction between aluminum with metal additives and polymeric matrix decay products.

Metal added	$\sum Q$ , cal/g	$\bar{V}_q$ , cal·g/s	$V_q^{\max}$ , cal·g/s	$T_{os}$ , °C
initial	1410	1.146	3.08	700
Ti	1695	1.378	4.84	570
Fe	1774	1.440	9.90	560
Ni	1556	1.265	5.66	580
Cu	1912	1.608	6.00	460
Zn	1575	1.280	7.31	580
alloy	1526	1.241	7.01	580

Table 5: Position of heat release peaks of mixtures of polymeric matrix and aluminum with addition of other metals.

Metal added	Temperature of peak, °C				
	1	2	3	4	5
initial	208	300	396	635	absent
Ti	206	304	385	623	837
Fe	208	307	373	617	849
Ni	206	305	386	626	836
Cu	199	absent	403	615	812
Zn	207	308	382	612	833
alloy	207	303	377	611	841

### Results and discussion

The rapid heating of the polymeric matrix results in its decomposition with the release of oxidizing agents. Being under such conditions, the metal oxidizes with evolution of heat. This process is similar to the initial stage of explosion and combustion of energetic condensed systems, and is a means of controlling the latter.

The obtained results show that all the studied metal powders are more reactive in such processes than aluminum. The temperature of the start of their oxidation is 200 to 240°C lower than that of aluminum, but the maximal heat release rate is higher. The position of peak  $V_q^{\max}$  also shifts to the region of lower temperatures.

The replacement of a part of the aluminum by more reactive metals leads to a significant increase in  $V_q^{\max}$ . The total heat release ( $\sum Q$ ) under other equal conditions increases non-additively by 100 to 440 kcal·g for additives of different metals. The latter can be considered as earlier in time for heating aluminum particles and introducing them into the oxidation reaction, resulting in an increase of the total balance of released heat at a constant time.

### Conclusion

The conducted experiments have established a dependency on the rate of metal oxidation by polymeric matrix thermal decomposition products on its chemical nature. Aluminum was found to be the most favorable from the thermodynamic point of view, however, it is less reactive in the beginning process. It is established that the aluminum reaction can be promoted by adding other more reactive metals, which can serve as a means of controlling the process of explosion and combustion of energetic condensed systems.

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# IMPROVEMENT OF A TURBINE ENGINE START BY AN EXTERNAL OXYGEN-RICH GAS GENERATOR

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## EXTENDED ABSTRACT

The starting of turbine engines is often desired when the ambient temperature and pressure are far below their design values. Under such adverse conditions, the combustion process may fail to produce the energy necessary for accelerating the turbine engine to a steady operational regime, unless additional provisions are provided. In small turbine engines, the limitations in space and weight leave no room for ancillary equipment to assist the starting process, thus making the problem of a reliable starting even more difficult.

The turbine engine starting difficulties are related to the fact that for most small turbine engines, stable and self-sustained operation is obtained only above a certain rotational speed (so-called "idle speed"), which depends on the ambient conditions. As long as the actual rotor speed is lower than the idle speed and the air compression remains weak, the amount of air driven into the engine by the compressor is low and may be insufficient for enabling the combustion process to supply the energy required for acceleration of the engine up to a self-sustained operational regime. This occurs due to an insufficient amount of oxygen in the primary combustion zone. The situation is further worsened by harsh ambient conditions, such as low ambient-air density or pressure.

Various measures to improve the starting of a turbine engine under adverse ambient conditions have been proposed, including a pre-combustor for hot gases production<sup>1</sup>, pre-heating of a combustion chamber with a solid fuel tablet<sup>2</sup>, or the addition of gaseous oxygen to the combustion process<sup>3</sup>, which is in common use.

It is well known that the addition of oxygen into the combustion chamber drastically improves the ignition and starting processes of turbine engines<sup>4,5</sup>. A typical starting system for expendable turbine engines may include a bottle of oxygen at high pressure (200 to 400 bars) and associated accessories for proper oxygen feed and injection, which become deadweight after the completion of the starting process. The density of molecular oxygen in the bottle is 0.25 to 0.50 grams per cubic centimeter, or less than 0.2 g/cm<sup>3</sup>, when taking into account the total bottle volume.

The present paper describes an advantageous method and means\* for enhancing the starting process of a turbine engine by introducing into the combustion chamber hot oxygen gas, or hot gaseous oxidizing species, which are generated from a mass of solid substance. The latter is placed on the exterior of the engine, allowing easy replacement and retrofit, such as that performed when, for example, running an Acceptance Testing Procedure (ATP) on an engine. The added oxygen or oxidizing species improve the ignition process, prevent "oxygen starvation" of the combustion chamber and enable the rotor acceleration to the operational-regime speed.

One possible implementation mode of the proposed method can be achieved by the thermal decomposition of a mass of solid oxidizer; when heated, this material releases hot decomposition products rich in gaseous oxygen or oxidizing species. Another possible implementation mode calls for the release of hot gaseous oxidizing species from the combustion of an oxygen-rich solid-propellant grain. In both implementation modes hot gas, rich in oxidizing species is generated and introduced into the combustion chamber to enhance the ignition and combustion processes and thereby improve the starting of the turbine engine.

The solid oxidizer can be made of a material that contains a large portion of oxygen (e.g. perchlorate, nitrate, peroxide, or chlorate compound) and is manufactured by consolidation, or hot isostatic pressing (HIP) of oxidizer particles in a suitable device. A small amount of an appropriate polymer or co-polymer can be added to enable the compaction of particles.

Screening of solid oxidizers with high oxygen content provides a few potential candidates for selection. One of them is potassium perchlorate (KP). The density of the oxygen inside KP in the solid state is about  $1.0 \text{ g/cm}^3$ , much higher than in the pressurized oxygen bottle and without significant safety, storability, and reliability issues.

Various configurations of the proposed technical solution are possible. A variety of external oxygen-rich gas generators for production of hot gases rich in oxidizing species are proposed. One variant, designed for experimental verification, is presented in Figure 1. It has been shown that it is possible to achieve stable combustion of an oxygen-rich solid propellant, based on a mixture of potassium perchlorate and ammonium perchlorate as an oxidizer.

The proposed device may also simultaneously serve as an igniter for the combustion chamber.

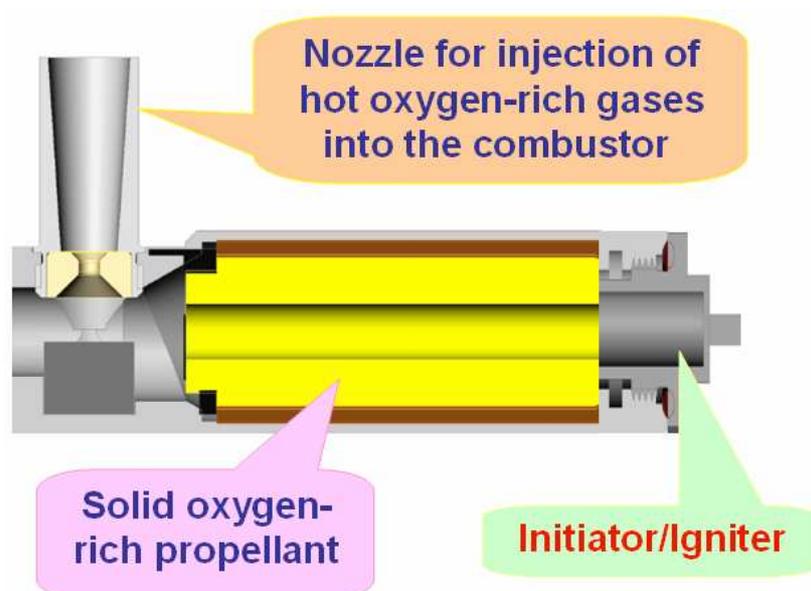


Figure 1: Selected configuration of external oxygen-rich gas generator

The present work includes a discussion of the pros and cons of existing means for improving the starting capability of small turbine engines, an analysis of a possible implementation of the proposed concept, its advantage over other solutions, and a feasibility study: including an evaluation of the amount of oxygen necessary for a reliable starting of a small turbine engine under various conditions.

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## CONVECTIVE BURNING STUDIES OF PYROTECHNIC POWDERS

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### ABSTRACT

This paper describes an experimental study to determine the response of two porous pyrotechnic powders to mechanical impact. A Piston Driven Compaction (PDC) experiment is being used in this study to first gain an understanding of the ignition thresholds of the materials and secondly, to examine the velocity and behavior of the luminous convective flame front as it proceeds through the bed<sup>1-3</sup>.

The pyrotechnic powders are composed of a mixture of ingredients including an oxidizer, a fuel, and a binder. Two pyrotechnic powders are being studied to determine the effect of oxidizer type on the ignition threshold and propagation rate. Potassium perchlorate is the oxidizer used in Pyrotechnic A, and a combination of ammonium and barium nitrate are the oxidizers in Pyrotechnic B.

In this experiment a LEXAN tube is filled with the pyrotechnic powder and a piston is driven into the bed at velocities up to 300 m/sec. The effect of piston velocity on the flame propagation rate can be seen in Figure 1.

The high level of condensed phase products resulting from the combustion of these materials present a challenging contrast to the gas phase dominated energetic materials. These materials are formulated to burn rather than explode or detonate and due to the heterogeneity of the powders, the reaction rates depend on migration or diffusion distances between the particles; hence, the critical need to understand the initiation and combustion behavior under dynamic conditions.

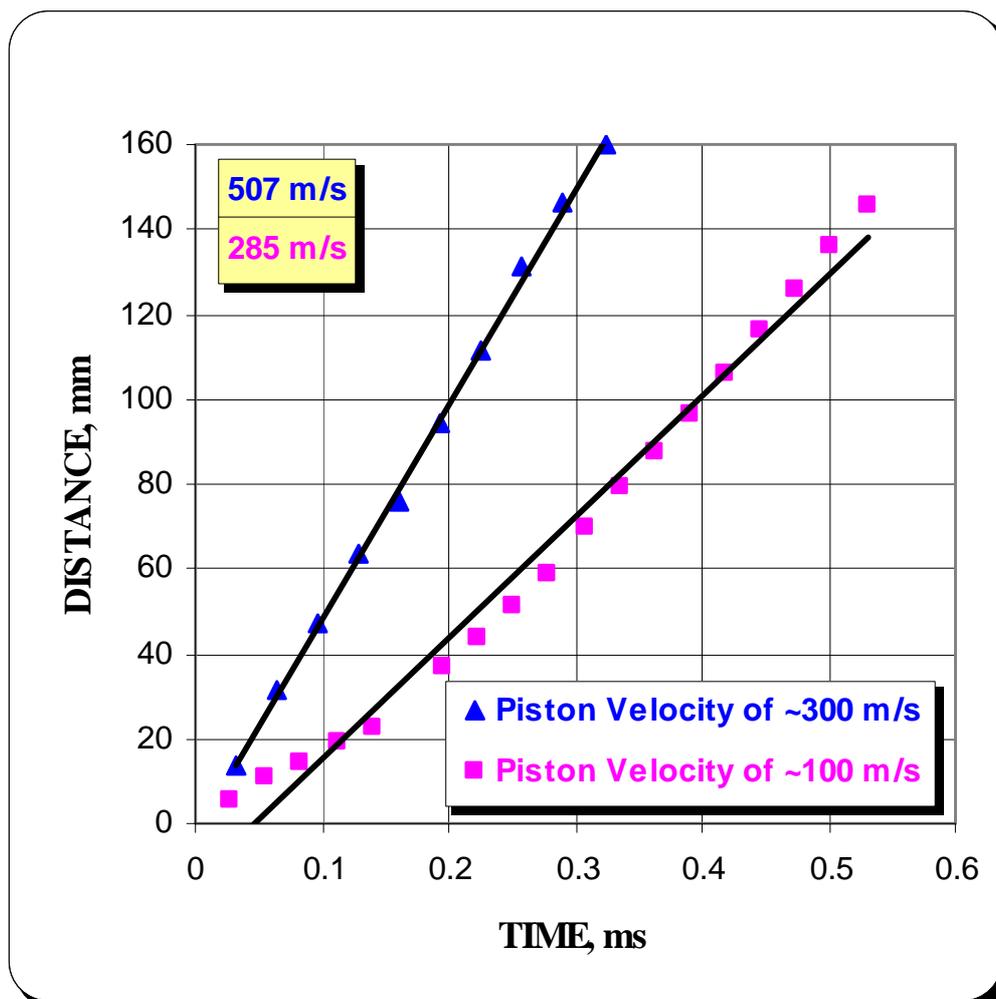


Figure 1: Pyrotechnic A flame propagation rates at two impact velocities.

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## SUPPRESSION OF DUST EXPLOSIONS BY MEANS OF ACTIVE SUPER FAST EXPLOSION SUPPRESSION SYSTEM OF 5 LITERS VOLUME

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### ABSTRACT

#### *Introduction*

In industrial conditions, there are different kinds of installations endangered by explosions of dust-gas mixtures. In order to prevent them from any consequences of potential explosions, active protection systems which use extinguishing powders as the suppressing material are becoming more widely applied. It often happens that the industrial installations are additionally endangered by mechanical vibrations. In the above mentioned conditions, the extinguishing powder tends to agglomerate, making the process of dispersing it in the protected areas more difficult. The presented research was aimed at the development and testing of a super-fast explosion suppression system using smokeless powder or pyrotechnic material as an explosive charge and sodium bicarbonate or water as a suppressing material.

#### *Experimental Apparatus*

The experiments were carried out on a prototype device: – a steel container with a capacity of five liters, closed by means of an aluminum membrane. Below the membrane, there was an exhaust connector pipe with a dispersing head. Inside the container about 1.75 kg of extinguishing powder or water was located. The membrane was ruptured by the explosion of a specially developed smokeless powder charge, located inside perforated steel combustion chamber and mounted over the suppressing material surface. The amount of gases produced during the combustion of the explosive charge was sufficient to perforate the membrane and to disperse the extinguishing material into the protected volume. There was no overpressure inside the container during the watch time. The overpressure was produced only after triggering the system by the signal from the protected volume, sent by the pressure transducer or by a photodiode reacting to a developing flame.

The investigations of efficiency of the developed active explosion suppression system were carried out in the 1.25 m<sup>3</sup> explosion chamber. The explosion was initiated in the corn starch-air mixture of 0.2 kg/m<sup>3</sup> concentration, dispersed pneumatically inside the chamber. The suppression system was triggered at different overpressures inside the protected volume. The dust explosion suppression process occurred as a result of activity of extinguishing powder blown out from the extinguisher, after membrane perforation by means of the compressed combustion products.

#### *Experimental Procedure*

In the course of the research, complex analysis of the system efficiency was carried out. The influence of the parameters and components as:

- type, mass, and shape of explosion charge,
- number, energy, and configuration of the chemical igniters,
- shape of the perforated combustion chamber,
- geometry of the outlet system from the container,
- membrane thickness and its primary incisions,
- shape of dispersion heads,
- value of overpressure inside the extinguisher

was taken under consideration.

The main considered parameters were:

- sensitivity of system response to the developing explosion (in the 1.25m<sup>3</sup> explosion chamber)
- final explosion pressure (in the 1.25m<sup>3</sup> explosion chamber)
- pressure inside the extinguisher

During the research, several sets of tests were carried out. After every set, the obtained results were discussed and new solutions were tested. The above mentioned procedures resulted in the development of an efficient and reliable explosion suppression system.

During the research, the course of overpressure was measured in the explosion chamber and inside the extinguisher.

The extinguishing system was started after reaching a threshold overpressure inside the explosion chamber of 1.25 m<sup>3</sup> volume. The threshold overpressure was counted from the overpressure level resulting from the corn starch dispersing process. The reference overpressure is the sum of the pressure growth from the pneumatic dispersion of the combustible dust (~ 0.24 bar), and the pressure growth from the activation of extinguisher (~0.18 bar). Pressure increases above the reference overpressure resulted from the developing explosion inside the chamber.

The exemplary results of the explosion suppression process are presented in Figure1. Finally, the process of dust explosion suppression by means of extinguishing powder was modeled and the numerical simulations were carried out.

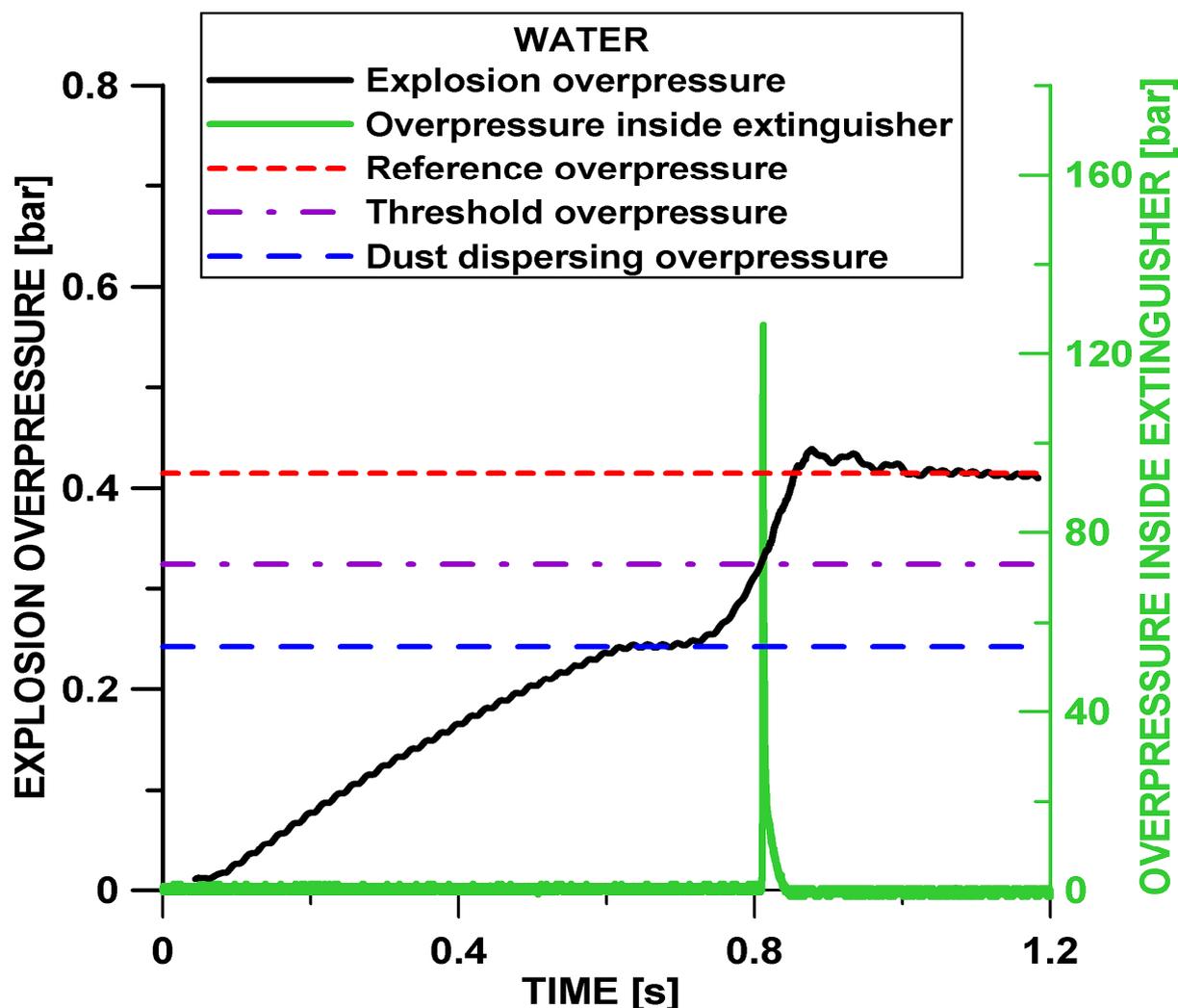


Fig. 1. Course of the overpressure inside the 1.25m<sup>3</sup> test chamber during explosion of the corn starch ( $C=0.2 \text{ kg/m}^3$ ) and inside the extinguisher. Activating threshold overpressure  $\sim 0.08 \text{ bar}$ .

### Conclusions

The final outcome of the work is a suppression system, characterized by high efficiency and reliability, independent from applied extinguishing substance. Research proved also that for dust explosions, water is a very good suppressing medium. In this case there are two suppressing mechanisms: cooling the flame by evaporating water droplets and moistening of unburned dust particles, which delays their ignition and slows down or even stops the flame propagation process.

The tests carried out for containers of 2 dm<sup>3</sup>, 5 dm<sup>3</sup>, and 10 dm<sup>3</sup> volume show that if the system is constructed properly, the dispersing time of the suppressing material is independent of the container volume.

## INTERNAL BALLISTIC SIMULATION OF A 40MM ROUND

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### ABSTRACT

The need arose for reliable simulation software that can be used as a tool to assist in the optimization of the propulsion system of the new medium calibre 40-mm cartridges, which is currently under development at RDM. The 40-mm cartridge functions on the dual chamber blow-down (or hi-low pressure) concept. After ignition, the powder charge cup, containing the propellant in the high-pressure chamber, bursts open at a certain threshold pressure to vent through the connecting holes to the low-pressure chamber. The existing internal ballistic simulation program (0-D thermodynamic model) at RDM was modified to include this dual chamber function.

Firings from an instrumented 40-mm gun and a static test rig were conducted to obtain the relevant data for calibration of the simulation model. The pressure vs. time measurement in the primary chamber and the burst pressure investigation were taken in the test rig, which has an open-air vented secondary chamber. The pressure vs. time in the secondary chamber, combined with muzzle velocity and exit time measurements were obtained during dynamic firings. Different configurations were tested, including the evaluation of different propellants. The simulated pressure curves were then fitted to these experimentally measured curves by adjusting several calibration factors until the best possible fit and correct muzzle velocity was obtained.

The present work reports both the experimental results and the experience gained in the calibration of the software. After completion of this work, a simulation tool will be available, which can be used to expedite new product development in applications making use of the dual-chamber concept.

## **DYNAMICAL SIMULATION OF BURNT ZONE OF METALIZED COMPOSITE PROPELLANTS**

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The method of numerical simulation of the structure and temporal evolution of the burnt zone of metalized composite propellants is developed. The method under consideration falls into three stages.

For the first stage, a simulation of composite solid propellant structure is performed. An analysis of the propellant structure obtained in calculations is carried out. It is shown that the contacting aluminum particles form lengthy clusters in the propellant volume. The role of the clusters in formation of burnt zone structures is discussed. It is shown that aluminum particles inside the clusters can both sinter in particle heating and merge in particle melting.

For the second stage, the thermal conductivity of propellant is calculated. It is shown that there are two types of thermal conductivity of propellant: fast and slow ones. In the fast processes (e.g. combustion), a heat flux goes through the chains of contacted aluminum particles in propellant while a binder and oxidizers do not practically participate in thermal conductivity of propellant. This mechanism of heat exchange takes place in propellant combustion and essentially differs from thermal conductivity of propellant under slow change of propellant temperature. Simulation of temperature fields in propellant both in fast and slow processes is carried out. It is shown that the temperature field has a corrugated shape in heterogeneous propellant even in steady-state conditions.

For the third stage of simulation the thermal, chemical, and mechanical evolution of aluminum particles above the propellant burning surface is considered. The adhesive forces between aluminum particles in the burnt zone result in the formation of coral-like structures above the propellant burning surface. A simulation of the coral-like structures above the burning surface is carried out. A method for modeling the evolution of the coral-like structures under the action of gas-dynamical forces and adhesive forces is suggested. It is well-known that interaction of aluminum particles with each other and gaseous products lead to their agglomeration.

It is shown that the method under consideration allows for calculating aluminum agglomeration in composite propellant combustion. Two kinds of agglomeration are considered: fast agglomeration and slow agglomeration. Calculations of aluminum agglomeration under different conditions of combustion were made. The results of calculation are dynamically represented and compared with the experimental data, obtained by a high-speed digital recording of aluminized composite solid propellant combustion.

## MODELING OF SELF-IGNITION, STRUCTURE AND VELOCITY OF FREE PROPAGATION FLAME OF HYDROGEN AZIDE

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### ABSTRACT

Modeling of combustion processes (such as ignition, flame propagation, and so on) is a powerful method of investigation of combustion kinetics and prediction of behavior of combustion under other initial conditions. Modeling allows us to find out some new effects, which cannot be detected in hard experimental conditions.

In this paper, a mechanism of decomposition of hydrogen azide ( $\text{HN}_3$ ) at low pressure, reproducing the experimental data on velocity of free propagation of  $\text{HN}_3$  flame [1] and on limits (critical pressure and temperature) of self-ignition [2], was proposed and tested. Hydrogen azide is well-known as an endothermic explosion gas for a long time, but there is a lack of understanding about the detailed kinetics of its decomposition.

The CHEMKIN II package was used for modeling. The obtained calculated results were compared with experimental data available in literature [1, 2]. The proposed kinetics mechanism contained 60 reactions for 14 species ( $\text{H}_2$ ,  $\text{H}$ ,  $\text{N}$ ,  $\text{NH}$ ,  $\text{NH}_2$ ,  $\text{NNH}$ ,  $\text{NH}_3$ ,  $\text{HN}_3$ ,  $\text{N}_3$ ,  $\text{N}_2$ ,  $\text{Ar}$ ,  $\text{N}_2\text{H}_2$ ,  $\text{N}_2\text{H}_3$ , and  $\text{N}_2\text{H}_4$ ). The mechanism includes the reactions of hydrazine decomposition [3] and 8 additional reactions with the participation of  $\text{HN}_3$  и  $\text{N}_3$ . The initial stage of  $\text{HN}_3$  decomposition was investigated more carefully. A model of unimolecular decomposition of  $\text{HN}_3$  was created on the basis of existing data of the potential energy surface, and rate constants were obtained as functions of temperature and pressure through Master Equation modeling.

The velocity and structure of a freely propagating flame of  $\text{HN}_3$ -containing mixtures at a pressure of 50 torr and limits of  $\text{HN}_3$  self-ignition were calculated. The calculated width of the zone of intermediate species in  $\text{HN}_3/\text{N}_2$  (30/70 vol. %) flame coincides with the experimental width of luminous zone of the same flame [1]. The analysis of flame structure of  $\text{HN}_3/\text{N}_2$  and  $\text{HN}_3/\text{Ar}$  mixtures shows that the maximum temperature in front of the flame exceeds the calculated adiabatic equilibrium flame temperature by up to 160-650 degrees if the concentration of  $\text{HN}_3$  in mixture exceeds 50%. This phenomenon is known in literature for hydrocarbon gaseous flames as super adiabatic flame temperate (SAFT).

The developed mechanism can be used for describing the combustion and thermal decomposition of gaseous or condensed combustible systems (for example, 5-aminotetrazole), containing  $\text{HN}_3$  as a main or intermediate product.

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# FACTORS AFFECTING COMBUSTION BEHAVIOR OF METAL POWDERS IN FUEL-RICH PROPELLANTS FOR RAM ROCKETS: A FRESH LOOK

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## EXTENDED ABSTRACT

Fuel-rich solid propellant based ramjet rockets offer a combination of higher range, high speed, continuous power and compactness. They have a specific impulse comparable to liquids, while retaining other advantages like simple design, self-throttling etc. of solid propellants. Invariably, fuel-rich solid propellants for ram-rockets use high metal contents (>30%). Combustion of metalized fuel-rich propellant in ramjet mode uses a primary chamber, where fuel-rich propellant is pyrolyzed, or partially burnt to give a fuel-rich gaseous product, which is expelled to undergo full combustion in the secondary chamber with ram-air coming from air-intakes. Since fuel-rich solid propellants have high metal powder loading in an organic binder matrix, combustion mechanism of fuel-rich propellant is affected to a large extent by the combustion of metal powder.

Three major aspects for combustion of metal powders in ram rockets consist pyrolysis of fuel in primary chamber, good expulsion efficiency, and turbulent mixing. For maximum specific impulse ( $I_{sp}$ ) in the secondary chamber, propellant should undergo pyrolysis with limited combustion of metal components, high expulsion efficiency and initiation in the secondary chamber at stoichiometry leading to the highest possible combustion temperature. Overall tailoring of the propellant formulation needs a selection of metallic fuel, a compatible binder system, favorable geometry of propellant in the primary chamber, and very efficient combustion in the secondary chamber.

Selection of metal for fuel-rich propellants has several governing criteria. In general, oxidizer efficiency is highest for fluorine mono-oxide, followed by fluorine, trifluorine nitrogen, and ozone followed by oxygen. Accordingly, the best fuels are lithium, beryllium, boron, aluminum and magnesium. However, in terms of volumetric heat of oxidation, boron is much superior to the other metal powders and, hence, it is the most versatile metallic fuel used in fuel-rich propellant for ramjet application. This paper reviews and analyzes factors affecting combustion of metal powders in fuel-rich propellants for ram rockets.

Boron has very high heat of oxidation by weight, as well as by volume and the reaction  $2B + 3/2 O_2 = B_2O_3$ , produces an enthalpy value of 58 kJ/kg. However, boron should be expelled out of the primary chamber in unburnt condition, so that maximum energy can be extracted by oxidation in the secondary chamber. Boron expulsion efficiency is governed by the nature and quantity of the binder, which makes expelled boron loose, hard, or fluffy. When boron particles are heated to 1800-2000 K, they are ignited and burn with brighter luminosity. Generally, two combustion phases are identified. First is the burning of boron in the presence of semi-protective oxide coating, and the second is prolonged combustion of a pure metal surface with formation of sub-oxides and formation of final products of combustion. Due to low thermal conductivity, boron poses a problem of ignition. Two mechanisms of combustion of boron particles have been suggested in literature<sup>1-5</sup>. The first is oxygen diffusion in metal through liquid oxide layer, and the second boron dissolution and diffusion in oxide layer. Experimental observations support the second combustion mechanism, where boron dissolves in liquid oxides, forming BO, which is attacked by gaseous molecules of  $O_2$  and  $H_2O$  at the gasliquid interface. This forms  $BO_2$  and HOBO;  $B_2O_3$  evaporates from the surface. The main governing mechanism for boron combustion is a product of pressure (P in atm) and particle size (d in mm). It is observed that for  $P \cdot d < 75$  atm.mm, the combustion of boron is kinetically controlled, whereas for higher values of the product, the combustion is limited by oxygen diffusion. Burning the same propellant composition at high pressure results in higher amounts of residue in the primary chamber. Coating boron particles by oxidizer like ammonium perchlorate can increase reaction heat. It improves the condensed phase reaction and increases the burning rate in low-pressure conditions<sup>2</sup>. On further investigation, three

different types of structures have been observed in SEM study of boron combustion surface. The formation of a reaction-less segment, where gas phase reaction is confined is observed<sup>7</sup>. Another approach could be to assess boron-based, fuel-rich propellants using the parameters including: energy input, combustion efficiency, and propulsive performance. It is observed that low oxidant with high boron content is best from an energy point of view at low pressures, but complete combustion is difficult to achieve<sup>8</sup>.

Magnesium is another metallic particle, which is investigated widely for application in fuel rich propellants. However, below 700 K magnesium has a protective oxide layer, which thickens and loses its inhibition properties on a rise in temperature. Combustion of magnesium particles shows several features like irregular particle combustion and retention of irregular shape during combustion, metal jetting in initial stages of combustion, gradual ignition without flash in low oxygen concentration, rotation of irregularly shaped particles and tremendous rise in volume, resulting in cracking the oxide layers during heating.<sup>9-14</sup> Desh Deepak et al<sup>15</sup> have tested magnesium-based fuelrich propellant containing 40% magnesium, 26% HTPB and 34% ammonium perchlorate in a connected mode of primary and secondary chambers. They changed the primary nozzle parameters to conduct a series of tests and considered the rise in temperature as an indication of the efficiency of the propellant in the secondary chamber. It was observed that length of secondary chamber can be reduced with more air inlet points, but it leads to sharp fall in temperature along the chamber.

In Al-Mg alloy, magnesium is generally coupled with aluminum in solid propellant formulations. It is observed that use of magnesium and aluminum together changes combustion mechanism completely. No accumulation of metal at the surface is observed and no trace of metal dripping is seen from burning surface of fuel-rich propellants. This indicates higher efficiency of magnesium-aluminum powder as compared to pure magnesium powder in the fuel-rich propellants<sup>16</sup>.

Zirconium (Zr) and titanium (Ti) are attractive as fuel for ramjet rockets because of the advantages of solubility of their oxides in the molten metals and moderate ignition temperature, thereby ensuring sustained combustion, even at very high metal loading. Zr and Ti have the potential to offer high volumetric impulse due to a much higher density than Al and Mg. However, during initial phase of development, chances of observing high mean molecular weight of combustion product negatively affected their use in fuelrich propellants. But for low air-to-fuel ratios, higher performance from Zr-based fuelrich propellant is expected. Theoretically, 60% Zirconium in a double base matrix is capable of giving flame temperature of about 3400°C.

We have conducted combustion studies on Zr-based fuel-rich propellants in the primary chamber. A composition with 50% Zr loading produced a pressure exponent of 0.6 in the pressure range of 30-70 kg/cm<sup>2</sup>. A similar trend was obtained with HTPB based fuel-rich propellant. For Zr loading of 65%, the calorific value was found to be comparable to Zr loading in a double-base matrix. The pressure exponent was found to be above 0.6 in the pressure range of 30-110 kg/cm<sup>2</sup>. As loading of Zr is increased, formation of long chain agglomerates of fused zirconium oxide caused a short circuit of the burn rate measurement, using nichrome wires. DSC/TG studies indicate that propellants undergo a two-step decomposition and temperature decrease with increasing percentage of zirconium. FTIR revealed that acetone soluble organic materials remain even after combustion of propellant in the primary chamber. The main functional groups identified are -OH, -NH, aliphatic =CH and -C=O (carbonyl). Zr based formulations show lower values of low-pressure combustion limits and sustained stable combustion is observed with 30% Zr even up to 10 atmospheric pressures compared to corresponding aluminized composition.

Although different metal powders have been investigated by various researchers for assessing their combustion behavior in ramjet and scramjet applications, it is not the propellant alone which governs the energy output and utility of the ingredients. Single metal fuel in the propellant formulation cannot be a panacea for all the combustion problems of fuel-rich solid propellants in ramjet and scramjet modes.

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# HIGH-NITROGEN-METAL COMPLEXES AS BURNING-RATE MODIFIERS FOR THE ALUMINUM-WATER PROPELLANT SYSTEM

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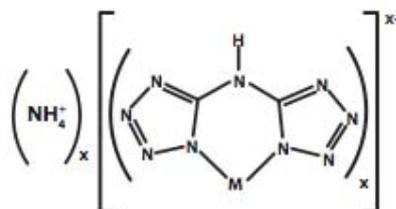
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## ABSTRACT

The reactions of electropositive metals, such as aluminum, with water have long been utilized in explosive and propellant formulations, but until recently this has mostly been limited to the water formed as a product gas from the decomposition of another energetic system. Recently, however, with the increased availability of nano-particulate materials, the direct reaction of nano-aluminum (nAl) with water as an oxidizer has been investigated as a propellant system due to high reaction temperatures and the production of hydrogen as the primary gaseous species. This system could be useful for intra-planetary travel where non-terrestrial water is harvested for the oxidizer.

Here we present the study of nAl, mixed at a stoichiometric ratio with water ( $\Phi = 1$ ) with the highly water soluble metal complexes of bis(tetrazolato)amine (BTA) added at 5, 15, 30 and 50 wt% in the case of FeBTA and 5 and 15 wt% in the case of NiBTA and CoBTA. The basic structure of the BTA complexes is shown below where M = Fe, Ni or Co, and  $x = 3$  for Fe and Co and  $x = 2$  for Ni. The particle size of nAl studied was primarily 38 nm with various



studies with the particle size of 80 nm.

The FeBTA at a loading of 15 wt% gave the highest burning rate enhancement (4.6x at ~6.8 MPa), while retaining a low pressure exponent (0.21 compared to 0.24 for nAl/H<sub>2</sub>O). At 15 wt% the Ni and Co increased the burning rate, but also increased the pressure exponents.

The work presented here began as a method for the combustion synthesis of metal-metal oxide composites (cermets), but it was found that even at relatively low levels of MBTA loading, a dramatic increase in the burning rate of the nAl-H<sub>2</sub>O system was observed, thus providing another degree of engineering control for propellant uses. The primary focus of this paper will be upon burning rate modification of the nAl-H<sub>2</sub>O system with these materials and with a secondary focus on the material characterization of the cermets produced.

## COMBUSTION OF BIMODAL AL AND ICE MIXTURES

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### ABSTRACT

The combustion of aluminum with ice is studied using various mixtures of nanometer and micron sized aluminum particles as a means to generate high temperature hydrogen for propulsion and power applications. Bimodal distributions are of interest in order to vary mixture packing densities and nascent alumina concentrations in the reactant mixture. The effects of the bimodal distributions on ignition, combustion rates, and combustion efficiency are investigated in strand experiments at constant volume and constant pressure and in small-scale (1.5" diameter) combustion chambers with center-perforated propellant grains. The aluminum particles consist of nanometer-sized particles with a nominal diameter of 80 nm and micron sized particles with a nominal diameter of 2 micron. In addition, various additives dissolvable in the water, including ammonia borane and hydrogen peroxide, are examined. Burning rates from near atmospheric pressure to 2000 psi and chemical efficiencies based on percent water conversion to hydrogen are presented. From the small scale motor tests, thrust, C\* and Isp efficiencies are provided. From these results, mechanistic issues of the combustion process are discussed.

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## THERMAL DECOMPOSITION BEHAVIOUR OF AMMONIUM NITRATE AND CARBON MIXTURES

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### ABSTRACT

Since ammonium nitrate (AN) has been used as a suitable oxidizer because of its smaller impact to the environment, ammonium nitrate and combustible mixtures are expected as a combustible composition for propellants and air bag inflators of the next generation. Thermal decomposition behaviour of AN and carbon mixtures were experimentally investigated and the influence of the physical characteristics of carbon was discussed. In this paper, four kinds of carbon which have different physical characteristics were used; such as, activated carbon, graphite, carbon nanotube, and fullerene.

To understand the influence of physical properties of carbon on the thermal decomposition behavior of AN and carbon mixtures, Raman spectroscopic analysis, differential scanning calorimetry (DSC), thermogravimetry-differential thermal analysis with infrared spectrometry (TG-DTA-IR), thermogravimetry-mass spectrometry (TG-MS), and flash pyrolysis mass spectrometry (Py-MS) were carried out. From the result of DSC scanning analysis, AN mixed with activated carbon and AN with carbon nanotube showed a violent reaction after melting of AN; whereas AN mixed with graphite, and AN with fullerene showed a mild exothermic peak, the same as shown for pure AN. From the result of TG-IR, carbon dioxide was determined more remarkable for AN and activated carbon, and AN and carbon nanotube mixtures than other mixtures. TG-MS spectrum of decomposition gases for AN and activated carbon, and AN and graphite mixtures showed a different pattern at a heating rate of 100 K/min with TG-MS, but they showed a similar spectrum when instantaneous heating with a flash pyrolyzer was performed. It is concluded that AN mixed with carbons with low crystallinity showed a violent reaction after melting. AN mixed with carbons with high crystallinity showed the same behavior as pure AN. Thermal decomposition behavior of AN/carbon mixtures was hardly influenced by the crystallinity of carbon when heated instantaneously.

## COMBUSTION CHARACTERISTICS OF HAN SOLUTIONS

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### ABSTRACT

Hydroxyl ammonium nitrate (HAN) based liquid propellant has been investigated as a candidate for the monopropellant of reaction control system (RCS) of satellites as an alternative to hydrazine. The propellant which contains ammonium nitrate (AN), methanol, and water has moderate burning characteristics, sufficiently low freezing temperature, high density and low toxicity, and its calculated density\*Isp is 70% higher than hydrazine. In a previous study, the combustion characteristics of the propellant were reported by Katsumi et al.<sup>1</sup> The composition of the propellants are HAN/AN/Water/Methanol = 95/5/8/0 (Control), and 95/5/8/21 (SHP163) in mass ratio. SHP163 is the candidate for monopropellant and includes methanol content at the stoichiometric ratio against "HAN+AN". However, the inclusion of AN or methanol in the propellant can influence and complicate the combustion mechanism.

In this paper, the interest is focused on the combustion characteristics of HAN-water solution. The sample solutions whose HAN concentrations were 95mass%, 85mass%, 80mass%, 77.6mass%, 64mass%, and 50mass% were prepared. Linear burning rates of these HAN-water solutions in the glass tube were obtained as functions of the mass concentration of the HAN and of pressure. The result is shown in Figure1. The burning rate of the 95mass% HAN solution is equal to the HAN crystal. This fact shows that the combustion mechanism of the 95mass% solution might be the same as the HAN crystal. The burning rate has a peak at around 80mass%. In the case of a high burning rate, more than 100mm/s, the burning rate depends hardly upon pressure. The mechanism of this characteristic will be presented.

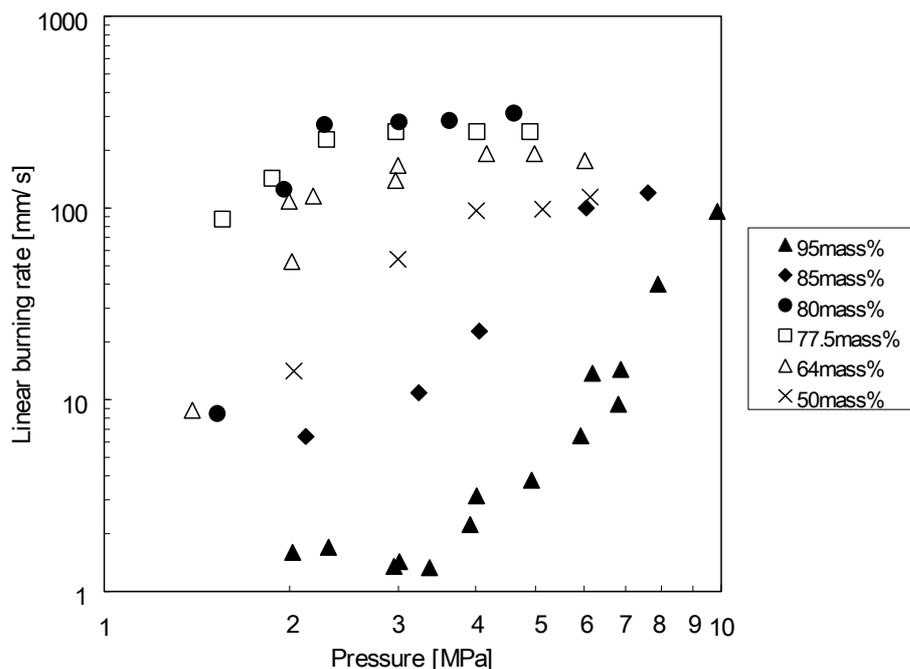


Figure 1: Linear burning rate of the HAN-water solutions

Further, the observation with the high-speed video camera (250fps~), the temperature measurements with fine thermocouple, and the measurement of the burning rate as a function of the diameter of the glass tube and pressure were conducted. In the observation, the characteristics of each combustion wave at 3MPa were obtained in a glass tube. In general, there were three phases in the combustion wave: liquid, two-phase and gas-phase. The gas-phase is brown, which may be evidence of  $\text{NO}_2$  generation. In the case of the 95mass% HAN-water solution, there are both fine and transparent bubbles (less than 1mm diameter) and large and brown bubbles (more than 2mm diameter) in the two-phase region. The interface between liquid and two-phase region vibrates strongly. In the case of the 85mass% solution, two combustion modes appear alternately. The first mode is that there are fine and transparent bubbles in the liquid phase above the interface between the liquid and gas-phase, and the burning rate is slow, less than 3mm/s. The second mode follows the first one. The brown bubbles grow very rapidly, and the burning rate was very high, more than 100mm/s. The first mode maintains for 500~600ms, and the second mode for about 100ms. The burning rate of the 85mass% solution is 10~20mm/s in overall burning. In the case of 80mass%, the brown bubbles grow quickly, and new bubbles generate in the vicinity of the large bubble and grow very fast. This manner supports an extremely high burning rate, more than 100mm/s. In the case of 77.6, 64 and 50mass%, the phenomena were nearly same as the case of 80mass%. This fact may indicate that HAN concentration changes the structure of the combustion wave, and the structure character governs the burning rate. Combustion mechanism of HAN-water solution based upon these experimental results will be discussed in detail.

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## EFFECT OF REACTION KINETIC SCHEMES ON GRAPHITE ROCKET NOZZLE EROSION RATES

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### ABSTRACT

Understanding the thermo-chemical erosion of graphite nozzles is an important step in designing high-performance solid-propellant rocket systems. The propulsive performance of solid rocket motors experiences degradation due to the erosion of the exposed internal surface of the rocket nozzle. Generally, the AP/HTPB composite propellants used in the rocket motors generate high concentrations of oxidizing species such as H<sub>2</sub>O, OH, and CO<sub>2</sub> in the combustion products at temperatures ranging from 2,800 to 3,100 K. The combined high temperature and high oxidizing species concentration provide detrimental conditions for the graphite material erosion via heterogeneous chemical reactions. Recently, a comprehensive numerical program called graphite nozzle erosion minimization (GNEM) code was used for prediction of graphite nozzle throat erosion rates as a function of pressure and propellant composition. The GNEM code is a comprehensive predictive code for simulation of compressible turbulent reacting boundary layer flows. The GNEM code uses a second-order k- $\epsilon$  turbulence model to achieve closure of the turbulent flow in the core region. In the near-wall region, a wall function based approach by using the modified Van Driest formula is utilized for calculating the turbulent viscosity. From this study, it was found that the magnitudes of nozzle throat erosion rate strongly depend on the chemical kinetic scheme when non-metallized solid propellants were used under relatively low operating pressures ( $P < 8$  MPa). However, at higher pressures, the nozzle throat erosion process was found to depend more on the rate of diffusion of oxidizing species from the core region to nozzle surface. For metallized solid propellants with higher flame temperatures, the nozzle surface temperature was calculated to be much higher; thereby, the thermo-chemical erosion of nozzle was governed by the diffusion process. This observation stresses the importance of using more accurate and definitive kinetic parameters for graphite oxidation reactions, especially at conventional rocket motor operating pressures.

In order to accomplish this objective, a comparative study of the heterogeneous reaction kinetic schemes has been carried out. The graphite oxidation mechanism has been studied by various research groups over many years. However, heterogeneous reaction kinetics should be coupled with the realistic simulation of turbulent reacting boundary layer flow to answer the pertinent questions related to graphite nozzle throat erosion. Therefore, in this work, the high-temperature semi-global reaction kinetics recently developed by Culbertson et al. will be coupled with the GNEM code and compared with the lower temperature reaction kinetics established earlier by Libby-Blake and Bradley et al. This analysis will provide improved prediction of the nozzle throat erosion rates and quantify the significance of chemical kinetics in the nozzle throat erosion process. In addition, it is also important to identify the most reactive oxidizing species under the rocket motor operating conditions. This information will greatly aid in the nozzle throat erosion minimization techniques and design of advanced solid rocket propellants. Therefore, the second objective of this study is the implementation of elementary reaction kinetics obtained by Lin et al. with quantum chemical calculations into the GNEM code to establishing the importance of oxidizing species in the thermo-chemical erosion of graphite nozzles. The predictions from the GNEM code will be compared with the available experimental data and discussed in the full paper.

## COUPLING OF TRANSIENT HEATING AND INDUCED STRESSES COMPUTATIONS IN GRAPHITE NOZZLE MATERIALS

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### ABSTRACT

Synthetic graphite materials (*e.g.*, G-90 grade manufactured by Metaullics, Inc.) are typically composed of filler particles in a binder matrix. Though macroscopic properties of high-density graphite are approximately isotropic, graphite nozzle erosion has been observed to occur preferentially around filler particles in the binder material.[1] This places an additional importance on the effect of binder material behavior on nozzle-throat erosion rate. Under solid-rocket motor operating conditions, nozzle materials undergo rapid heating as the propellant products flow over the surfaces. The nozzle throat experiences the most intense heating since the mass flux, and therefore heat-transfer rate, is the highest in this region. The rapid heating of the nozzle material generates high thermal stresses and may induce microstructure cracking in the binder material of synthetic graphite. The fracture of binder material can lead directly to bulk material removal, as well as increased reactive surface area for thermochemical attack by oxidizing species.

The effects of induced thermal stresses and the contributions to the overall nozzle-throat erosion process is the focus of this paper. The study represents a strong coupling of the fluid flow behavior of the propellant products through the nozzle with the mechanical response of the nozzle material under severe convective heating by the flow. First, the heat-transfer rates to the nozzle material are calculated using the graphite-nozzle erosion minimization code (GNEM)[2,3] and Bartz correlation[4] for solid-propellants burning under a range of chamber pressures from 6.9 to 48.3 MPa. The GNEM code uses a second-order  $k-\epsilon$  turbulence model to achieve closure of the turbulent flow in the core region. In the near wall region, a wall function based approach by using the modified Van Driest formula is utilized for calculating the turbulent viscosity. The convective heat fluxes to the nozzle surface are determined at all axial locations by using GNEM code. The calculated heat-transfer rates are used as boundary conditions for a brittle material damage model to predict induced stresses and graphite material response.

The combustion products of solid propellants contain oxidizing species like H<sub>2</sub>O, OH, and CO<sub>2</sub>, which react with the graphite nozzle surface and result in thermo-chemical erosion of the rocket nozzle. In order to react with the solid graphite surface, the gas molecules adsorb onto the active sites of the graphite surface and dissociate upon adsorption. In the dissociative adsorption process, the rate of chemical reaction strongly depends on the concentration of active sites on the graphite surface, which is a function of exposed surface area. This area is the total area including those generated from the induced thermal stresses. Therefore, the surface temperature and surface area of the graphite nozzle are two major parameters for quantifying the graphite nozzle-throat erosion rates. This additional area evaluated from the material model is used in the GNEM code to predict the nozzle erosion rate. The calculated erosion rate together with the heat flux and surface temperature distributions along the nozzle surface provide the required boundary conditions for the material-damage model simulation. Damage evolution in the graphite nozzle is in turn assessed by the combined effects of shear and thermal stresses.

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# COMPATIBILITY OF AMMONIUM DINITRAMIDE (ADN) WITH POLYMERIC BINDERS STUDIED BY THERMOANALYTICAL METHODS

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## ABSTRACT

Ammonium dinitramide (ADN) is a promising energetic oxidizer actively being considered as a potential replacement for ammonium perchlorate (AP) and ammonium nitrate (AN) in composite propellants and explosives. The study of chemical compatibility of ADN with polymeric binders is of prime importance for a thorough understanding on ageing, shelf-life and safety aspects during their production, storage, and use. The compatibilities of ADN with energetic and inert binders were studied in order to detect any interaction between the contact materials. Differential scanning calorimetry (DSC) and dynamic thermogravimetric analysis (TGA) methods according to STANAG No. 4147 were used for the compatibility test measurements. Glycidyl azide polymer (GAP) and a copolymer of GAP and poly(bis(azidomethyl)oxetane) (GAP-PBAMO (80:20)) were used as energetic binders, while hydroxylterminated polybutadiene (HTPB) and polyethylene glycol (PEG1500) were used as inert binders. Both TGA and DSC analyses results of ADN with GAP, GAP-PBAMO, and HTPB showed that these mixtures are highly compatible. TGA measurements on the compatibility of ADN with PEG1500 indicated that these were incompatible, while DSC measurements on the interaction between the two indicated a small degree of incompatibility. Since the compatibility of ADN + PEG1500 could not be confirmed by the TGA and DSC methods, detailed kinetic analyses using a variable heating rate (Kissinger method) were carried out. The activation energy ( $E_a$ ) was lowered from 173.2kJ/mol for ADN to 86.8kJ/mol for the admixture, while the rate constant value for the mixture was several orders of magnitude higher than that for ADN. The lowering of the activation energy and the higher rate constant values obtained for ADN + PEG1500 admixture suggest that these are incompatible.

Table 1: Summary of STANAG dynamic TGA and DSC results on the compatibility of ADN with polymeric binders

	<b>GAP</b>	<b>GAP-PBAMO</b>	<b>HTPB</b>	<b>PEG1500</b>
<b>ADN (TGA)</b>	Obs.WL =13.2% Calc.WL =16.4% Obs < Calc	Obs.WL =13.2% Calc.WL =18.7% Obs < Calc	Obs.WL =3.9% Calc.WL =14.9% Obs < Calc	Obs.WL =39.2% Calc.WL =14.6% Obs > Calc
	COMPATIBLE	COMPATIBLE	COMPATIBLE	Difference = 24.6 INCOMPATIBLE
	<i>* Obs.WL= Observed weight loss; Calc.WL=Calculated weight loss</i>			
<b>ADN (DSC)</b>	$T_{dE}=174.3^{\circ}\text{C}$ $T_{dM}=177.7^{\circ}\text{C}$ $T_{dM} > T_{dE}$	$T_{dE}=174.6^{\circ}\text{C}$ $T_{dM}=181.1^{\circ}\text{C}$ $T_{dM} > T_{dE}$	$T_{dE}=174.3^{\circ}\text{C}$ $T_{dM}=181.7^{\circ}\text{C}$ $T_{dM} > T_{dE}$	$T_{dE}=174.3^{\circ}\text{C}$ $T_{dM}=158.1^{\circ}\text{C}$ $T_{dM} < T_{dE}$
	COMPATIBLE	COMPATIBLE	COMPATIBLE	Difference = 16.2 Degree of INCOMPATIBILITY
	<i>* <math>T_{dM}</math>= Peak temperature of ADN + binder; <math>T_{dE}</math> = Peak temperature of ADN</i>			

In the present study a good agreement was observed in the conclusions drawn from DSC & TGA experiments on the compatibility of ADN with GAP, GAP-PBAMO, and HTPB. Only PEG1500 gives a variable result for the different test methods. Kinetic analyses were performed on the ADN + PEG1500 binary systems. The binary systems of ADN with GAP, GAP-PBAMO, and HTPB are compatible, while the ADN with PEG1500 system is incompatible. A detailed discussion on the experimental results of the compatibility of ADN with polymeric binders will be presented in this paper.

**Keywords:** activation energy, ammonium dinitramide, compatibility, DSC, energetic binders, kinetics, TGA, thermal decomposition.

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## BORON-RICH FUELS FOR GAS GENERATORS AND PROPELLANTS

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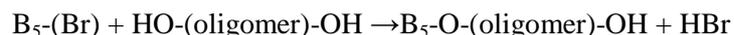
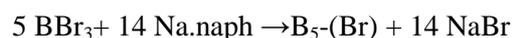
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### ABSTRACT

Metals can provide energy for fuels in excess of that provided by hydrocarbons, making them attractive for use in gas generators and propellants. By using the metals in the form of ultrafine metal particles, both burning surface area and reactivity can be greatly enhanced, which explains recent interest in aluminum nanoparticles. However, because of its high gravimetric and volumetric heats of combustion, boron may be a better choice than aluminum for volume-constrained systems. Unfortunately, experience has proven that B particles are often difficult to burn efficiently due to various physical-chemical phenomena that occur during combustion. These phenomena can be roughly divided into two problem areas. The first area comprises the oxide layer around the particle and how it affects ignition and combustion. Aging of the bare metal particles produces a surface oxide layer that not only reduces the energy available, but acts as a barrier to ignition. Once ignition does occur, an additional liquid oxide layer is produced ( $B_2O_3$ ) which leads to a reduction of the reaction rate. Once the local temperature gets close to the boiling point of  $B_2O_3$ , the oxide layer starts to evaporate. The evaporating oxide layer establishes another barrier, reducing the oxidant diffusion (oxygen) to the boron surface and further limits the reaction rate. The second area comprises the problem of agglomeration. Because of their small size, nanoparticles offer a very large total burning surface which can accelerate burning of the fuel. However, besides the oxide layer problem, boron nanoparticles have an increased agglomeration tendency not only during dispersion in a fuel, but during ignition and combustion. This agglomeration of boron particles can lead to incomplete combustion. The larger the agglomerates get, the longer the time required for complete combustion. Any unburned boron particles will diminish performance of the platform of interest.

As a solution to this problem, we investigated previous in-situ polyolefin coating processes for boron nanoparticles. While this approach helped to prevent the aging of the particles, the agglomeration problem was not completely eliminated. In this paper, we study a different approach to create a boron-hybrid energetic binder, where boron atoms are directly incorporated in the polymer structure. While organo-borane molecules were studied many years ago, they were difficult to handle and use since they are pyrophoric and toxic. This research aims at producing compounds that address the safety and handling issues of organo-borane compounds, the aging problems of metal nanoparticles, and the ignition and combustion difficulties of boron due to the oxide layer. To achieve these objectives, we relied on a direct chemical synthesis approach. Modifying a synthesis scheme recently published in open literature, we prepared boron-rich, metal-hydroxy-terminated glycidyl azide polymer (GAP) composites using a reduction process starting from a halogenated boron precursor. By this process, low molecular weight diol molecules have been attached to clusters of five boron atoms:



The resulting organo-boron compound is an oily product that could easily be mixed, dispersed, and copolymerized within a polyurethane-based polymer binder. The characterization of the reaction products using <sup>11</sup>B NMR confirm that the desired structures were obtained. Different types of oligomers were tried and GAP based polyurethane binders were prepared with up to 20% of their contents with the synthesized molecules. Strand burner measurements and other thermal characterization have been conducted and the results were compared to non-modified GAP formulations.

## CHARACTERIZATION AND COMPARISON OF TWO HTPE PRE-POLYMERS

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### ABSTRACT

Composite rocket propellants with improved insensitive munitions (IM) characteristics can be produced using cross-linked Hydroxyl Terminated Polyether (HTPE) binders, which are potential alternatives to Hydroxyl Terminated Polybutadiene (HTPB) compositions. Some characteristics of propellants based on this binder have been presented, but there has been no report on the comprehensive chemical characterisation of the pre-polymer. In this paper, we report a preliminary study on the characterization and comparison of two different HTPE pre-polymers, one synthesised in our laboratory and the other obtained from a commercial source. Analyses were carried out to determine molecular weight, molecular structure, glass transition temperature (T<sub>g</sub>), melting temperature (T<sub>m</sub>), impurities, and density. These properties were determined by using a range of techniques including: Size Exclusion Chromatography (SEC), Nuclear Magnetic Resonance (NMR) Spectroscopy, Differential Scanning Calorimetry (DSC), Gas Chromatography-Mass Spectrometry (GC-MS), and Fourier Transform Infra-red (FTIR) Spectroscopy.

## UNIFORM AND HIGH YIELD CARBON NANOTUBES WITH MODULATED NITROGEN CONCENTRATION FOR NANOENERGETIC MATERIALS

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### ABSTRACT

It is well known that pure poly-nitrogen systems are meta-stable. Polymeric nitrogen was theoretically predicted in 1992 and experimentally synthesized in 2004, but under high temperature and pressure, as well as mechanical confinement, which is not desirable for practical applications of polymeric nitrogen used as an energetic material. So far, no one has managed to synthesize one that remains stable at ambient temperature and pressure. Recently, a theoretical study shows that when a polymeric nitrogen chain is encapsulated in a carbon nanotube (CNT), it will be stable at ambient pressure and room temperature [see ref: About-Rachid H. et al., Phys. Rev. Lett. 2008; 196401:100], which makes CNTs new promising materials in nano-scale energetic materials. In this study, we report a systematic study of multi-walled carbon nanotubes with different nitrogen-doping produced by chemical vapor deposition (CVD). The morphological and compositional changes of N-doped carbon nanotubes (N-doped CNTs) were characterized by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). Figure 1 shows SEM and TEM images of N-doped CNTs. The detailed investigation of N-doped CNTs will provide a route to obtain evidence of the above theoretical prediction.

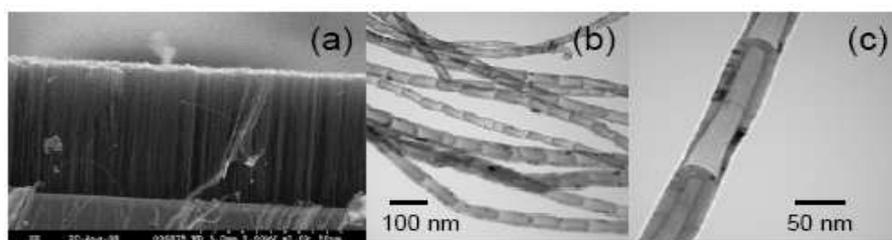


Figure 1: SEM and TEM images of N-doped carbon nanotubes synthesized by CVD. (a) Showing aligned CNTs grown on silicon substrate, (b) and (c) showing typical TEM images of the bamboo like structured nitrogen-doped CNTs

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## **REDUCED AGGLOMERATION RESULTING FROM NICKEL COATING OF ALUMINUM PARTICLES IN SOLID PROPELLANTS**

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### **ABSTRACT**

Reduction in aluminum agglomeration is the main motivation for the use of nickel-coated particles. This paper will present the effect of nickel-coating of aluminum particles on the combustion of aluminized solid propellants, with an emphasis on the agglomeration phenomena.

Previous works indicated that reducing the time and temperature of ignition of aluminum particles should result in reduced agglomeration. Nickel-coated aluminum produced via a unique method developed in-house has demonstrated a substantial decrease of ignition temperature and time versus regular aluminum powders, both in air and in nitrogen atmospheres. The exothermic reaction between nickel and aluminum could not provide the sole reason for the promotion of ignition, since the small fraction of nickel (5% mass-wise) limits the total reaction heat evolved. Experiments show that nickel-coated aluminum powders exhibit violent ignition at about 1000K, whereas regular aluminum powders do not ignite even at temperatures as high as 1500K. Nickel-coated aluminum was less inclined to form large agglomerates than regular aluminum powders.

The propellants tested were composed from 15% aluminum, 55-65% AP, and 30-20% HTPB, respectively (mass-wise), at various particle diameters. Comparison was made between propellants of the same composition, prepared at the same time and in the same conditions, differing only in the aluminum component – regular (as received) or nickel-coated. Experiments have been conducted in both pressurized (up to 32atm) and atmospheric environments, with an initial propellant temperature of 15 – 28°C. A fast-view video camera, *FASTVIEWER-XL* of FastVision, was used during the experiments, taking pictures at a rate of 1000-3000 fps. A windowed, pressure-controlled strand burner was used. A vast amount of photos were reviewed. The main and most evident finding has been that the use of nickel-coated aluminum causes a substantial decrease in agglomeration with respect to the use of regular uncoated aluminum in the same composition and under identical conditions. The recorded combustion images were analyzed, mainly by particles count and size measurements, revealing that the initial general prediction of reduction in agglomeration due to nickel coating was correct.

In each and every experiment a median particle diameter was calculated, for which half of the aluminum mass is concentrated in larger particles, and the other half is concentrated in smaller particles. Figure 1 demonstrates a definite reduction in median agglomerate diameter due to nickel coating. It can be seen that, on average, the diameter of agglomerates resulting from nickel-coated aluminum is around 60% of the diameter of agglomerates resulting from regular aluminum. This finding is very important when the mass reduction is taken into consideration; the “reduced” agglomerate constitutes approximately 20% of the “original” one. This reduction is expected to lead to better and more complete combustion of aluminum particles within the solid rocket motor.

For both atmospheric and higher pressure series, a calculation for the aluminum mass flux was conducted, based on the counted aluminum particles ejected from the propellant samples. The results obtained were in the same order of magnitude as a matching calculation based on the propellant burning rate and burn time.

The test result of reduced agglomeration of nickel-coated aluminum is of great significance in solid rocket motors for both improving combustion efficiency and reducing slag accumulation.

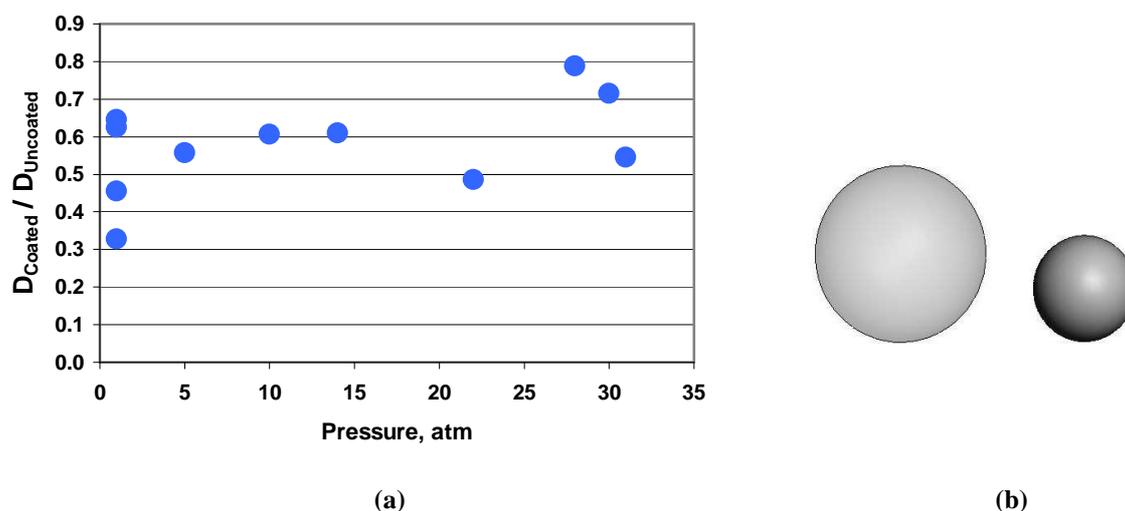


Figure 1: Ejected aluminum agglomerate diameter ratio between coated and uncoated aluminum particles vs. pressure (a), and illustrated characteristic diameter reduction (60% of the "original") due to nickel coating (b).

## BALLISTICS OF METALLIZED SOLID ROCKET PROPELLANTS

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<sup>2</sup>*MACH I, USA*

### ABSTRACT

Boron presents a very interesting combustion ingredient in propellants, explosives, and pyrotechnics. The energy density of boron is very attractive for energetic combustion applications. However, the oxide coating formed on the surface of elemental boron inhibits combustion and delays ignition in these systems. Several attempts were already made in the past to improve the ignition and combustion characteristics of boron.

Under the sponsorship of the US Office of the Secretary of Defense, MACH I, Inc. has recently developed a proprietary technology to coat boron with magnesium to form a MgB composite on the surface of the boron particle which reduces the combustion problems associated with neat boron substantially. Testing at the New Jersey Institute of Technology (NJIT) has shown that the ignition temperature of boron has been reduced from about 2000 K to about 1000 K when boron is coated with magnesium to form MgB composites. A supplemental benefit of the coating process according to the MACH I technology is that by forming the MgB composite coating, the reactivity of boron with hydroxyl containing binders such HTPB is reduced substantially, and hence, viscosity problems associated from using boron in HTPB binders are also reduced.

This paper will discuss a systematic ballistic characterization of solid rocket propellants using different B-based metallic alloys. In particular, with reference to the currently standard formulation AP/metal/HTPB in the mass ratio 68/18/14, the MgB composites produced by MACH I were investigated as fuel powders and compared to a micrometric Al powder (30  $\mu\text{m}$  grain size) taken as reference. The experimental studies carried out include the characterization of the tested powders in terms of chemical composition, morphology and grain size distribution, determination of propellant densities and ballistic properties (steady burning rate), high-resolution visualization of the combustion surface, and analyses of the combustion residues (by means of XPS, SEM, and XRD techniques). The oxidizer grain size effect was taken into account by considering two bimodal AP distributions (58/10; 48/20) including a coarse (160-200  $\mu\text{m}$ ) and a fine (5-10  $\mu\text{m}$ ) fractions. Steady burning runs were effected both under  $\text{N}_2$  and Ar inert gases to verify the occurrence of possible interactions between the analyzed powders and the surrounding atmosphere.

Further tests to evaluate the agglomeration phenomena were performed under  $\text{N}_2$  atmosphere at 5, 10, 20, and 25 bars; some tests were repeated in Ar without noticeable changes. For each test, the size of 200 incipient agglomerates was manually measured and the  $d_{43}$  mean diameter calculated. For all experimental series, the minimum distinctly observable diameter was around 30  $\mu\text{m}$ . The experimental error was estimated by a bootstrap method generating 100,000 quasi-random parent populations.

## ON THE INFLUENCE OF MICROSTRUCTURE OF HETEROGENEOUS EXPLOSIVE MATERIALS ON THEIR DETONATION BEHAVIOUR

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### ABSTRACT

According to the Zeldovich – Von Neumann – Döring (ZND) model, the detonation wave consists of a shock jump and a chemical reaction zone where the pressure decreases and the matter expands, i.e. the Von Neumann spike is formed. Numerous experimental data confirm the validity of this model for most high explosives. However, in recent years a number of detonation effects that don't correspond to classical ZND model have been found in several heterogeneous explosive materials (EM).

One of the effects is the unusual reaction zone structure and detonation velocity dependence on initial porosity of samples in pressed TNETB high explosive. With the use of the VISAR laser interferometric system, it was found that in the range of initial porosity of 3.3 to 15.2% propagation of a steady-state detonation wave without the Von Neumann spike predicted by the classical detonation theory was possible in “coarse” (mean particle size of initial powder  $r_{av} \sim 120 \mu\text{m}$ ) TNETB. In samples of “fine” ( $r_{av} \sim 5 \mu\text{m}$ ) TNETB, the upper limit of porosity range increased to 29%. The discontinuities of the dependence of detonation velocity on initial density near the lower and upper limits of the specified range of porosity were also found. This observation can be the witness that the detonation regime without the Von Neumann spike is the steady-state underdriven detonation, which is fundamentally impossible according to the ZND detonation model.

In similar VISAR experiments with the mixture of RDX and silicon nitride  $\text{Si}_3\text{N}_4$  which acted as hard and inert additive, the Von Neumann spike was observed at all studied mixture ratios. However, its duration was significantly shorter and its amplitude was significantly higher than that of the pure RDX of the same density as it was in studied mixtures, whereas it was expected intuitively that the addition of inert material to the reacting media would extend the duration of chemical reaction, and thus lengthen the Von Neumann spike and decrease its amplitude.

One of the general principles of the ZND model is that both the width of a shock jump in the reacting media and the initial rate of chemical reaction in it must be equal to zero. But the analysis of the measured experimental data with the use of the acclaimed theoretical concept of “hot spots” mechanism of detonation of heterogeneous EM showed that in the studied EM this assumption seems to cease being realized due to extremely strong spatial inhomogeneity of matter and energy distribution. So, in particular, the anomalous detonation behaviour of TNETB and RDX/ $\text{Si}_3\text{N}_4$  mixture can be explained by the presence of a great number of effective “hot spots” that provide fast burning—and therefore a higher initial rate of chemical reaction—of EM directly within a shock compression zone, which in this case has a non-zero thickness. This shows that for an explanation of a full spectrum of the observed phenomena that doesn't correspond to the classical ZND detonation, a new model that takes the influence of EM microstructure on the detonation behaviour into account is required.

# THE INFLUENCE OF SPHERICAL GRANULAR PROPELLANTS ON THE COMBUSTION PROPERTIES OF HIGH-BURNING-RATE PROPELLANT

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## ABSTRACT

The novel spherical grain-binding, high-burning-rate propellant is a kind of compound structure propellant (called consolidated propellant), which is prepared with spherical granular propellant (spherical propellant grains) as dispersed phase and colloidal binder as continuous phase. The effects of composition, particle-size, and morphology of spherical propellant grains on the combustion performance of propellants were investigated. The results show that the burning rate of the propellant decreases with the increase of the burning-rate of spherical propellant grains. The greater the difference in burning rate between the spherical propellant grains and the binder; the higher the burning rate of propellant will be. The burning rate of the consolidated propellant increases with the decrease of the particle size. Compared with that of the propellants prepared with smooth-faced spherical propellant grains, the burning rate of the propellants prepared with the shaggy spherical propellant grains is much higher; however, the combustion can become less stable.

**Keywords:** *Spherical Propellant Grains; Burning-Rate; Particle-Size; Morphology; Porous Permeability Combustion Layers*

## TEMPERATURE INSENSITIVE PROPULSION SYSTEM (TIPS®) BASED ON SCDB® PROPELLANT AND NEW CCC DESIGN OF CARTRIDGE 120MMX570 DM63

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<sup>2</sup>*Nitrochemie Aschau GmbH, Germany*

### ABSTRACT

TIPS® is the first propulsion system for large calibre applications with a nearly temperature independent muzzle velocity. In 2005 TIPS® has replaced the propulsion system of the predecessor KE round DM53 to allow for unrestricted use in the full temperature range from -46 to +71 °C and in the L44 and L55 weapon systems of Leopard 2 tanks.

TIPS® is based on the surface coated double base (SCDB®) technology combined with a new combustible cartridge case (CCC) design with improved burning characteristic and refractory metal oxide additive to reduce barrel wear.

#### ***SCDB® Technology***

For high performance applications the SCDB® technology is typically based on propellant grains with a circular cross section, 19 perfs and L1 recipe. These so-called base grains show a quite normal burning characteristic with a monotonous increase in burning rate with increasing ambient temperature. Even after the surface coating process this burning behavior remains essentially unchanged but depends on the surface coating strength (SCS) of the gas production rate and is an increasing, approximately constant or decreasing function of temperature. This implies that the form function (ratio of actual burning and initial surface) must have changed from a pure function of geometry to a function of geometry and temperature, which compensates for the temperature dependency of the burning rate – not as an exact counterbalance but in a statistical sense.

For an optimum performance of the propulsion system, the SCS must be fine-tuned according to the properties of the igniter and the burning characteristic of the CCC.

#### ***Wear Reducing CCC Technology***

The combustion gases of CCC form a layer of “cold” gases which protect the barrel wall very efficiently from the hot combustion product gases of the propellant.

At first glance a “very cold CCC recipe” may look like the best choice in order to have the maximum advantage from this effect. But going into the details of the involved physics, it can be seen that the formation of the cold gas layer from a “very cold CCC” takes place too late within the interior ballistic cycle to efficiently protect the barrel wall. Therefore the CCC recipe optimization process is not straight forward and requires complex simulations and experimental investigations and simulation.

Furthermore a refractory metal oxide was incorporated into the CCC to increase the wear reducing properties of the CCC combustion gases by lowering the amount of hydrogen and the heat conduction, at least in the vicinity of the barrel wall. Estimates showed that compared to the propulsion system of the predecessor cartridge, a decrease in erosion by a factor 3 should be expected.

***Performance of the Cartridge 120mmx570 DM63***

According to the demand of the German customer, the DM63 has the same performance as the predecessor cartridge at ambient temperature where a weakly marked maximum of the muzzle velocity occurs. The spread of muzzle velocities between -46 and +63 °C is typically less than 45 m/s. This implies that the centers of impact of hit patterns at different temperatures show a clearly smaller spread compared to a conventional propulsion system.

The cartridge DM63 is safe to fire up to +71 °C and can be stored under the conditions of climatic category A1 for at least 3 years without degradation of the ballistic stability or significant changes in performance.

Barrel wear was shown to be almost 5 times lower than with the propulsion system of the predecessor cartridge DM53.

The cartridge DM63 fulfills all standard IM requirements and complies with the ICD which guarantees the interchangeability of ammunition for 120 mm smooth-bore guns.

Finally, when tapping the full growth potential of TIPS®, an approximately 80 m/s muzzle velocity increase should be possible.

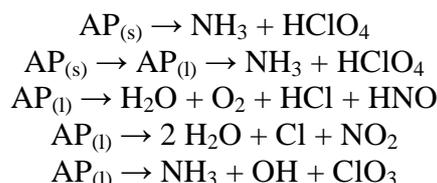
# FIRST-PRINCIPLES STUDY OF WATER EFFECT ON THE SUBLIMATION OF AMMONIUM PERCHLORATE

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## ABSTRACT

Experimentally, the mechanisms for the decomposition and combustion of ammonium perchlorate (AP) have been extensively studied over the past few decades, as summarized in detail in the overviews by Jacobs and Whitehead<sup>1</sup> and Tanaka and Beckstead<sup>2</sup>. The latter authors reviewed various assumed initiation reactions and put forth a three-phase combustion initiation model:



to account for the observation of Brill et al<sup>3</sup> acquired from a time-resolved FTIR measurement at high pressure and that of Ermolin and coworkers<sup>4</sup> for species detected by mass-spectrometry near a burning AP surface. To fully substantiate the 3-phase combustion model is experimentally very difficult and theoretically requires a systematic study of the chemistry occurring in each of the three phases by high-level quantum-chemical calculations for the key processes involved. In the model, all processes, except that for sublimation from solid AP, are unknown.

In this work, the kinetics and mechanism for the sublimation/decomposition of ammonium perchlorate (AP) with and without water present on the decomposing surface have been investigated by first-principles calculations, using a generalized gradient approximation with the plane-wave density functional theory. Calculated results show that H<sub>2</sub>O can enhance the sublimation of AP; the sublimation energies of AP with (H<sub>2</sub>O)<sub>n</sub> (n = 0, 1, 2, 3) from the AP surface were predicted to be 28.1, 21.4, 18.6, and 14.2 kcal/mol, respectively. Notably, H<sub>2</sub>O was found not to affect the proton transfer between the NH<sub>4</sub><sup>+</sup>/ClO<sub>4</sub><sup>-</sup> ion pair, but was found to significantly enhance the sublimation of AP by co-desorbing with the ion pair. The rate constants for the dominant sublimation processes, the desorption of the molecular complex, H<sub>3</sub>N•••HOClO<sub>3</sub>, and the co-desorption of H<sub>2</sub>O with AP, (H<sub>2</sub>O)<sub>n</sub>•••NH<sub>4</sub>ClO<sub>4</sub> (n = 1, 2), predicted by canonical variational transition state theory can be presented by:  $k_{\text{des}} = 6.53 \times 10^{12} \exp(-28.8 \text{ kcal/mol/RT})$  (n = 0),  $1.69 \times 10^{10} \exp(-20.3 \text{ kcal/mol/RT})$  (n = 1), and  $1.08 \times 10^{11} \exp(-17.7 \text{ kcal/mol/RT})$  (n = 2) s<sup>-1</sup>, respectively, with a significant enhancement by the H<sub>2</sub>O molecules. Interestingly, the structures of AP in the water complexes are more ionic than that without H<sub>2</sub>O in the gas phase. In addition, the energy changes for proton transfer on the surface have been compared with those in solution. The calculated proton transfer energies on the crystalline AP surface with (H<sub>2</sub>O)<sub>n</sub> (n = 0, 1, 2), 31.1, 29.7, and 32.5 kcal/mol, were found to be close to the corresponding values, 30.8, 30.5, and 30.4 kcal/mol, calculated by the (H<sub>2</sub>O)<sub>n</sub>-NH<sub>4</sub>ClO<sub>4</sub> complexes with the Polarizable Continuum Model. These calculated proton transfer energies on the surface and in solution are close to the experimental values inside AP solid, 26 - 31 kcal/mol. Furthermore, the energies for the desorption of H<sub>2</sub>O, (H<sub>2</sub>O)<sub>2</sub>, and (H<sub>2</sub>O)<sub>3</sub> from the AP surface were found to be 5.2, 12.8, and 9.5 kcal/mol respectively. They are much lower than that required for the sublimation of AP. This result clearly suggests that

water cannot favorably form solution on a decomposing AP surface under combustion conditions in the way that it can effectively desorb molecularly or desorb with AP as ionic complexes with much lower energies than the neat AP surface.

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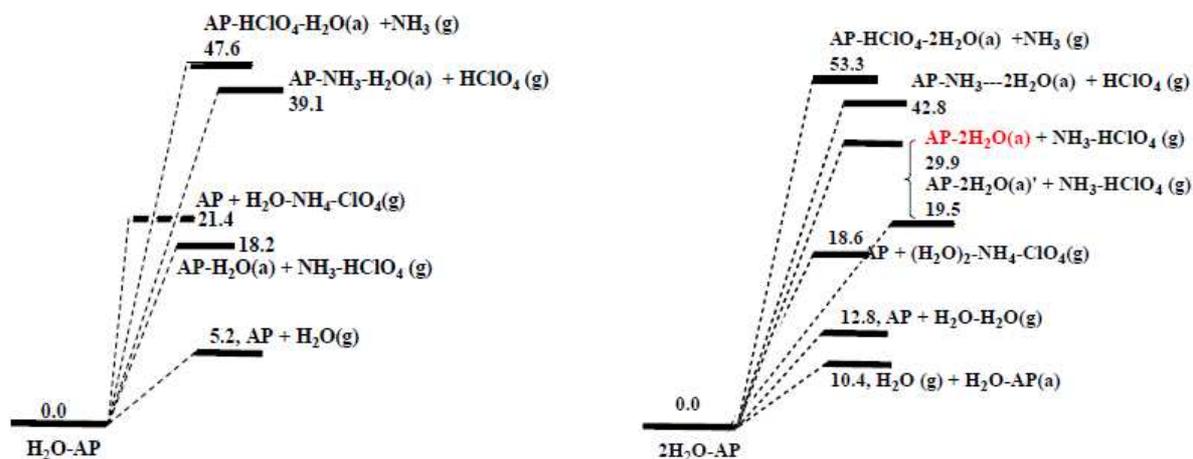


Figure 1: Schematic energy diagram (in unit kcal/mol) for the sublimation/dissociation processes of  $\text{H}_2\text{O-AP}$  (left) and  $(\text{H}_2\text{O})_2\text{-AP}$  (right); where  $\text{H}_2\text{O-AP}$  and  $(\text{H}_2\text{O})_2\text{-AP}$  represent the initial relaxation AP surface with one and two  $\text{H}_2\text{O}$  molecules; “a” represents the adsorbed state and “g” represents the gas phase.

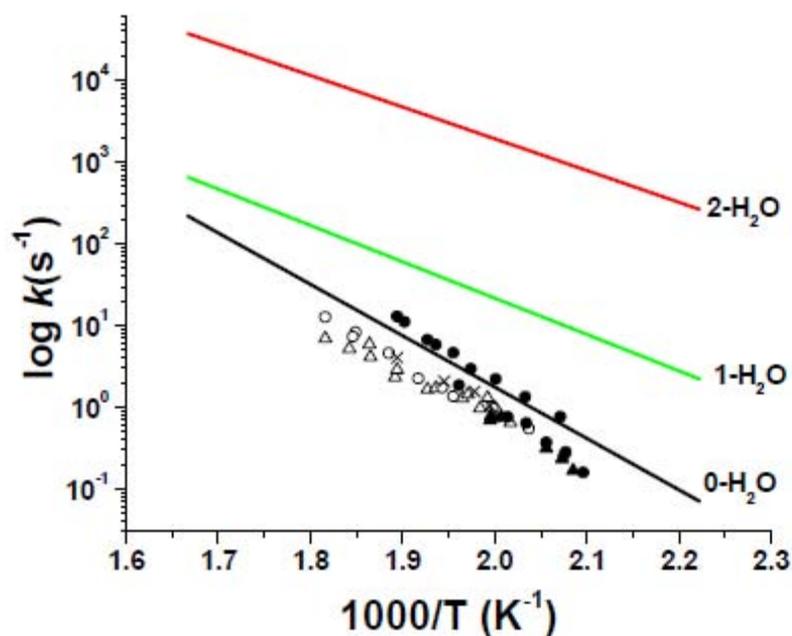


Figure 2: Predicted  $(\text{H}_2\text{O})_n\text{-AP}$  ( $n = 0, 1, 2$ ) sublimation/dissociation rate constants. Solid, dotted, and dashed lines are the calculated values; symbols are the experimental values taken from reference 5.

### *Acknowledgments*

This work was supported by the Office of Naval Research under grant No. N00014-02-1-0133. We are very much indebted to Taiwan's National Center for High-Performance Computing for the extensive number of CPU's needed in this work.

## NUMERICAL CALCULATIONS PREDICTING SOLID PROPELLANT INGREDIENT INTERACTIONS

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### ABSTRACT

The complexities of the flame structure above multi-ingredient solid propellants have been elucidated using a two-dimensional, detailed kinetic model. The model utilizes a vorticity formulation of the transport equations and includes mass and energy coupling between the condensed and gas phases. The condensed-phase decomposition is based on previously reported one-dimensional models and includes distributed decomposition and multi-step reaction kinetics. The model uses detailed gas-phase kinetic mechanisms and species transportation to allow for a prior calculation of the flame structure. Numerical studies have been performed to examine AP particle size and pressure effects on the flame structure above an AP/HTPB propellant. The combination of AP with a binder/fuel results in a significantly enhanced burning rate relative to monopropellant AP, and this effect increases as AP particle size decreases. The modeled flame structure was found to be qualitatively similar to the BDP model. Three different combustion zones, based on particle size, were predicted: the AP monopropellant limit, the diffusion flame, and the premixed limit. Calculations varying pressure further illustrate the dynamic nature of AP propellant combustion; as pressure increases, the impact of increasingly smaller AP particles becomes significant. A pseudo-propellant consisting of RDX/GAP was also examined. Unlike AP/HTPB, the combination of RDX and GAP results in a diminished burning rate relative to the individual monopropellants. These flame structure calculations give a mechanistic understanding of AP particle size effects and the diminished burning rate of RDX/GAP and are a significant step toward simulating propellant combustion.

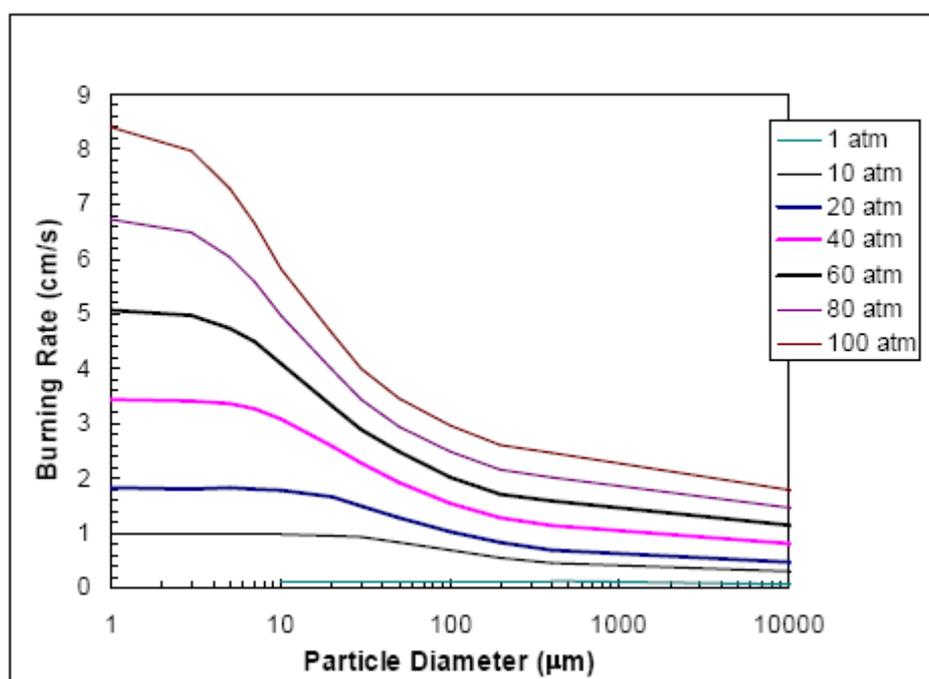


Figure 1: Calculated AP/HTPB burning rate with pressure and AP particle size.

## MECHANICAL PROPERTIES OF COMPOSITE PROPELLANTS AND EFFECT OF PROPELLANT STRETCH ON ITS BURN RATE

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### ABSTRACT

Propellant stretching in combustion leads to an essential increase (up to 50% and more) in burn rate. The analysis of existing representations about the influence of stretch deformations on propellant burn rate is carried out. It is shown, that for composite solid propellants the basic mechanism of increase in the burn rate under stretch conditions is detachment of the binder from particles of oxidizers, formation of additional burning surface, and change of structure of a burnt zone.

For description of this effect a rheological model of composite solid propellant is developed. The model takes into account a detachment of the binder from particles (oxidizers, coolers, metals, etc.) under action of stretch deformations. The criterion describing distinction in behaviors of propellant in stretch conditions with detachment of the binder from particles in comparison with a stretch of the same material without occurrence of internal defects is established. The method for experimental determination of the amount of the defects arising in the propellant in stretch, based on the analysis of the diagram of material stretch is suggested.

The mathematical model of combustion of composite propellant in stretch conditions, taking into account a detachment of the binder from particles of oxidizers, and formation of an additional burning surface is developed. The model considers heterogeneous structure of a propellant, a burning surface, and a gas phase. The analysis of ignition of the cracks formed on the binder-particles border, as a result of detachment of the binder from particles in propellant stretch, is carried out.

It is shown, that an inverse effect when a burn rate decreases little in propellant stretch can be observed in certain conditions. It is shown, that this effect is connected with incomplete burn-out of oxidizer particles on propellant burning surface as a result of their detachment from a surface.

Parametrical research of composite propellant combustion under action of stretch deformations is carried out. Results of calculations are compared with well-known experimental data.

Correlation between changes in propellant burn rate in stretch conditions and parameters of propellant stretch diagram without combustion is established. The method is developed, that allows for predicting the change in propellant burn rate in stretch conditions by using the diagram of propellant stretch without combustion.

# EXCITATION OF HYDRODYNAMIC MICRO-STRUCTURES DURING ENERGETIC MATERIALS UNSTEADY COMBUSTION AND PHENOMENON OF WAVES OF NEGATIVE EROSION

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## ABSTRACT

Despite intensive work spanning five decades, the problem of combustion instability of high energy solid propulsion systems is still an important engineering problem. The phenomenon of reduction of the burning rate as a result of blowing of the solid-propellant burning surface with low velocity of the combustion products from the same composition refers to as the effect of "negative erosion". The phenomenon of "negative erosion" is one of the typical anomalies of burning.

The necessity of revision of the "negative erosion" models is determined by the fact that the mathematical apparatus of the present-day models does not contain the necessary elements to obtain solutions that adequately describe these phenomena. It is desirable to base a new "negative erosion" model on experiments in which the temporal stepwise nature and the spatial non-uniformity of the torch micro-structures on the burning surface are pronounced most clearly.

A suggested new concept of the phenomenon of "negative erosion" is developed on the basis of the universal concept of the spatial-periodic micro-structure excitation on the energetic material (EM) burning surface<sup>1</sup>. Excitation of the spatial-periodic micro-structures in ionic fusion with thermo-electric properties on the burning surface is a main source of development of the synergetic phenomena in the EM burning zone. Separate fragments of the new mechanism of the phenomenon of "negative erosion" have been presented on the 7-ISICP in Kyoto, Japan (2007)<sup>2</sup>. In the given paper, the detailed mechanism of development of the phenomenon of "negative erosion" is considered.

It is proposed that the phenomenon of excitation of periodic toroidal vortex micro-structures over the burning surface plays a key role in the realization of the phenomenon of the "negative erosion". Physical laws of formation of the toroidal vortex micro-structures over the burning surface has been considered during analysis of the experimental results, which have been obtained under conditions of blowing<sup>3</sup>. Pulse-wise effusing jets of the micro-torches from the burning surface induce around themselves surrounding medium fluxion. As a result of interaction of the pulsing jets with this induced flow of a surrounding medium, the toroidal-shaped micro-vortexes are generated.

An anomalously long lifetime and stable high-temperature toroidal vortices are related to the toroidal configuration of the vortex motion of the plasma or gas. In the course of its formation, the high-temperature toroidal vortices accumulate rotational and translational kinetic energy. The high-temperature toroidal vortices can be regarded as a self-organized dynamic system. The lifetime of the vortex as a self-maintained hydrodynamic structure increases due to the forces arising in it. For the same Reynolds numbers, the value of the drag coefficient for toroidal vortices may be much smaller than the drag coefficient for an axis-symmetric, drop-shaped body, which is known to be the best streamlined object. The

consecutive stages of the high-temperature toroidal vortices formation are considered (Figure 1).

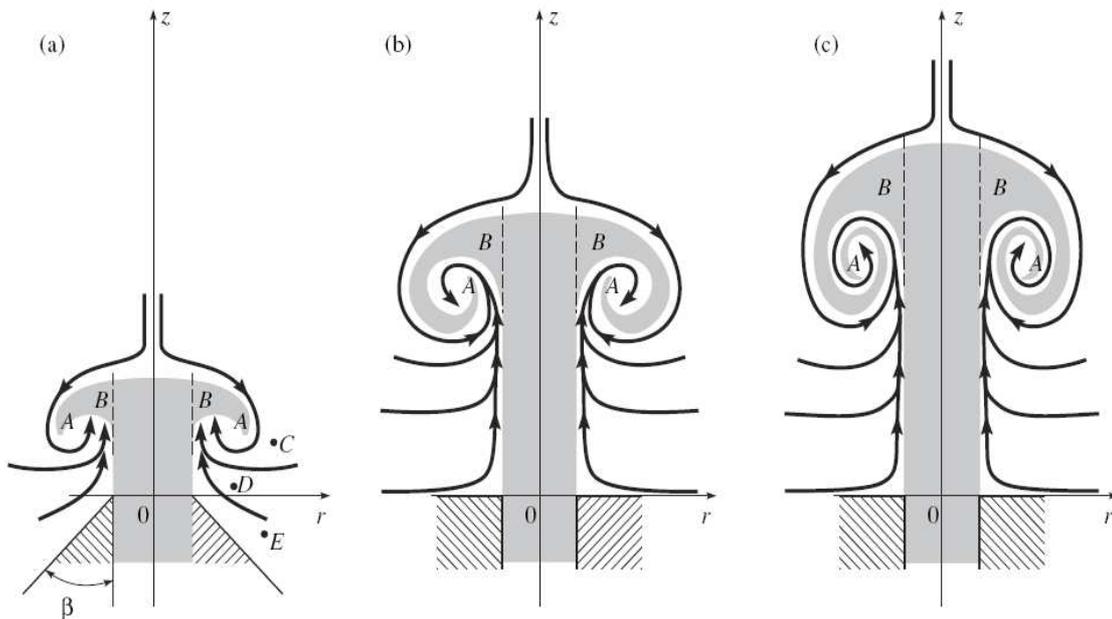


Figure 1: The qualitative pattern of the toroidal vortex formation and generation of the induced ambient air flow about the pulsed jet: (a) beginning of the formation of a toroidal spiral and the generation of the induced ambient air flow, (b) formation of the first turn of the toroidal spiral and (c) the entrainment of the ambient air into the formed toroid<sup>4</sup>.

Also the phenomenon of excitation of micro-plasma structures over the EM burning surface is considered. This effect becomes significant only at relatively high (above 1600 K) temperatures. In accordance with numerous experimental data, for "ignition" of a plasmoid, the presence of various initiators (catalytic agents) is necessary. The carbon micro-particles at the burning surface and agglomerates, in the conditions of intensive chemical ionization, can be catalytic agents and active centers for excitation of micro-plasma toroidal vortex formations over the burning surface at the combustion products temperatures above 1600 K.

The toroidal-shaped vortex micro-structures forms the system of thermal channels over the burning surface. The boundary of existence of the phenomenon of "negative erosion" is determined by stability of toroidal-shaped vortex micro-structures in the stream of the combustion products which is blowing the burning surface of the EM.

Within this new concept, the phenomenon of excitation of the waves of "negative erosion" is analyzed. Propagation of the pressure waves in the stagnation zones will induce waves of "negative erosion" that leads to the mode of pulsating ignition of the EM. Within the suggested concept, the experimental results obtained in the Scientific-Research Institute of Polymeric Materials (Perm, Russia), and partially presented in the paper<sup>5</sup>, have gained a new explanation.

Understanding of mechanism of excitation of hydrodynamic micro-structures over the EM burning surface leads to a new technological opportunity, which is reduction of possibilities for excitation of combustion instability.

Suggested earlier theoretical concepts for description of the phenomenon of "negative erosion" did not give theoretical possibility for development of the technologies providing minimization of this phenomenon. Active controlling by self-organizing processes of the spatial-periodic micro-structures in the EM liquid-viscous layer and on the EM burning surface opens possibilities for efficient control by the boundary layer over the burning surface of the EM, and by development of the phenomenon of "negative erosion".

**Keywords:** *Combustion Instability, "Negative Erosion" Phenomenon, Periodic Toroidal Vortex Micro-Structures, Micro-Plasma Structures, Waves of "Negative Erosion"*

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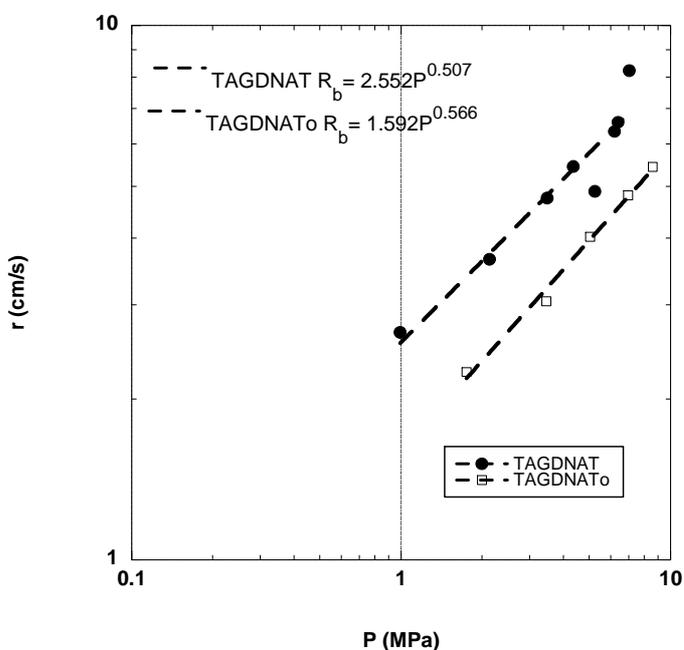
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# SYNTHESIS AND COMBUSTION CHARACTERISTICS OF NOVEL HIGH-NITROGEN MATERIALS

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## ABSTRACT

The synthesis of high-nitrogen energetic materials has been of ongoing interest at the Los Alamos National Laboratory (LANL). We have discovered that high-nitrogen materials can offer interesting performance and sensitivity properties not accessible through conventional energetic materials. For example, some of the high-nitrogen materials developed at LANL have extremely fast burn rates and very low dependence of the burn rate on pressure. Examples of this include BTATz and DAATOx materials. In this paper, we will discuss our recent developments in our continuing efforts towards the synthesis of new high-nitrogen materials that feature interesting combustion and explosives properties. In particular, we will describe the synthesis of the high nitrogen materials dinitroazotriazole (DNAT), dinitroazoxytriazole (DNATO) and the corresponding triaminoguanidinium salts (TAGDNAT, TAGDNATo), and present chemical properties such as density, and heat of formation, as well as their sensitivity properties. Thermo-equilibrium calculations (Cheetah Code) were used to predict decomposition products as well as propellant and explosives behaviors. Finally, we will present burning rate data for these new materials. A typical burning rate plot versus pressure is shown in the figure below.



## REDUCTIVE DEBENZYLATION OF 2,4,6,8,10,12- HEXAAZAISOWURTZITANE

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V.V.

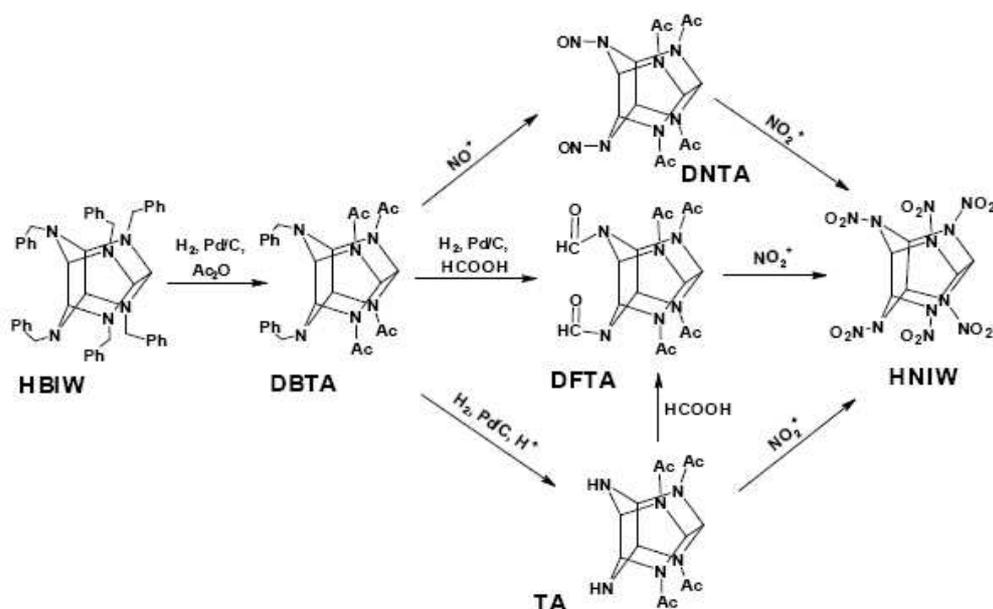
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### ABSTRACT

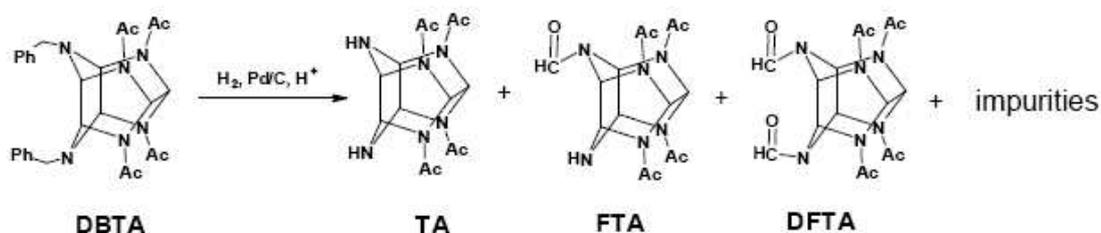
The composition of products from catalytic hydrogenolysis of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane and 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane is studied by HPLC method. In the process of hydrogenolysis of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane, there are all the possible directions of the reaction. Debenzylation of 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane in a mixture of formic acid with acetic, propionic, and isobutyric acids leads to a mixture of 4,10-diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane with 4-formyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane. In aqueous solutions of formic acid, there is formed a mixture of the same products, but the process becomes complicated due to the hydrolysis of amide groups.

The known methods of obtaining 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HAW, CL-20, **HNIW**) [1] are based on a three-stage chemical transformation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (**HBIW**) [2]. For removal and replacement of benzyl groups, a method of catalytic hydrogenolysis over Pd/C is widely used. The main relationships of hydrogenolysis are described in literature [2, 3]; however, the process is accompanied by the formation of other products that have not been described in literature.



4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**DBTA**) is obtained in 80% yield during the hydrogenolysis of **HBIW** in a mixture of acetic anhydride with dimethyl formamide in the presence of bromobenzene. A study of the composition of products left in the solution by means of HPLC with mass-selective detector (APCI) shows the formation of a number of compounds which may be proposed to the following structures: benzylacetamide, pentaacetylbenzylhexaazaisowurtzitane, two isomers of ethyltetraacetylbenzylhexaazaisowurtzitane, two isomers of **DBTA**, and dibenzylethyltriacylhexaazaisowurtzitane. This indicates that during the process there are a number of directions taking place at the same time: - destruction of **HBIW** to form benzylacetamide; - hydrogenolysis of the benzyl groups both in the positions 2, 6, 8, 12 (mainly) and in positions 4, 10; - reduction of the acetyl groups not only in the positions 4 and 10, but in 2, 6, 8, 12.

The ratio of by-products is little influenced by the process pressure (0.01–0.5 MPa), number of catalyst cycles ( $n = 1-10$ ), and excess of brominating agent. The solvent composition and concentration of initial **HBIW** have a greater effect. The hydrogenolysis of **DBTA** in the medium of acids is also accompanied by the formation of a series of products, the ratio of which is defined by water content and medium acidity.



Thus, in the process of hydrogenolysis of **HBIW** there are all the possible directions of the reaction; - hydrogenolysis of **DBTA** in the medium of formic acid affords a mixture of products, the ratio of which depends on the concentration of water, and is complicated by hydrolysis; - hydrogenolysis of **DBTA** in the mixtures of formic acid with acetic, propionic and isobutyric ones gives only formyl derivatives of hexaazaisowurtzitane. A decrease in the concentration of formic acid results mainly in the formation of the monoformyl derivative of **FTA**.

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**Keywords:** *4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-2,4,6,8,10,12-hexaazaisowurtzitane, 4,10-diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane, -2,6,8,12-tetraacetyl- 2,4,6,8,10,12-hexaazaisowurtzitane,4-formyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12- hexaazaisowurtzitane, hydrogenolysis, hydrogenation, hydrolysis, debenzilation*

## MECHANISMS AND METHODS OF SUPPRESSION OF COMBUSTION INSTABILITY

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### ABSTRACT

Suppression of oscillatory burning may result from two sources: (1) attenuating the acoustical wave by absorption, reflection, or scattering; and (2) altering the feedback path by changing the physical and/or chemical requirements for reaction. The latter source may be further subdivided by considering the site of the controlling feedback reaction as either the condensed phase or the gas phase. The majority of recent models have focused on the first source and the concept of "particle damping", where solid particles suspended in the reaction products absorb energy through viscous drag. There is, however, considerable experimental evidence that the second source of suppression is dominant for many motor designs.

A series of experiments was conducted to provide further input to the resolution of this question. These experiments comprised laboratory experiments where high-speed cinematography was employed to study the combustion of metallic additives at or near the burning surface of solid propellants, as well as motor firings in a standard test motor equipped with close-coupled pressure transducers and recording equipment capable of providing an accurate record of any oscillations with frequencies characteristic of the test motor, i.e., less than 40 kHz.

Two high-energy binder systems were employed in this study: (1) one based on polypettrin acrylate with TEGDN as the plasticizer and (2) a plastisol nitrocellulose system incorporating TEGDN. Ammonium perchlorate was the oxidizer. Fourteen additives were evaluated at the two-percent level in the first binder system and twenty-two additives in the second system. The effects of particles containing several types of reactive metals such as aluminum, magnesium, boron, and magnesium/aluminum alloys were evaluated, as well as some non-reactive particles of aluminum oxide and silica.

The most significant finding of these experiments was that the results of motor firings correlate well with photographs of the burning process of those additives that liberate large amounts of energy, i. e., the additive must ignite and burn near the burning surface to be effective. In fact, it appears possible to make predictions of the effectiveness of such additives based solely on photographs of their combustion. In addition, energetic additives are far more effective than inert ones, based on the extent to which "particle damping" was able to diminish the extent of pressure oscillations.

## **IMPROVING THE METHOD FOR DETERMINATION OF AN ADMITTANCE FUNCTION FROM PULSED TUBULAR GRAIN MOTOR TESTS**

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### **ABSTRACT**

Combustion instability is a common problem experienced in solid rocket motors. The ability to accurately predict the combustion stability of a motor is strongly influenced by the quality of the available experimental data for a given propellant. T-burners are the industry standard but they require a large test matrix. This makes it expensive to operate and maintain.

A new method for determining the acoustic admittance or response function of a solid propellant has been developed. Extending the basic concept of the T-burner to a tubular grain motor, it is now possible to obtain such data for multiple modes during a single test. The continuing improvements in the understanding and mathematical description of the physical mechanisms that contribute to combustion instability allows for their calculation with a degree of uncertainty. It is therefore possible to calculate the admittance of the propellant without having to obtain the loss mechanisms experimentally as with the T-burner.

A cylindrical grain motor is pulsed three times during the burning period. If the motor does not go unstable, it is possible to determine the growth or decay constants,  $\alpha$  for multiple longitudinal modes at three different pressures. When the motor is linearly stable, the classical linear analysis and Flandro's energy balance analysis can be used. Both Culick's and Flandro's non-linear method were applied when the motor is unstable after pulsing.

The initial study showed that it is possible to obtain good results; however, the analysis is constrained to 3-5 modes due to the assumption of small penetration number ( $\xi < 1$ ). The energy normalization, which has been found to be  $E_m^2 = \frac{5}{8} \pi \frac{L}{R}$ , has been integrated with this working range in mind. This viscous parameter constrains the applicability of the analytical results for a tubular grain motor obtained by Flandro and co-workers to a range that is not applicable to high frequencies or to small motors. This study will extend this new method so that higher modes can be evaluated; in this way, the admittance function can be obtained for a wider frequency spectrum per test. This will reduce the total number of tests required, as well as negate the need to modify the motor to fit within the small  $\xi$  assumption.

## **BURNING BEHAVIOR OF NITRAMINE GUN PROPELLANTS INFLUENCED BY PRESSURE OSCILLATIONS**

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### **ABSTRACT**

It seems to be that the combustion of propellants in guns and closed vessels is very well known. In the last few years, however, some new findings have been made concerning the burning of propellants.

For some propellants burned in closed volumes, measurement results have been obtained which have not been expected and which do not conform with the geometry of the propellant grains. They show excessive values in the first half of the dynamic vivacity. Sometimes they even last until half of the charge has been burned.

This accelerated combustion in connection with an intensified generation of gas has been observed at low loading densities and low propellant temperatures in particular.

For the dimensioning of a gun ammunition propellant the knowledge of the burning behavior and the burning rate respectively is very important, not only for the prediction of the effectiveness of the propellant, but also for ammunition safety purposes. For this reason, systematic experimental and theoretical studies were performed.

These investigations, which were conducted by the WTD 91 and the German-French Research Institute-Saint-Louis (ISL), show that the observed intensified combustion is directly related to gas-dynamic oscillations, which are generated inside the perforations of the propellant grains. Besides the well known "Vieille oscillations," other types of pressure oscillations have been shown to exist in closed volumes with burning propellants. The properties of these pressure oscillations are determined by the geometry of the gun propellants. The amplitudes of these oscillations also depend on the propellant temperatures and the loading densities used. Hints as to the mechanism and the effect of the pressure oscillations on combustion were obtained from topographical measurements on grains after an interrupted burning.

In this paper, new results of investigations in nitramine propellants are presented. With parts of DNDA and RDX in the formulation, gun propellants can be realized with an approximate temperature independent burning. The reason behind that behavior is not clear so far. To get findings about the influence of pressure oscillations on the burning of such nitramine propellants, investigations were performed with two different propellants. It could be shown in both cases that the pressure oscillations have a determinant impact on the temperature behavior.

## LESS SENSITIVE AND “GREEN” PROPELLANT

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### ABSTRACT

Single base propellants that contain approximately 10% DNT (di-nitrotoluene) are not IM compliant and are especially sensitive to shock. Such propellants normally fail the insensitive munitions (IM) tests for Bullet Impact (BI), Fragment Impact (FI) and Shaped Charge Jet Impact (SCJI). The DNT and other typical single base propellant ingredients such as DBP (di-butyl phthalate) and other phthalates and DPA (di-phenyl amine) are all suspected to be carcinogenic substances. Some still contain lead or other heavy metal salts. A further problem associated with these propellants is the large quantities of solvents released into the atmosphere during the processing of the propellants. There is a world-wide drive towards “Green” propellants as well as less sensitive propellants and we have launched a program to develop a less sensitive, green propellant to replace the existing S760 single base propellant.

We have theoretically and chemically evaluated various formulations with the aim of replacing the DNT, DBP and DPA with “green” substances. These substances must not only be “green” but also less sensitive to shock so that we can comply with the IM specifications as well. A further aim was to reduce or totally eliminate the large quantities of solvents normally released into the atmosphere during the processing. In these formulations we have replaced the DPA as stabiliser with EC (ethylcentralite) or Acardite II. The DNT and DBP were replaced as plasticisers with TEGDN (tri-ethylene glycol dinitrate) or DEGDN (di-ethylene glycol dinitrate). We also replaced the mechanical mixture NC (13.15% N), typically used for single base propellants, with Piro M30 type of NC (12.6% N). Although the mechanical mixture NC has more energy than the Piro M30 type of NC, it does not process as well nor does it have the same mechanical properties.

Three different propellant families were proposed as possible candidates to replace the S760 propellant formulation. The 1st formulation was intended to reduce the sensitivity only and it comprised a single base formulation with the DNT directly replaced with an increase in the DBP concentration and an increase in the NC concentration to maintain the required energy level. The 2nd and 3rd propellant families were intended to be both “green” and less sensitive. The 2nd formulation was a double base formulation containing DEGDN instead of NG. The 3rd formulation contained the energetic plasticiser TEGDN. All 3 formulations processed well and were evaluated for their sensitivity properties. The TEGDN formulation was processed conventionally with the solvent process, but the DEGDN formulation was processed solvent-free with the aim of reducing the quantities of solvents used. The DEGDN and TEGDN formulations showed reduced sensitivity properties and performed very well when submitted to IM testing according to STANAG 4491. Both formulations are also “green” and the DEGDN formulation has the added benefit of being solvent-free as well.

## FATE AND BEHAVIOR OF PROPELLANT RESIDUES IN WATER OF THE UNSATURATED ZONE UNDER AN ANTI-TANK FIRING POSITION

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### ABSTRACT

The main goal of this paper is to study the fate of propellant residues on large soil columns. The study is aimed at characterizing the impact on soil and groundwater of military activities related to antitank firing positions. The type of ammunition used at the antitank ranges is the M72 66 mm and the 84 mm Karl Gustav shoulder rocket, containing a double base propellant comprising nitrocellulose (NC), nitroglycerin (NG), and potassium perchlorate in the case of the M72. The compounds of interest were NG and its metabolites (1,2-dinitrolycerine, 1,3-dinitrolycerine, 1-mononitrolycerine, 2-mononitrolycerine, nitrites, and nitrates) and perchlorate. A solid-phase extraction method coupled with HPLC-UV analysis was developed to monitor both NG and its degradation products at a trace level in water samples. The soil behind a firing position was sampled. Initial concentrations of NG and perchlorate in the surface soil were 3145 mg/kg and 3.52 µg/kg. Nitrite and nitrate initial concentrations were 307 mg/kg and 296/mg/kg.

The soils containing propellant residues were spread on the surface of two columns containing uncontaminated soils. Soil consisted of sand with negligible silt and clay fractions, low cation exchange capacity (CEC), and negligible total organic carbon content (TOC). The soil was watered following the recharge patterns of its location for two years (two spring seasons and two fall seasons). Effluent of the columns was sampled in order to evaluate the contaminants transported through the unsaturated zone. Percentage of recovery of chemicals was evaluated and defined as the total mass of the chemical in the effluent to the initial mass in the propellant residues at the surface of the column.

A significant nitrate concentration at the beginning of the experiment appeared in the effluent and reached a maximum of 128 mg/L. The maximum concentration level for drinking water (MCL) is 45 mg/L. Percentage of recovery of nitrates was around 130%, indicating a slight production from, possibly, oxidation of nitrites. The nitrite concentration in the effluent has shown a significant wash out at the beginning of the experiment and has reached a maximum of 45 mg/L. The MCL is 3.2 mg/L. Percentage of recovery of nitrites was around 60%, because of nitrite oxidation into nitrate. The NG, DNG, and MNG concentrations in the effluent have presented a peak of concentration at one pore volume, meaning that dissolved NG and its metabolites is transported at the same velocity of water, and not absorbed into the soil matrix. The following successive peaks of NG could be explained by its release from the nitrocellulose matrix during dissolution events. NG concentrations have reached a maximum of 174 mg/L. The MCL is 0.28 mg/L. The low percentage of recovery of NG (around 12%), is explained by NG degradation in the effluent along the flow path.

## COMBINED EFFECTS ALUMINIZED EXPLOSIVES

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### ABSTRACT

This paper reports on the development of theory and performance for recently developed combined effects aluminized explosives. Traditional high energy explosives used for metal pushing incorporate high loading percentages of HMX or RDX, whereas traditional blast explosives commonly incorporate some percentage of aluminum. Although these high blast explosives produce increased blast energies, they normally produce reduced metal pushing capability due to the relatively late time aluminum reaction. Metal pushing capability refers to the early volume expansion work produced during the first few volume expansions associated with cylinder wall velocities and Gurney energies. Recently developed combined effects aluminized explosives (PAX-29C, PAX-30, PAX-42) achieve both excellent metal pushing and high blast energies. This ability to achieve both excellent metal pushing and high blast energies has been demonstrated in a number of different experimental configurations. The excellent metal pushing capability of the combined effects explosives is due to the earlier exothermic conversion of aluminum to aluminum oxide, as compared to traditional blast explosives. However, the traditional Chapman-Jouguet detonation theory does not explain the observed detonation states achieved by these combined effects explosives. As a result, the detonation behavior of these combined effects explosives have been studied using detonation velocity and cylinder expansion experimental data with JAGUAR and CHEETAH thermochemical modeling. This work demonstrates that eigenvalue detonation theory explains the observed behavior and that both high metal pushing capability and high blast are achieved using these new explosives. Cylinder Expansion Testing and modeling results will be presented.

## DEVELOPMENT, OPTIMIZATION AND APPLICATION OF COMBINED EFFECTS EXPLOSIVES

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### ABSTRACT

This paper reports on the recent developments, optimization, and application of combined effects aluminized explosives. Traditional high energy explosives used for metal pushing (the ability of an explosive to push metal) incorporate high loading percentages of HMX or RDX, whereas traditional blast explosives commonly incorporate some percentage of aluminum. Although these high blast explosives produce increased blast energies, they normally produce reduced metal pushing capability due to the relatively late time aluminum reaction. Metal pushing capability refers to the early volume expansion work produced during the first few volume expansion associated with cylinder wall velocities and Gurney energies. Recently developed combined effects aluminized explosives (PAX-29, PAX-30, PAX-42) achieve both excellent metal pushing and high blast energies. This ability to achieve both excellent metal pushing and high blast energies has been demonstrated in a number of different experimental and munition configurations. The excellent metal pushing capability of the combined effects explosives is due to the earlier exothermic conversion of aluminum to aluminum oxide, as compared to traditional blast explosives. However, the traditional Chapman-Jouguet detonation theory does not explain the observed detonation states achieved by these combined effects explosives. Eigenvalue detonation theory explains the observed behavior and has been incorporated into the computational design process for warhead configurations. High performance combined effects shaped charges and EFPs have been developed and demonstrated. Excellent penetration has been achieved, as well as exceptional blast capability from the same combined effects warheads. Computational and experimental results are presented.

## FORMIC ACID INVESTIGATION FOR THE PREDICTION OF HIGH EXPLOSIVE DETONATION PROPERTIES AND PERFORMANCE

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### ABSTRACT

Thermodynamic equations of state for explosives products which are accurate for wide ranges of specific volumes, including overdriven and expansion regions, are required for the accurate continuum modeling of high explosive systems [1]. Traditionally, thermo-chemical equations of state, such as the BKW and JCZ3 relationships, do not result in sufficiently accurate detonation properties for the required volume range. In order to improve the accuracy of calculated detonation properties of explosives and of the resulting thermodynamic equations of state, research studies have been previously conducted. The ARDEC-developed JAGUAR computer program was used for the determination of optimized procedures of an extended JCZ3 thermo-chemical equation of state, including EXP-6 potentials for the individual product gaseous species. The JAGUAR computer program uses direct minimization of free energy to calculate chemical equilibrium for dissociated detonation product species of explosives. In particular, variable metric optimization routines were utilized for the optimization of the JCZ3 EXP-6 potential parameters for H-C-N-O explosive product species. When these studies were done, no experimental data were available for the parameterization of formic acid (HCOOH). As a result, the EXP-6 parameters of formic acid were originally optimized by minimizing the difference of experimental detonation velocities to predicted C-J detonation velocities for PETN with initial densities from 1.26-1.77 g/cm<sup>3</sup> and later modified to reproduce experimental overdriven detonation pressures [2]. JAGUAR was subsequently demonstrated to provide accurate detonation properties for wide ranges of conditions including the C-J state, overdriven detonation, and at seven volume expansions for near ideal H-C-N-O based explosives. The resulting JAGUAR capability is now used as a standard process to generate accurate JWL and JWLb thermodynamic equations of state [3].

As part of the new joint ARL/ARDEC Software Application Institute for Multi-Scale Reactive Modeling (MSRM), recent work focused on predicting formic acid thermodynamic properties, including the Hugoniot behavior using molecular dynamics modeling [4]. During the course of this work, ARL identified a set of formic acid Hugoniot data. Both the molecular dynamics and experimental data have been used to parameterize new sets of EXP-6 potential parameters for use with the extended JCZ3 JAGUAR equation of state. This provides a means for comparison of predicted detonation properties using either the empirically-derived or theoretically-based formic acid potential parameters. The computed formic acid results are in good agreement with the experimental data for both the empirical and molecular dynamics modeling approaches. The resulting JAGUAR formic acid EXP-6 parameters were subsequently used for explosive detonation and performance calculations for a variety of H-C-N-O explosives. Detonation velocities and copper cylinder expansion test data were used for the comparisons. In addition, eigenvalue detonation states [5,6] and cylinder test velocities were predicted for a small set of high performance combined effects aluminized explosives (PAX-29, PAX-30 and PAX-42) [7] to assess effects produced by using the more accurate formic acid descriptions. The results show the benefits that are now being achieved from improved accuracy descriptions for detonation products equations of

state used or explosive systems modeling, as well as the growing importance of multi-scale modeling approaches and validity.

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# FUEL REGRESSION RATE BEHAVIOR IN SWIRLING-OXIDIZER-FLOW-TYPE HYBRID ROCKET ENGINES

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## ABSTRACT

### *Introduction*

In hybrid rocket engines, it is difficult to achieve the theoretical maximum specific impulse obtainable in the fuel-rich side due to low fuel regression rates. We proposed a unique technique, a swirling oxidizer injection at fuel grain head, to improve the poor property of hybrid combustion, and showed that applying swirl to an oxidizer flow increased the overall fuel regression rate of the engine up to about 3 times [1]. Using this type of engine, we succeeded in the first launch of a small hybrid rocket in Japan. In order to put the engine into practical use, the fuel regression rate behavior for various conditions in the engine needs to be clarified in detail, which is the focus of this study. Thus, in this paper, the effects of the oxygen mass flux, fuel grain length, burning duration, fuel type, and swirl intensity on the overall and local fuel regression rates were examined.

### *Experimental apparatus*

The swirling-oxidizer-flow-type hybrid rocket engine used in this experiment was fundamentally the same in configuration as the previous engines [1]. The oxidizer was gaseous oxygen. The engine consisted of a miniature rocket type igniter using black powder, a swirling type injector having 8 rectangular slits with the geometrical swirl number, which indicates the strength of swirling flow, of  $Sg=19.4$ , a fuel grain, and a carbon nozzle. The fuel grain was made of PMMA (acrylic) and PP (polypropylene), and had a single port with an inner diameter of 40mm. The length of the grain,  $L$ , was varied from 150 to 1000 mm. The throat diameter of the nozzle was selected from 10 to 17.8 mm, depending on the specified thrust level. Burning experiments were carried out for the combustion chamber pressure range of 1 to 4 MPa and the burning time up to 27 sec. The time-averaged oxidizer mass flux,  $G_o$ , defined as  $G_o = 4 \dot{m}_o / (\pi d_{ave}^2)$ , was varied up to about 200 kg/(m<sup>2</sup>-s), where  $\dot{m}_o$  was the time-averaged oxygen mass flow rate and  $d_{ave}$  was the time-averaged port diameter estimated by the initial and final diameters of the fuel grain port.

### *Experimental results*

For all the experimental parameters within the range tested in this study using swirling oxidizer flow, the relationship between the time-averaged overall fuel regression rate,  $\dot{r}_{over}$ , and  $G_o$  could be expressed by a conventional hybrid regression rate formula as  $\dot{r}_{over} = a G_o^n$ ; where  $a$  and  $n$  were experimental coefficients. However, the values of  $a$  and  $n$  differed according to the fuel type; for PMMA,  $\dot{r}_{over}$  [mm/s] =  $0.0345 G_o^{0.778}$  and for PP,  $\dot{r}_{over}$  [mm/s] =  $0.0826 G_o^{0.550}$ . Thus, PP grains had lower fuel regression rates than PMMA grains at  $G_o$  regions higher than about 50 kg/(m<sup>2</sup>-s).

Figure 1 shows the time-averaged local fuel regression rate,  $\dot{r}_{loc}$ , of the PP fuel against distance from the grain leading edge,  $x$ , for  $L = 600$  mm during the period from 9 to 27 sec. For all the experiments, the values of  $\dot{r}_{loc}$  between  $x = 0$  and 100 mm were considerably large due to the formation of impinging jet flames by swirling oxygen flow, and they decreased

sharply as  $x$  increased. From  $x = 100$  mm (even as  $x$  increased downstream) the values of  $\dot{r}_{loc}$  remained mostly constant, and their distributions over the flow direction did not change regardless of burning duration. However, as the burning duration increased, both  $\dot{r}_{over}$  and  $\dot{r}_{loc}$  decreased slightly due to a decrease of  $G_o$  with time.

For long burning durations of about 17 sec or more, the burn-out of the grain leading edge occurred due to higher  $\dot{r}_{loc}$ . The burn-out distance from the grain leading edge increased almost linearly with time.

Although the grain shape changed with time, there was no large influence on engine performance which was independent of burning duration.

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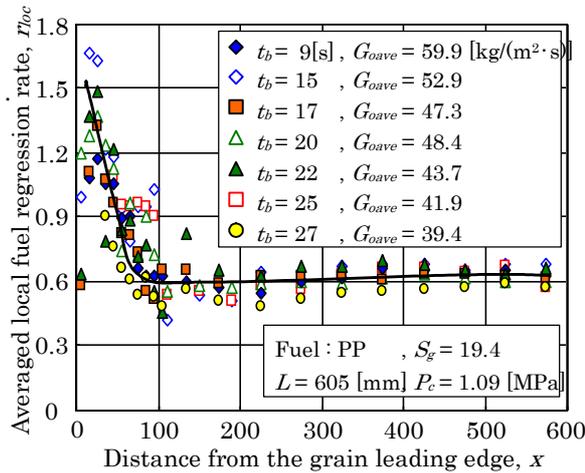


Figure 1: Time-averaged local fuel regression rate.

# INVESTIGATION OF PARAFFIN-BASED FUELS IN HYBRID COMBUSTORS

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## ABSTRACT

### ***Introduction***

Hybrid propulsions main potential is implementation in space launchers. It is very attractive due to the combination of safety, “green” propellant system, and high energetic performance. Space launchers require high thrust. However, classic hybrid rocket fuels are characterized by a low fuel burning rate and, hence, a low thrust level. To increase the burning rate, liquefying fuels (mostly paraffin-based fuels) have been suggested and studied during recent years.

In our work we execute a parametric experimental investigation of paraffin as a hybrid motor fuel. Our goal is to characterize the regression rate, the energetic performance, and combustion efficiency of paraffin-based fuels with and without additives. The experimental results are being compared to the information obtained from a thermochemical program.

### ***Experimental setup***

A laboratory scale static firing hybrid test system has been used for the experiments. The experimental setup includes a motor (combustion chamber), test stand, gaseous oxygen (oxidizer) tank, as well as thrust, pressure, and flow rate measuring gauges, and computerized data acquisition and control system. Oxygen flow rate is controlled and measured by oxidizer pressure and a choked nozzle in the oxygen supply line. Average fuel regression rate calculation is based on the overall fuel mass loss during the firing test. The combustion chamber pressure can be roughly estimated before the test by selecting the exit nozzle throat size.

### ***Experiments***

Several series of static firing tests have been conducted with different paraffin-based fuel formulations (Fig. 1). Gaseous oxygen has been used as the oxidizer for all the tests.

Plain paraffin exhibits high regression rate but low mechanical strength. Paraffin seems to undergo very severe melting, forming quite a thick layer of low viscosity molten paraffin on the burning surface during combustion. Part of this molten paraffin may leave the combustor unburned in the form of drops or vapors.

The regression rate of the paraffin-polymer mixture is lower than the rate for plain paraffin, but is still higher than that of a pure polymeric fuel. On the other hand, mechanical properties are improved significantly, whereas melting phenomena are reduced.

Figure 2 presents a summary of tests conducted with paraffin and mixed paraffin-polymer fuels.

### ***Physical-Mathematical model***

As was mentioned above, paraffin produces a liquid layer on the burning surface during combustion, enhancing the mass transfer and the apparent fuel regression rate via entrainment

of liquid droplets into the gas stream. A physical-mathematical model representing the combustion of paraffin in hybrid engine has been developed. The model is based on the heat transfer and mass loss balance in the liquid layer.

The full manuscript will present the research results in detail.



Figure 1: Static Firing Test of a Combustor Employing a Paraffin-Based Fuel

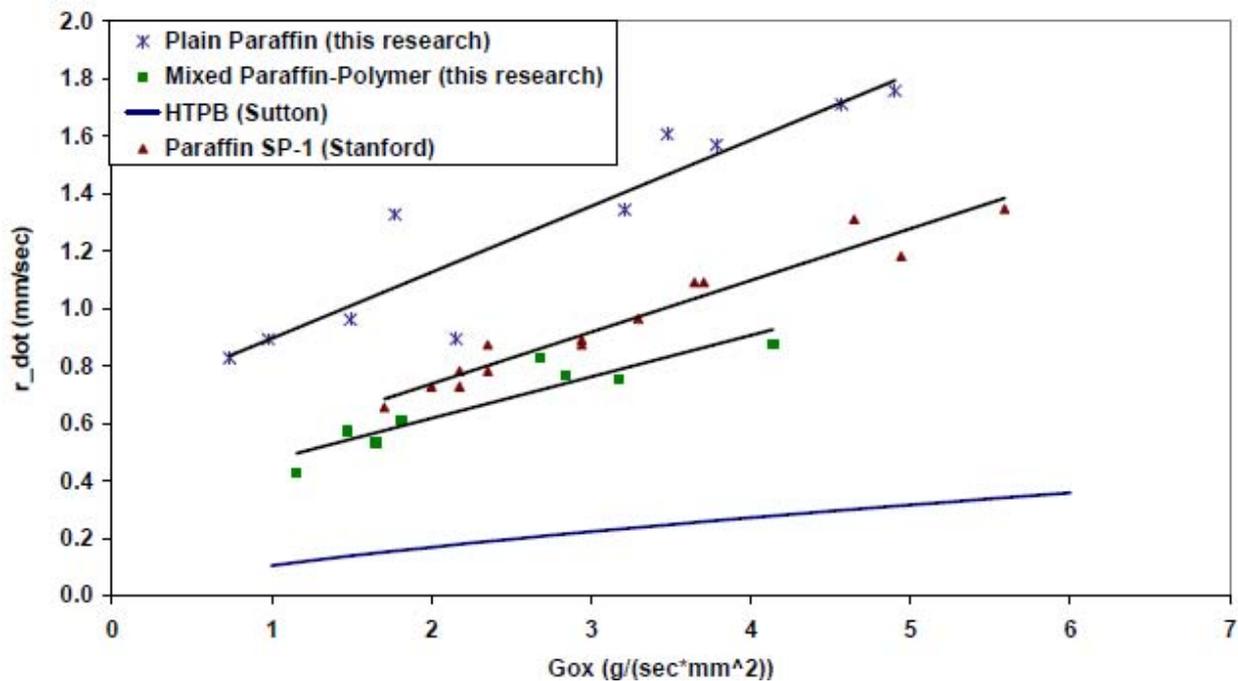


Figure 2: Regression Rate Results for Paraffin, Polymer, and Paraffin-Polymer Mixture

## HYBRID ROCKET USING GAP AS A SOLID FUEL

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### EXTENDED ABSTRACT

Two types of hybrid rocket motors which use Glycidyl Azide Polymer (GAP) as a solid fuel are proposed and the basic combustion characteristics are presented. Efforts were made to spread the burning rate spectrum of GAP to widen the design flexibility of propellant grain from a small sounding rocket to a large booster. Simple mixing with an inert polymer whose solubility parameter is close to GAP was found to be feasible, and polyethylene glycol (PEG) was selected among some candidates due to the good solubility with GAP, the same curing system with GAP, favorable density ( $1.17 \times 10^3 \text{ kg/m}^3$ ), and low cost. Burning rate was easily suppressed with higher amounts of PEG and the mechanical property of the mixture was significantly improved. GAP and PEG mixtures, with PEG concentrations higher than 50 wt%, lose self combustibility and are employed as a solid fuel of traditional hybrid rocket systems, which enable the versatility of the operation, such as extinction and re-ignition. GAP and PEG mixtures with lower than 50 wt%, can sustain self combustibility can still be used as a solid fuel for gas-generator type of hybrid rocket systems. This study categorizes the mixtures of GAP and PEG into two ways; self-combustible compositions for a gas hybrid rocket and non-self-combustible compositions for a conventional hybrid rocket, and then presents those combustion characteristics.

In the gas hybrid rocket system, GAP/PEG fuel burns in the primary combustor and its burning pressure is utilized to eject liquid oxidizer into the secondary combustor. Combustion products of GAP/PEG fuel are highly fuel-rich gases which flow into the secondary combustor, mix with liquid oxidizer there, and burn thoroughly. Test firings of the GAP/PEG gas generator (primary combustor) were conducted and  $C^*$  efficiency was evaluated as functions of test parameters and found to be in the range of 0.65 to 0.9; however, no combustion residue was found in the chamber after the firing tests. This efficiency is well predicted by the parameter,  $\phi_{cr}$  defined in our combustion model of GAP using a "Blow Off Mechanism". Combustion efficiency of this hybrid system (secondary combustor) was evaluated with gaseous oxygen and found to be high enough. Further, thrust controllability using both a change of O/F and a layered fuel grain with GAP and GAP plus a small amount of PEG was investigated, and the control from full to half thrust was experimentally attained.

Firing tests of a traditional hybrid rocket motor were also conducted. A pure PEG sample was evaluated first as a control and the comparisons were made with other samples including GAP. The effect of GAP addition to PEG is obvious and GAP enhances the regression rate of solid fuel grain, and makes the burning surface "dry". The effects of pressure, O/F ratio, and oxygen mass flux on the regression rate will also be presented.

## **DETERMINATION OF TOTAL SURFACE HEAT FLUX TO THERMAL PROTECTION MATERIALS IN SOLID ROCKET MOTORS VIA INVERSE HEAT CONDUCTION ANALYSIS**

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### **ABSTRACT**

In testing the capability of solid rocket motor thermal protection materials (TPMs), it is useful to measure the total surface heat flux to the TPM. Many solid rocket motors are propelled by metalized propellants, which contain condensed phase products. For multi-phase flows with extremely high flame temperatures, conventional heat-transfer correlations (e.g. Bartz correlation) are not applicable. One of the reasons for the inexistence of a suitable heat-transfer correlation is due to the harsh flow environment in the rocket motor for conventional heat flux gauges to survive. The other challenge is the selection of a suitable high-temperature material, which is compatible with the heat flux gauge so that the film coefficient at the gauge location does not have a discontinuity, caused by the mismatch of thermal conductivities between the gauge and the surrounding high-temperature material. In this study, a total heat flux gauge using pyrolytic graphite as the sensor material has been designed, fabricated, and tested. Multiple micro-thermocouples are embedded at different depths in the graphite sensor, and their recorded traces are utilized in an inverse heat conduction analysis (IHCA) to deduce the total heat flux and temperature at the graphite surface. This gauge is inserted in a slab of the same material as the sensor element. An analysis has also been developed to deduce the heat flux to the TPM from the measured heat flux to the graphite gauge.

With the measured temperature-time traces at different depths, the IHCA utilizes an iterative non-linear ordinary least squares analysis for deducing the total surface heat flux to the graphite gauge. Using temperature-dependent thermal properties, the IHCA is able to determine both the heat flux at the surface of the graphite as well as the heat flux on the backside of the graphite sensor. The forward heat conduction solver of the IHCA employs a finite-volume method. The IHCA was tested by specifying a heat flux history and using the forward solver to generate a temperature history. This temperature history was then fed into the inverse solver as measured temperature data, and the resulting calculated heat flux history was compared to the one initially specified. The IHCA has been proven to replicate the specified heat flux histories almost exactly. In addition, the gauge was tested by applying a known heat flux to the surface of the gauge and using the IHCA to reproduce the measured power input curve. The calculated heat flux fell within the bounds of the experimental error, proving its accuracy. The gauge was then utilized in a series of subscale solid rocket motor firings, which were used to study the erosion behavior of TPMs. This heat-flux measurement technique has been proven to be robust, producing repeatable and reasonable results for each test. Therefore, this method has shown great potential in measuring the total surface heat flux inside a solid rocket motor.

# **A NOVEL RADIATIVE HEAT FLUX MEASUREMENT TECHNIQUE FOR COMBUSTION PRODUCTS FLOWING IN SOLID ROCKET MOTORS**

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## **ABSTRACT**

To assess the performance of thermal protection materials (TPMs), it is necessary to observe them in a well-characterized thermal environment. While it is important to know the total heat flux to the TPM, it is also necessary to know what fraction of that flux is due to radiation. In this paper, a new gauge has been designed, with its radiation-sensing element isolated from the convective combustion product flow by a sapphire window. To avoid damage to the window, the gauge is recessed below the surface of the TPM. This restricts the sensing element to viewing a narrow solid angle of the total hemispherical radiative heat flux incident on the TPM surface. The fraction of radiation incident on the detector is considered proportional to the solid angle viewed by the detector.

The combustion of metallized solid propellants generates condensed-phase  $\text{Al}_2\text{O}_3$ ; these particles can quickly coat the window of the radiometer if they are not purged away in some manner. For this purpose, a flow of cold helium gas is introduced above the window of the radiometer at an oblique angle to the combustion product flow. The helium purge gas flow can keep the window clean and maintain it at relatively cool temperatures. A series of CFD calculations was performed with varying He mass flow rates and  $\text{Al}_2\text{O}_3$  particle sizes. The results of these calculations demonstrate the ability of the angled He injection to prevent particles from impacting the window, and to prevent the hot combustion gases from heating the radiometer directly.

A radiometer was built for use in a laboratory-scale solid rocket motor. This gauge was then installed in a laboratory-scale solid rocket motor burning highly aluminized AP-based composite solid propellant. A series of rocket motor firings were performed that demonstrated that the He purge gas is capable of maintaining a clean window. The purge gas system also sufficiently protected the gauge from thermal damage. The measurements provided by the gauge lie within the range expected from theoretical calculations, and are, therefore, considered reliable. Thus, it is determined that this radiometer is robust and capable of providing accurate measurements of the radiative heat flux from solid propellant products inside a solid rocket motor.

# A STUDY ON THE FABRICATION PROCESS, THE HEAT TRANSFER AND ABLATION ANALYSIS FOR SOLID ROCKET MOTOR NOZZLE THERMAL LINERS

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## ABSTRACT

Nozzle thermal liners for rocket propulsion system are exposed to combustion gas with hot and high pressure. The function of thermal liners is to protect rocket motor structures from such situations. In this process, the materials for thermal liners are required properties which are of thermal/erosive resistance and high strength. The fabrication process has to be set up by material selection, heat transfer and fluid dynamics analysis, etc.

In the case of carbon/phenolic composite, phenol becomes char and forms char layer with temperature increase. Erosion occurs on the char surface and then the char layer increases more. Erosive polymers on the material surface are evaporated as temperature increases. The materials that evaporate first are mainly water (steam), solvent and low weight molecular polymers, and these suppress a large quantity of temperature increase. Gradually, thermal properties of polymers are getting worse and chains of polymers become broken off from branch to main as surface temperature increases. Finally, most chains only remain as carbon and form char layer.

This study is about the development of a large size solid rocket motor with sub-merged nozzle and composite propellant. The thermal liners consist of carbon/phenolic, silica/phenolic and glass/phenolic composites that are used for each part of the nozzle.

For the nozzle design, erosion by combustion gas flow and heat transfer was estimated by Hanwha's own S/W named as Advanced Structure Heat Transfer and Ablation Analyst. Tape wrapping method was applied for the fabrication by HYDRO-CLAVE of Thermal Equipment Corp, Ltd. Static firing tests on the ground of 60sec burning solid rocket motors were performed and presented the results of erosive phenomenon by analysis and ablation trend through real tests.

As a result of this paper, the performance of the software for nozzle erosion and heat transfer estimation was validated. Also, the fabrication method of nozzle parts was established to be proper to apply for large size solid rocket motors.



Figure 1: The Comparison to Results of Analysis Program and Real Ablation Configuration

## **MUNITION HEALTH MONITORING – PRINCIPLES AND EVALUATION OF AMMUNITION STRESS DATA GATHERED UNDER OPERATIONAL CONDITIONS**

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### **ABSTRACT**

Munition Health Monitoring (MHM) subsumes any measurement which yields relevant information on the state of ammunition during its life cycle, and of course, the assessment of the gathered data. Such measurements – typically temperature, relative humidity, vibrations and shock events – can be performed for in-service ammunition by external sensors and for future ammunition by embedded sensors. The benefit of such measurements is the possibility to predict remaining safe-operational life times, performance changes, and in the future, the remaining functional reliability of ammunition, or to make sure that objects which have experienced the highest stress will be chosen for classical ammunition surveillance.

Gathering and evaluating data of external sensors - Data Logger situated close to the ammunition – is the more difficult method due to a complex logistic chain and the necessity of correlating the measured data to the conditions seen e.g. by the explosives of a propulsion system. But the necessary tools to assess such data have been developed at RWM during the last years and are now available for different 30, 120 and 155 mm ammunition.

As an example, temperature and relative humidity data gathered inside 120 mm Leopard 2 tanks with heat protection during operations in Afghanistan by the Danish Army are used to calculate stabilizer depletion and performance changes of 120 mm KE ammunition stored in the ammunition rack of the turret. The results of the evaluation correlate very well with predictions made on the basis of “climate models” derived for hot, dry areas and they show the importance of heat protection measures with respect to safe-operational life time of ammunition.

Even if the described life cycle management system for in-service ammunition has the disadvantage of a manual assignment of ammunition to data loggers for every step in the logistic chain. The assessment of the gathered data is not fully automated up to now and it seems to be the only system which has proven its suitability for use under operational conditions. It allows a quasi-real-time monitoring of the state of ammunition with respect to safe-operational life time and performance changes and enables the user to keep ammunition much longer in service than it would be expected by rough estimates based on the climatic categories defined in STANAG 4370 / AECTP 200.

# LIDAR DETECTION OF EXPLOSIVES VAPORS USING EXCIMER LASER

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## ABSTRACT

Recently much attention has been paid to the developments of opto-electronics systems for remote detection of terroristic threats. Of course, this is based on the advances in laser and electronics technologies, as well as on the prospects of using numerous effects of interaction between radiation and matter aimed at solving certain practical problems.

**LIDAR (Light Detection and Ranging)** methods that are based on the principle of pulsed laser and radar, which enables one to acquire comprehensive information on the spatiotemporal characteristics of the environment. It is just for this reason that development and use of LIDAR methods in the systems of counter-terroristic measures have become an urgent task.

This contribution presents a discussion of the efficiency of using LIDAR methods for remote detection of various manifestations of terroristic activities. The effects of radiation interaction with matter are classified; sensitivity of the methods that use these effects is an estimate, and potentialities of the LIDAR technologies are assessed. Also, various scenarios of using the LIDARs are being discussed in this paper. The sensitivity of the LIDAR methods for detection of chemical agents and explosives based on fluorescence and Raman scattering of laser radiation is estimated. As a result, the LIDAR explosives detector, based on the application of specially designed KrF laser is described. The LIDAR detection principle is based on the combination of the one color laser fragmentation and laser induced fluorescence of explosives fragments. This is a very promising technique proposed by T. Arusi-Parpar.

But the problem is that it takes more powerful laser sources to obtain necessary sensitivity and to reduce the measurement time. That is why we had proposed to apply a powerful tunable excimer KrF laser, which should have a narrow line (3pm) at the fringe of the amplification envelope. Such a laser was developed in the Institute of High Current Electronics, SB RAS. This allows us to detect TNT and TG vapors at distances of about 5m at the room temperature in first experiments. We hope that further development and modification of the LIDAR system will allow us to reach higher sensitivities at longer distances. The research problems that are to be addressed in further development of the LIDAR detectors of explosives are formulated.

**Keywords:** *explosives, LIDAR, laser, stand off detection.*

## REGRESSION RATES AND CCPS MEASUREMENT OF METALIZED SOLID FUELS

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### ABSTRACT

Experimental investigations on regression rates and combustion condensed products (CCPs) of metalized solid fuels for hybrid propulsion systems are presented in this paper. Influences of oxidizer flow rate, pressure, and fuel-grain composition were investigated using three different laboratory-scale burners designed and developed at the Space Propulsion Laboratory (SPLab) of Politecnico di Milano.

The first rig includes a pressurized test chamber (up to 30 bar) equipped with a video acquisition system for quasi-steady measurement of the solid fuel regression rate. An axial symmetric (axisymmetric), cylindrical, solid fuel grain, with a single central port, is accommodated in a cylindrical case; combustion pressure is kept constant by means of an automatic pressure control system. The grain is ignited by a laser-activated solid propellant primer charge. Quasi steady regression rates were measured by a proprietary video technique.

The second rig is a 2D slab burner designed to investigate the boundary layer and the flame structure, the metal powder behaviour, and the development of the combustion process. Video recording techniques allow for the measurement of the instantaneous, local regression rate along the grain surface; the grain geometry is rectangular with a length up to 160 mm. The grain ignition is obtained by a pilot flame; the oxidizer flow rate is measured by a calibrated nozzle. A special collection device was designed to collect the combustion condensed residues; their chemical analysis gives the relative combustion efficiency of different solid fuel formulations and allows for the measurement of the condensed residue's size distribution curve.

The third rig allows for the burning of small-size slabs of solid fuels under controlled pressure and oxidizer flow rate. This micro burner allows for the observation of the details of the resulting flame with high-resolution video-recording. Ignition was performed using a hot wire; pressure was kept constant during the combustion test by means of an automatic pressure control system.

These experimental rigs were used with reference to a series of solid fuel compositions, including pure HTPB (hydroxyl-terminated-polybutadiene), HTPB + LP (liquid paraffin), and mixes of these fuels added with micro-aluminum, nano-aluminum and magnesium-hydride powders. Regression rates were measured for a wide range of grain compositions, oxidizer compositions, flow rates and pressures. Effects of metal nature, and metal powder mass fraction and size are discussed. A detailed analysis of the condensed combustion products was performed, and the combustion efficiency of the investigated compositions was estimated.

# ANALYSIS OF THERMOPLASTIC PROPELLANTS BASED ON NOVEL BINDER SYSTEM

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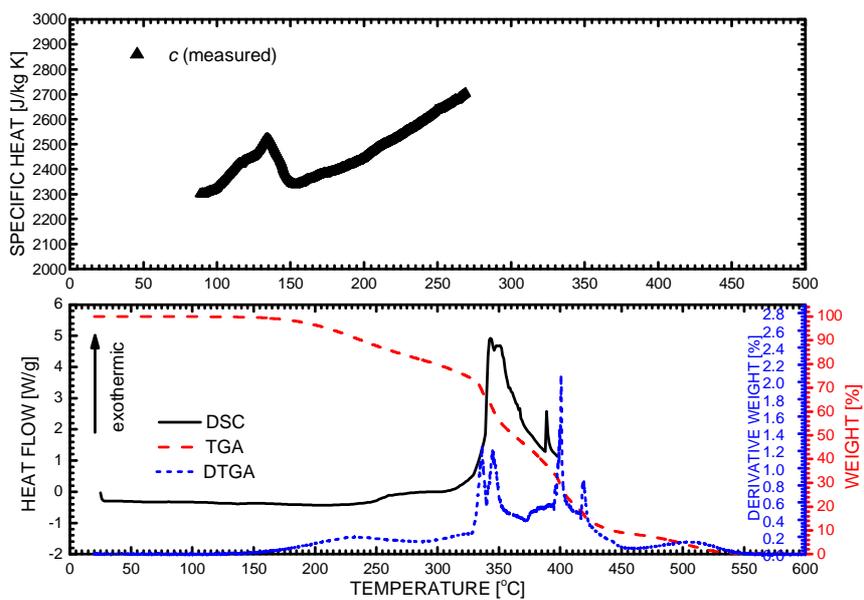
## ABSTRACT

The objective of this paper is to present a new binder system that can be applied in composite rocket propellants to improve properties of these propellants, not only for better performance, but also to reduce waste and pollution. This novel system is based on the oxygenated thermoplastic elastomer (TPE) binder, which consists of a multi-block segmented copolymer (alternating hard and soft segments) with the addition of a plasticizer, wetting agent, and an anti-oxidant. The tensile and tear strengths of this binder system can be compared to other binder systems, which are applied in composite propellants. The dynamic behaviour is particularly good with low hysteresis, high resilience, and good flex fatigue.

Propellant compositions using the novel TPE binder system can be processed with up to 90% of solids in the formulations, which depends on the type of process used. Temperatures of processing can be between 95-130°C depending, again, on the manufacturing method. Viable commercial processing techniques could be used for loading propellants with a high percentage of filler such as extruding, injection molding, two-roll milling, or pressing.

All polymerization reactions are completed before propellant manufacture begins, and post-process curing is eliminated during the processing of the propellant with the novel binder. Due to this, electrical consumption, which during processing is necessary only during heating, can be decreased in comparison with processing techniques applied in thermoset propellants, which require to be held several days at elevated temperatures to cure properly. By applying the novel binder system, scrap and composition errors could be reformulated by heating and reprocessing or blending again to meet the specific requirements. Another advantage is that after mixing, the excess product can be reheated and used again, unlike the current cross-linked systems where the excess simply becomes waste. In this way, waste and pollution during processing of grain can be reduced. Also, the ability to recycle or reuse decommissioned ordnance at the end of its life use is possible, through modification of the binder, plasticizers, or additives, and such ability can have the most significant effect on pollution prevention and waste minimization.

The effect of the novel TPE binder system on the burning rate and mechanical properties of AP based propellants is demonstrated. Also, thermal behavior of these propellant compositions was studied. As physicochemical characteristics of propellants do depend on the nature of their ingredients, especially the binder, thermal behavior of the binder has also been investigated (Fig. 1). Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) have been applied for this. It turns out that propellants based on the novel TPE binder have a better energy performance than HTPB/AP, and show good processing and aging characteristics at low cost.



**Figure 1: DSC, TGA, and DTGA plots of TPE binder at a heating rate of 10 K/min, and specific heat**

## **A NEW CLASS OF BONDING AGENTS FOR HIGH ENERGY PROPELLANTS**

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### **ABSTRACT**

Bonding agents are critically important components of solid propellants. They affect processing, mechanical properties, ballistics, safety, aging, temperature cycling, and insensitive munitions (IM) propellant characteristics. A bonding agent interfaces with the surface of the oxidizer and chemically reacts to the polymeric binder during the propellant cure process. The bonding agent typically doubles the stress, triples the strain, and maintains the modulus of propellants at a fairly uniform value at room temperature.

There is a need for effective bonding agents that function effectively in different oxidizers. Bonding agents have been developed and are typically used in AP oxidized propellants using a hydroxyl terminated polybutadiene (HTPB) binder. However, effective bonding agents do not exist for multi-functional oxidizers AP, AN, ADN, etc. with nitrate esters and GAP in polyether binder systems.

MACH I, Inc. presents a new concept in bonding agents where the bonding activity is directly reacted with isocyanates to produce a combination of bonding agent and curative. Solubility is increased, reactivity decreased, binder filler interaction is optimized, and the bonding agent is an inherent part of the polymer matrix.

This paper will describe the new di-functional bonding agent DITBA and tri-functional bonding agent TITBA developed by MACH I, and now commercially available for evaluation of propellant formulators.

## **CONTROL OF MAIN CHARACTERISTICS OF COMPOSITE PROPELLANTS BASED ON AMMONIUM NITRATE BY NANOSIZED METAL POWDERS**

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### **ABSTRACT**

High energetic compositions based on ammonium nitrate (AN) and active binders are studied. Micron aluminium, nano-aluminium and nitramines were introduced into composite propellants. Results of comparative analysis of influence on compositions burning rate are adduced. Content limit of nano-metal effective use for control of main ballistic and technological characteristics of composite propellants is determined. Data of TGA for composite propellants and interrelation with burning parameters is presented.

AN is potentially able to provide the development of cheap and ecologically safe high energy materials (HEM) for space applications. Nevertheless combustion of compositions based on AN is less effective. One of the basic ways to increase the efficiency of combustion is the use of active binders and nano-sized metal powders, especially nano-aluminium particles.

As active binder tetrazole polymer plastisized by nitramine-nitroether agent was used. Basis HEM contents 25% mass. Active binders, up to 15% Al with different dispersity (ALEX was included), up to 15% HMX and AN as the remaining ingredients. The choice of binder is able to provide realization of burning rate base level and the possibility to control it.

It has been found experimentally the possibility of development of high effective HEM based on AN and nano-metals with variations of ballistic characteristics in a broad range: specific impulse up to 235-250 sec at combustion chamber pressure of 4 MPa, burning rate from 1-2 mm/sec up to 15 mm/sec at 10 MPa.

Interrelation of parameters of thermal decomposition of mixtures with combustion characteristics is shown. It can provide the possibility to control the burning rate by catalysts of thermal decomposition of mixtures, first of all by metal oxides.

The necessary structure-rheological characteristics are provided.

The area for developed HEMs is controlled SRM for space propulsion applications, gas generators for airbags, emergency safe systems, etc.

## EXPLOSIVE VENTING TECHNOLOGY FOR COOK-OFF RESPONSE MITIGATION

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### ABSTRACT

Insensitive Munitions (IM) requirements place a great demand on the ability of ordnance to withstand unplanned external stimuli. When subject to slow cook-off (SCO) for example, ordnance is required to exhibit a response no more severe than a burning reaction (type V by Mil-STD 2105C). Our current effort concentrates on developing a venting design capability through the use of laboratory characterization and computer modeling. Before designers can mitigate the response of munitions subject to SCO, they must first understand how confined explosives behave when heated. A variety of effects control the response, including venting, sample size, and heating rate. Small and large scale venting experiments have been conducted using highly controlled thermal cook-off test fixtures. The small scale test fixtures consist of a small diameter (25mm) explosive pellet, highly confined in a steel housing. The large scale test fixtures consist of a larger diameter (78mm) explosive pellet, highly confined in a steel housing. One end of the housing contains a vent disc with venting area of which is fixed for a given test but varies from one test to the next. The steel housing is then heated using electric heating bands or an oven and feed-back control, based on measured thermocouple temperatures, until a reaction occurs. These experiments allow us to characterize the explosive violence as a function of a known vent area and controlled heating rate. The required venting area is experimentally determined at different heating rates. Large scale hardware has been used to investigate scaling effects. The large scale hardware is essentially a scaled-up version of the small scale test, designed using a 78mm diameter billet. A variety of melt pour, cast cure and pressed explosives have been tested to date, including Composition B, PBXN-109 and PAX-28. Tests results indicate that some explosives (PAX-28 and PBXN-109) intrinsically require less vent area to achieve a non-violent response than others (Composition B). However, the results also indicate that for solid explosives, a violent reaction commonly occurs when the samples were heated without the use of a melt out liner which allows gaseous products to reach the vents. This is in contrast to melt cast explosives that seem to be able to respond in a non-violent manner without the use of a liner. Thermal modeling, including explosive kinetics, has also been conducted using ALE-3D and, for some solid explosives (PBXN-109), shows close agreement with actual test results. However, very limited modeling is available for melt pour explosives. A high temperature closed bomb is under development for the burn rate characterization of high explosives. In order to reach temperatures of up to 400°F, a heating system using oil has been employed. The testing results are also being used to parameterize and develop analytic burn modeling of vented warheads. The U.S. Army has traditionally performed slow cook-off testing at a heating rate of 50°F/hour. Recently, the U.S. DoD has standardized with NATO to a 6°F/hour test, now required on most U.S. Army programs. At 50°F/hour heat rate, pressed or cast cure explosive billets normally ignite near or on the billet surface, thus providing a geometry where the gas byproducts from the burning explosive can be more easily vented away from the explosive. However, at 6°F/hour heat rate, the ignition normally occurs near the center of the billet. In this case, gas products can be confined, resulting in a violent reaction. Recent work has concentrated on concepts for using energetic materials to force the reaction to the billet surface during 6°F/hour heating in order to produce a non-violent reaction.

## **FORMULATION AND DEVELOPMENT OF AN EXPLOSIVE THAT ALLOWS CONVENTIONAL 155mm PROJECTILES TO ACHIEVE IM STATUS**

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### **ABSTRACT**

An intensive effort is being made to develop a cost effective, IM compliant 155mm bursting projectile. Understandably, the desire is for performance and cost comparable to the current projectile, but, in addition, the ability to pass most, if not all, IM tests.

The Energetics & Warheads Division at ARDEC worked to develop an explosive formulation for this purpose which achieved good success at fulfilling all the goals, including passing IM tests. Achieving success in Sympathetic Detonation and Shaped Charge Jet was especially noteworthy. The formulation can be melt cast loaded in existing production facilities and uses readily available ingredients.

The formulation to be discussed utilizes a TNT melt phase component that is desensitized using a method identified at ARDEC in the late 1980's. Further shock desensitization was achieved by seeding the melt phase with NTO. It has an energy output similar to TNT and there is no performance degradation due to adding the TNT desensitizing ingredients that occurs, in fact, the detonation pressure actually improves. A method used to adjust shock sensitivity to the value needed to pass SD by varying the fractions of the ingredients will be discussed. Laboratory characterization of the explosive will be presented.

IM tests, sometimes with slight, cost reducing modifications from the STANAG's, were performed with the formulation loaded into M795 projectiles, a large 155mm bursting projectile having about 12 kg of explosive. The results will be presented.

**BOOSTER CANDIDATES FOR IM APPLICATION AT RHEINMETALL DENEL  
MUNITION (RDM)**

Christo Emile Du Toit

*RDM, South Africa*

**ABSTRACT**

Currently two formulations are being used for all IM applications at RDM. For missile warheads, a Hexanitrostilbene (HNS) based formulation is used, regardless of the warhead application, e.g., shaped charge or fragmentation. For high setback application, an HMX based formulation, originally developed as an IM main charge, is used. While the mentioned formulations are functional, the situation is not optimal. The focus of the reported investigations was two-fold: Firstly, alternative binders for HNS-based PBX were evaluated. Promising candidates would then be regarded as alternatives for application as boosters in shaped charges. Preparation of granular product, pressing, mechanical properties, and detonative evaluation were parts of the evaluation. The latter evaluation consisted of the small-scale gap test and some comparative initiation testing that may in future be used as the basis for statistical detonation train reliability testing. Secondly, some alternative HMX-based formulations were compared to the existing standard, which is a highly insensitive HMX-based formulation. The aim was to identify candidates for further evaluation that may ultimately find application in fragmentation missiles, as well as high setback munitions. New candidates had to initiate easier than the standard without negatively impacting the IM properties of the system. Manufacture procedures, mechanical properties, and detonative evaluations are reported, while IM properties are to be determined.

## **MITIGATION TECHNIQUES FOR REDUCED ROCKET MOTOR VULNERABILITY AGAINST EXTERNAL THERMAL STIMULI**

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### **ABSTRACT**

Solid propellant rocket motors used widely in conventional and state-of-the-art tactical missiles typically react violently when exposed to external thermal stimuli. Collateral damage caused as a result includes potential loss of life and compromised operational capability.

Basic reaction mechanisms of such rocket motors are described for certain cook-off scenarios. Various mitigation techniques devised to alleviate violent cook-off reaction are presented and its effectiveness against thermal stimulus extremities argued with supporting examples.

## PROBING REACTION DYNAMICS IN NANOTHERMITES

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### ABSTRACT

Nano-scale particles composed of a metal and metal oxide can undergo a violent thermite reaction. In these studies, we probe with time resolved mass-spectrometry and optical emission the speciation and reaction dynamics of these materials. Species of Al, Al<sub>2</sub>O<sub>3</sub>, and metals from the oxidizer were identified in mass spectra as reaction products. O<sub>2</sub> released from the decomposition of oxidizer particles was also observed during the course of the thermite reactions. We find a correlation between the onset temperature of O<sub>2</sub> release, and the ignition temperature suggesting that the formation of oxygen from oxidizer particles may be the important factor. An ignition delay is also observed from both optical and mass-spectrometry measurements. The delay increased with an increase in shell thickness of the oxide-on-aluminum nano-particles implying a diffusion mechanism, and from which an effective solid-state diffusion coefficient can be extracted. Using classical molecular dynamics simulations we have simulated the mechanochemical behavior of oxide coated aluminum nano-particles. The results show that the high temperature oxidation process is driven by the electric field present in the oxide layer and accounts for approximately 90% of the mass flux of aluminum ions through the oxide shell. This result is consistent with the very interesting observation that the thermite event leads to a very short (< 100 μs) current pulse of ions.

## **FORMATION OF NANOTHERMITE STRUCTURES USING VARIOUS SUPPORT SUBSTRATES AND BINDER MATERIALS**

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### **ABSTRACT**

This research effort investigates the use of a support substrate, along with the water-processing method and various binders, to form consolidated nanothermite structures of the aluminum-bismuth trioxide-iron oxide system. The types of support substrates used were in the form of a felt-like material. It is theorized that the high surface area of the fibers in the material acts as a deposition site for the nanothermite material during drying. The desired product is a consolidated material that is less sensitive to ignition than loose powder, and also less brittle than granules, due to the added internal support of the fibers. Multiple substrates were investigated including alumina felt, and polymeric materials, to determine which material was the most effectively infiltrated with the nanothermite slurry, and also provided the most structurally sound final product. Several different processing additives and binder materials are also used to determine their effectiveness in adhering to the substrate and preventing nanothermite material from breaking apart to form smaller, more sensitive particles. Aluminum powders, having both flake and spherical morphologies, are used in the nanothermite formulations to determine which is better suited for the formation of consolidated structures. The effect of support substrate and binder on the reduced sensitivity to ignition by both ESD and laser impulse is also presented. Combustion of the nanothermite felts in a closed-volume pressure cell is used to determine pressurization rate and peak pressure output, in comparison to loose powder and granular materials that are more sensitive to ignition. Gasifying agents can also be added as a surface coating on the nanothermite felts to further decrease ignition sensitivity and produce higher pressures upon combustion.

## THERMOELECTRIC PULSE POWER GENERATION USING SELF-SUSTAINING GASLESS NANO-REACTANT SYSTEMS

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<sup>2</sup>*Naval Surface Warfare Center, Indian Head, USA*

### ABSTRACT

Defense systems such as expendable weapons, and countermeasure devices often use and rely on pulse electric power. Thermoelectric (TE) modules, which convert heat into electricity and vice versa (Seebeck-Peltier effect), can be used for short-term power generation. Commercially available TE modules are manufactured with a series of p- and n-doped semiconductor materials inserted between two ceramic face sheets. The ceramic material on both sides of TE device adds rigidity and the necessary electrical insulation. The most common ceramic material used in these devices is alumina. However, this material has a relatively low thermal conductivity (28W/m-K), therefore it should be replaced with more thermally conductive material, e.g. aluminum nitride (180 W/m-K), especially when fast generation of electrical power is required. In addition, for the fast generation of electrical power, a strongly exothermic gasless reacting system is needed as a source of thermal energy. We investigated a self-sustaining nano-thermite reactive system containing Fe<sub>2</sub>O<sub>3</sub>/Al and coated directly on alumina plates of a TE module. Upon initiation this produced a pulse voltage of 1.5V with the rise time of about 200 milliseconds. In the experiments performed, we coated alumina plates of two TE modules and they were placed on top of each other with Ni/Al foil inserted in between the two coated surfaces. On initiation, this system produced about 4.5 V with a rise time of about 220 milliseconds. Experiments have shown that the replacement of alumina with aluminum nitride significantly reduces the rise time. The effect of TE configurations, reacting systems, and types of ceramic substrates on the dynamic voltage generation will be presented and discussed.

## HIGH-REACTIVITY ALUMINUM POWDERS

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### ABSTRACT

The need for advanced energetic materials has grown rapidly in recent years. There is an interest in low cost technologies as well as higher performance novel energetic materials, in particular the synthesis of energetic ingredients for application to explosives, propellants and pyrotechnics. An example of particularly interesting component is high-reactivity aluminum powders. There are many advantages associated with incorporation of high-reactivity aluminum powders into fuels, propellants, and pyrotechnic compositions such as the following: shorter ignition delay and burn times, and enhanced heat-transfer rates from the surface area. This paper presents some results regarding the processing and characterization of activated high-reactivity aluminum powders.

One possible approach to the development of activated high-energetic aluminum powders consists of a modification of the surface layer of the metal to improve its reactivity. Some methods of the aluminum surface layer modification were developed. One of them includes the coating of aluminum particles by a thin (about 100 nm) nickel, iron or copper layer. A controlled chemical deposition technique for coating aluminum particles by Ni, Fe and Cu was developed. Not only aluminum powders, but also aluminum flakes were coated by the thin nickel layer. Another method is based on the pitting corrosion of the aluminum oxide layer through a treatment of aluminum powder by sodium or magnesium chloride solution. Pitting is a type of localized corrosion in which a small portion of the exposed surface experiences very high corrosion rates that result in small pits in the metal surface.

Investigations of the behavior of the Ni, Fe and Cu-coated aluminum particles during their heating in nitrogen and air were carried out. Experiments demonstrated better ignitability of the coated Al particles in comparison with regular Al particles. The improved ignitability is explained by the exothermic reaction between Ni, Fe, Cu and aluminum and by thermal and mechanical properties of the formed intermetallics. It has also been demonstrated that during ignition in air the coated aluminum particles exhibit reduced agglomeration in comparison with regular Al particles. Improved ignitability was also found for the aluminum particles exposed to the pitting corrosion. It may be explained by the easier penetration of oxygen to the aluminum core through the defected oxide layer due to pitting corrosion.

Another possibility to get the high-reactivity aluminum powders is to increase their specific reaction surface. To do that, the nano-scale aluminum powders with particle size of about 100 nm were developed. However, complicated and power-consuming equipment is used to produce nano-scale aluminum powders (wire explosion, plasma evaporation, etc.); thus, making these powders is very expensive. In this work we have developed a simple thermochemical method for the production of highly-porous aluminum particles with porosity of 50-60% and specific surface area about 12-18 m<sup>2</sup>/g (Figure 1).

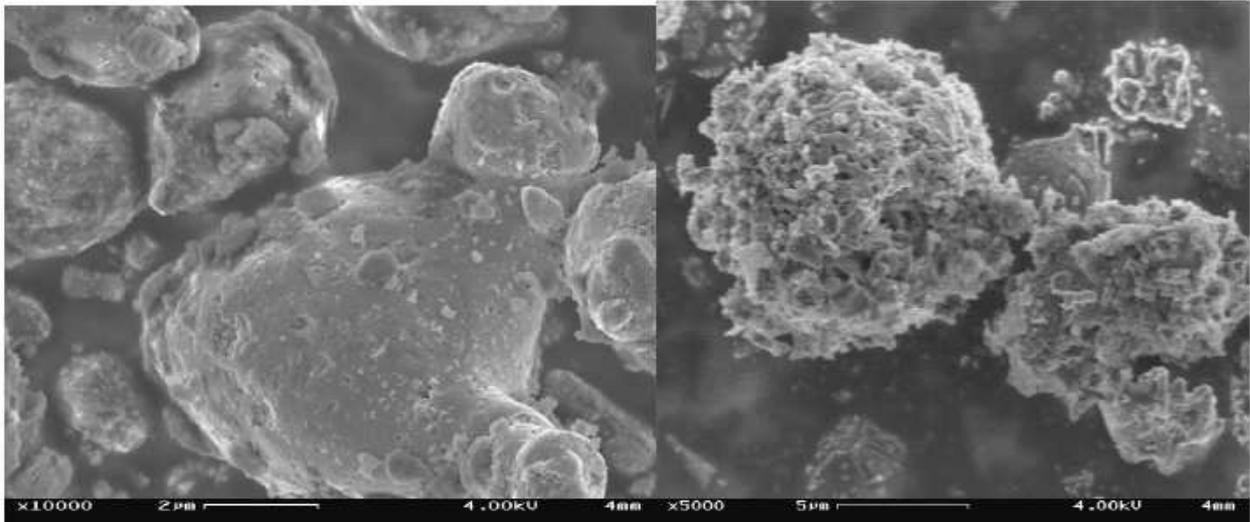


Figure 1: Regular (left) and porous (right) aluminum particles.

Study of the ignition behavior of the highly-porous aluminum powders with a mean particle size of 10 and 25  $\mu\text{m}$  revealed their very high reactivity and short ignition time, comparable with that of nano-scale aluminum powders.

# EXPERIMENTAL INVESTIGATION OF METALIZED SOLID FUEL RAMJET COMBUSTOR

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## EXTENDED ABSTRACT

### ***Introduction***

The need for long range, high speed flight vehicles has led to the search for a cost effective, high performance jet engine. The ramjet engines are the simplest among all air breathing jet engines, and give much better performance than rocket engines at high Mach numbers. The Solid Fuel Ramjet (SFRJ) is the simplest ramjet engine; the combustion chamber of the SFRJ is made of a hollow cylinder of solid fuel (typically based on a polymeric material). Air coming from the diffuser is slowed down by a series of oblique shock waves and a normal shock wave to subsonic speed before entering the combustion chamber and it flows through the solid fuel cylindrical port and reacts with the fuel. The combustion products accelerate through a nozzle in the rear part of the engine, producing jet thrust. This process is quite efficient in flight Mach numbers between 2 to 5 yielding a high performance in terms of specific impulse and specific fuel consumption.

### ***Objectives and motivation***

The objective of the present research is to investigate the characteristics of a metalized solid fuel ramjet combustor in comparison with non-metalized fuels. The research is motivated by the analysis that indicating a specific thrust (i.e., thrust per unit airflow rate) of a solid fuel ramjet vehicle employing common hydrocarbon fuels may not be sufficient to overcome the drag. One possible use of a solid fuel ramjet is for self-propelled gun-launched projectiles. The integration of solid fuel ramjet in a gun projectile can provide a remarkable improvement of the projectile's performance. To overcome the high drag that is generated during flight at speeds of around 1000 meter/sec, a very high specific thrust is required. One possible way of improving specific thrust of a polymeric fuel is by adding metal particles to the fuel. Previous theoretical studies show that metals such as magnesium, aluminum, and zirconium can provide much higher heat release per unit mass of air than hydrocarbon fuel; hence, substantially increasing the specific thrust of the engine.

### ***Test system***

To simulate the combustor inlet stagnation conditions in a high flight Mach number, a vitiated air heater was used. The heater uses hydrogen gas to heat the air to simulate air stagnation properties up to 1500K and 50 atm, and is capable of testing various combustion chamber configurations, as well as different fuel materials, both rigid (Plexiglas) and soft (HTPB). Pressure is measured along the combustion chamber and in the heater, and the thrust of the entire system is also measured. Airflow rate and both hydrogen and oxygen (makeup) flow rates are measured, as well. The solid fuel grain was made of a polymer-based material (HTPB) with or without metal additives.

### ***Preliminary results***

Tests have been conducted with an HTPB fuel grain with different percentages of metal powder (in this research we focused mainly on aluminum powder). Figure 1 shows one of the preliminary tests conducted with HTPB fuel containing 20% aluminum powder.

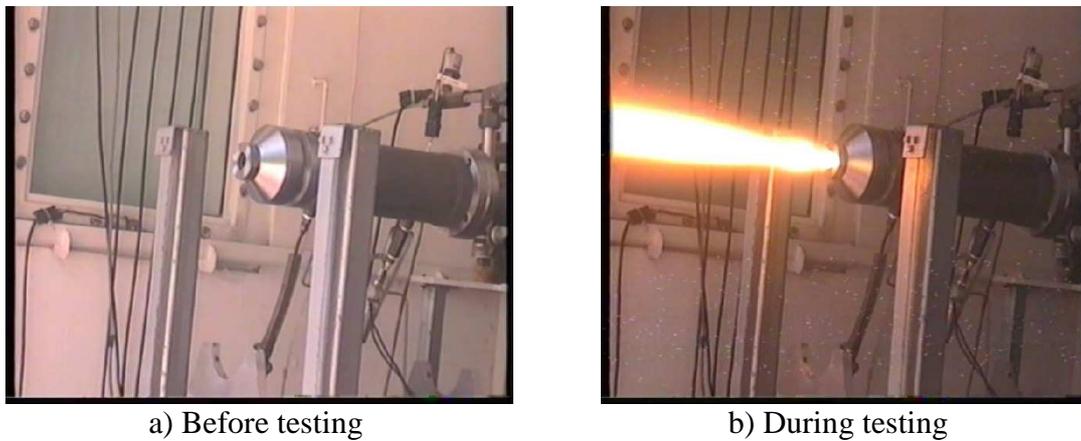


Figure 1: Solid fuel ramjet combustor before and during testing.

Theoretical calculations show that due to the aluminum additive, the thrust of the engine should increase; whereas the specific impulse is likely to decrease to some extent. The addition of metal particles will increase the difficulties in terms of combustion efficiency due to the complexity of metal combustion. Special metal treatment (nickel coating) developed in our lab has indicated reduced ignition delay time and temperature. Such coated particles have been used as well. Preliminary tests conducted with both metalized and non-metalized fuels show fair agreement with the model prediction (see Figure 2). The full paper will include more extensive test results in a wider operation range. If successful, the study will mark a significant step towards the actual use of solid fuel ramjet propulsion in practical supersonic projectiles and missiles.

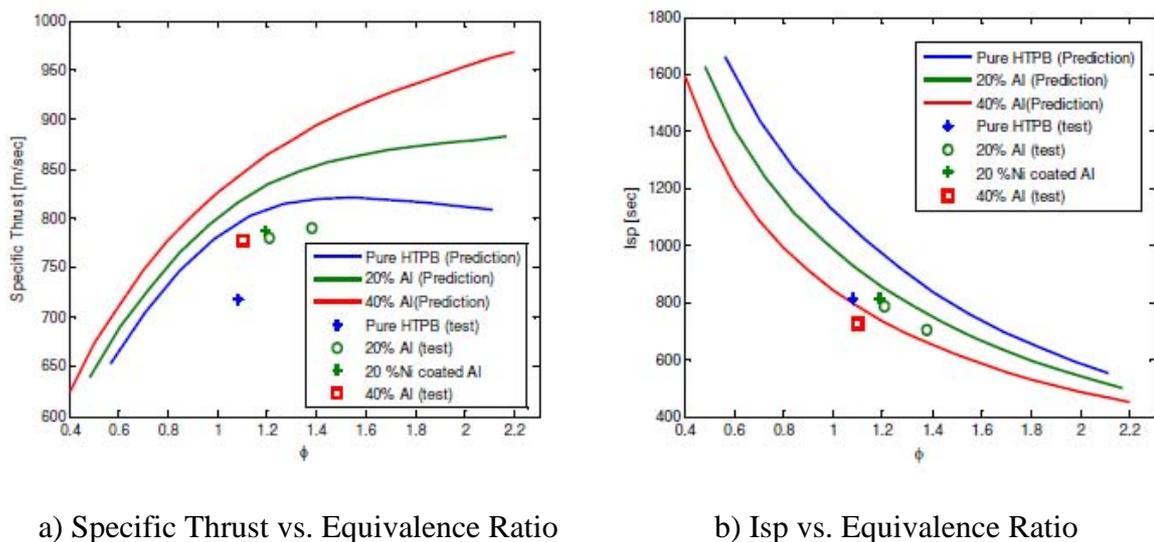


Figure 2: Model prediction and experimental results of a solid fuel ramjet for simulated flight conditions of Mach 3 at sea level.

## THERMAL REACTIVITY OF Al/Fe CORE-SHELL COMPOSITE

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### ABSTRACT

The Al/Fe core-shell composite has been prepared by a displacement method in which the micron Al particles were coated with a layer of nanometer Fe particles. Thermal analysis indicated that the reactivity of the Al/Fe composite was higher than that of the Al particles. When the Al/Fe composite reacted with O<sub>2</sub>, the DSC heat of Al/Fe-O<sub>2</sub> increased by 438.6%, and the apparent activation energy decreased by 152.54kJ·mol<sup>-1</sup>, as compared with the Al-O<sub>2</sub> system, and the weight increase of Al/Fe was 82.6% of its theoretical value in the TG trace. As the oxidizer was exchanged by CuO, the DSC heat of the Al/Fe-CuO system increased by 104.7%, and the apparent activation energy decreased by 222.58kJ·mol<sup>-1</sup>, as compared with Al-CuO. Additionally, the simple mixture of Fe nano-particles with Al powder did not exhibit high thermal reactivity. Finally, the role of Fe nano-particles acting in a thermal reaction for improving the reactivity of Al is discussed.

**Keywords:** *Thermite reaction; Al/Fe composite; Al powder; CuO; Thermal reactivity*

## PHASE TRANSFORMATION OF GRAPHITE AT HIGH SURFACE TEMPERATURES

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### ABSTRACT

In high performance rocket motors, the surface of graphite nozzle can reach very high temperatures, as the flame temperatures of solid propellants are as high as 3,600 K. Also, the heat flux to the graphite nozzle is increased substantially as the rocket motor operates at higher pressures. The combination of high surface temperatures and heat fluxes can lead to severe nozzle surface erosion, which can cause significant loss of propulsive performance. Generally, it is believed that the fundamental mechanism of graphite nozzle surface erosion is thermo-chemical. However, the experimental erosion study performed by Geisler (1970) using the Ballistic Testing and Evaluation System (BATES) rocket motors with the graphite nozzles showed an abrupt increase in the graphite nozzle throat erosion rate after the estimated surface temperature reached a value around 2,600 K. It was postulated that the graphite transitioned into a carbon allotrope called “carbyne.” Since carbyne is thermodynamically less stable than graphite, it was suggested that the higher erosion rate could be caused by this phase transformation. In order to investigate this interesting observation, a fundamental study was performed in this study to examine the effect of surface temperature on rate of mass loss of graphite samples and the mechanism(s) of mass loss.

To accomplish this objective, a windowed test chamber was designed for laser pyrolysis of a cylindrical graphite sample ( $d=3.18$  mm,  $L=3.18$  mm) irradiated by an 800 W continuous wave CO<sub>2</sub> laser. Two types of graphite samples were used in this study; one was high density graphite called G-90 (manufactured by Pyrotek Inc.) and the second sample was generic brand of graphite called GR008G (manufactured by Graphtek LLC). A D-type thermocouple bead was embedded in graphite sample. A 3- color pyrometer was used for measuring the instantaneous surface temperature of the heated graphite samples. Prior to laser heating, the test chamber was evacuated to remove any chemical species that could cause graphite oxidation. Inert argon gas (99% purity) was then introduced to the chamber. The graphite sample was irradiated with the CO<sub>2</sub> laser beam for a specified duration while in-situ surface temperature measurements were made by the 3-color pyrometer. In addition, a glass sampling probe was placed next to the graphite sample to collect the pyrolyzed material leaving the graphite sample. A paper filter was also placed in the sample collection line to capture any condensed-phase particles.

The surface temperature measurements with both types of graphite materials showed the attainment of 2,670 K with obvious mass loss; although the sublimation temperature of graphite is known to be at 3,915 K. Therefore, it can be concluded from these results that the graphite material demonstrates non-typical behavior at surface temperatures in the vicinity of 2,600 K. It is a possibility that the abnormal graphite nozzle throat erosion observed in BATES motor firings could be attributed to the same behavior of graphite sample observed in this study. During the mass loss process, fine condensed-phase particles were collected on the filter and sampling probe. Figure 1 shows an environmental scanning electron microscopy (ESEM) image of a recovered graphite sample with a laser beam induced crater near the

center of the sample. The deposits around the crater were believed to be formed from the vapor generated by graphite ablation, which was also recorded by a CCD camera.

Additional work is planned to include the examination of the effect of gases like N<sub>2</sub>, H<sub>2</sub>, and CO<sub>2</sub>, on the mass loss rates of graphite samples. A combined Gas Chromatography and Mass Spectroscopy (GC-MS) system will be used to analyze the gaseous samples from the test chamber.

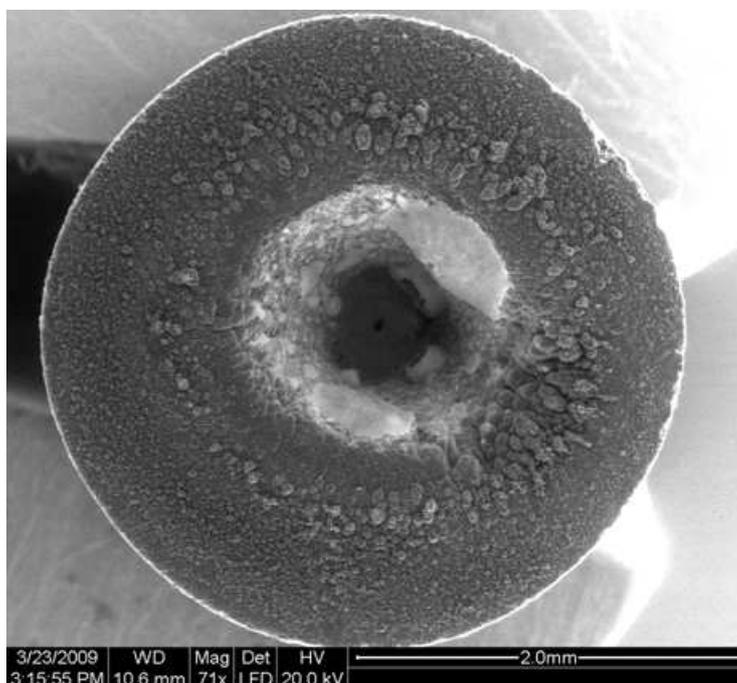


Figure 1: ESEM image of the recovered G-90 sample after laser heating.

## CHARACTERIZATION OF NOZZLE EROSION BEHAVIOR UNDER ROCKET MOTOR OPERATING CONDITIONS

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### ABSTRACT

The erosion of rocket nozzle throat can lead to performance deterioration, especially under high-pressure operating conditions. This is due to the extremely high heat-transfer rates to the nozzle throat surface and the heating of the nozzle material to elevated temperatures (>2,000 K). At high surface temperatures, oxidizing species such as OH, H<sub>2</sub>O, and CO<sub>2</sub> in the combustion products of solid rocket propellant are highly reactive with the graphite nozzle. The turbulent transport of these gas-phase oxidizing species to the heated nozzle surface leads to heterogeneous reactions and nozzle-throat material removal. When the propellant formulation contains metal additives like aluminum powders, additional effects must be considered. On one hand, the heat-transfer rates are increased due to the formation and coverage of a liquid Al<sub>2</sub>O<sub>3</sub>/Al layer on the throat surface. The liquid layer also impedes the diffusion of oxidizing species to the throat surface. Another major reason of reduced throat erosion rate for metallized propellants is caused by the reduction of concentrations of OH, H<sub>2</sub>O, and CO<sub>2</sub> in the combustion product for the formation of stable Al<sub>2</sub>O<sub>3</sub> species.

In this investigation, the erosion processes of high-density graphite nozzle materials (G-90 made by Metallurgical, Inc.,  $\rho = 1.92$  g/cc) have been studied using two rocket motors. The first one is an instrumented solid-propellant motor (ISPM), which has the capability for performing rocket motor tests at ultra-high pressure conditions up to 48.3 MPa, using either a metallized composite propellant (called Propellant M, containing AP, HTPB, and Al) or a non-metallized composite propellant (called Propellant S, containing AP and HTPB). The second rocket motor used in this study is a solid-propellant rocket motor simulator (RMS), which utilizes a bi-directional vortex reactant injection and combustion processes.<sup>1,2</sup> The oxidizing product-species concentration levels (*e.g.*, OH, H<sub>2</sub>O, and CO<sub>2</sub>) generated in the RMS can be systematically varied by controlling the flow rates of the gaseous reactants. The product species composition can also be adjusted to simulate the concentrations of oxidizing species of Propellant S, while maintaining the flame temperature. A real-time X-ray radiography system has been utilized with both test rigs for imaging the nozzle-throat contour variation during the test period, in order to deduce the instantaneous nozzle erosion rates. The nozzle assembly used for both the RMS and the ISPM tests can incorporate a specially designed nozzle boundary-layer control system (NBLCS), similar to that of Wolt and Webber.<sup>3</sup> This system uses several fuel-rich grains composed of succinic acid and polyvinyl acetate (SA/PVA)<sup>4,5</sup> to generate relatively cool products. These products also serve as oxidizer scavenging species in the flow passing through the nozzle throat region for reducing the severity of thermochemical attack. Successful demonstration of the NBLCS for mitigating nozzle throat erosion has been demonstrated in both RMS and ISPM tests with Propellant S.

Evaluation of G-90 graphite nozzle-throat erosion rates has been conducted with the data from RMS and ISPM for both non-metallized and metallized propellants at regular rocket motor operating pressures. A dimensionless erosion rate correlation was developed in terms of the chamber pressure, effective Reynolds number at the throat, and the mass fraction of an effective oxidizer, which is a linear combination of  $Y_{OH,th}$ ,  $Y_{H_2O,th}$ , and  $Y_{CO_2,th}$ . The effective Reynolds number is defined as the equivalent axial Reynolds number required for generating the same heat transfer rates as the RMS swirl combustor. The dimensionless erosion rate correlation was found to take the following form:

$$\frac{\rho_c \dot{r}_e}{G_{tot,th}} = 22.54 (\bar{p}_{th})^{0.510} \left( \overline{Re}_{D_{th,eff}} \right)^{-0.065} \left( Y_{OH,th} + 0.086 Y_{H_2O,th} + 0.022 Y_{CO_2,th} \right)^{1.587}$$

The above equation correlates quite well with both the erosion data from RMS and ISPM (for Propellant S and Propellant M) as seen in Fig. 1. All data points with error bars are within  $\pm 15\%$  boundaries, which correspond to an absolute error of only 0.05 mm/s. Additional ISPM test firings at conventional and elevated chamber pressure levels will be conducted, which will be used to form an erosion rate correlation, applicable to a broader range of operating pressures. The effectiveness of the NBLCS system at elevated pressure levels will be reported in the full manuscript.

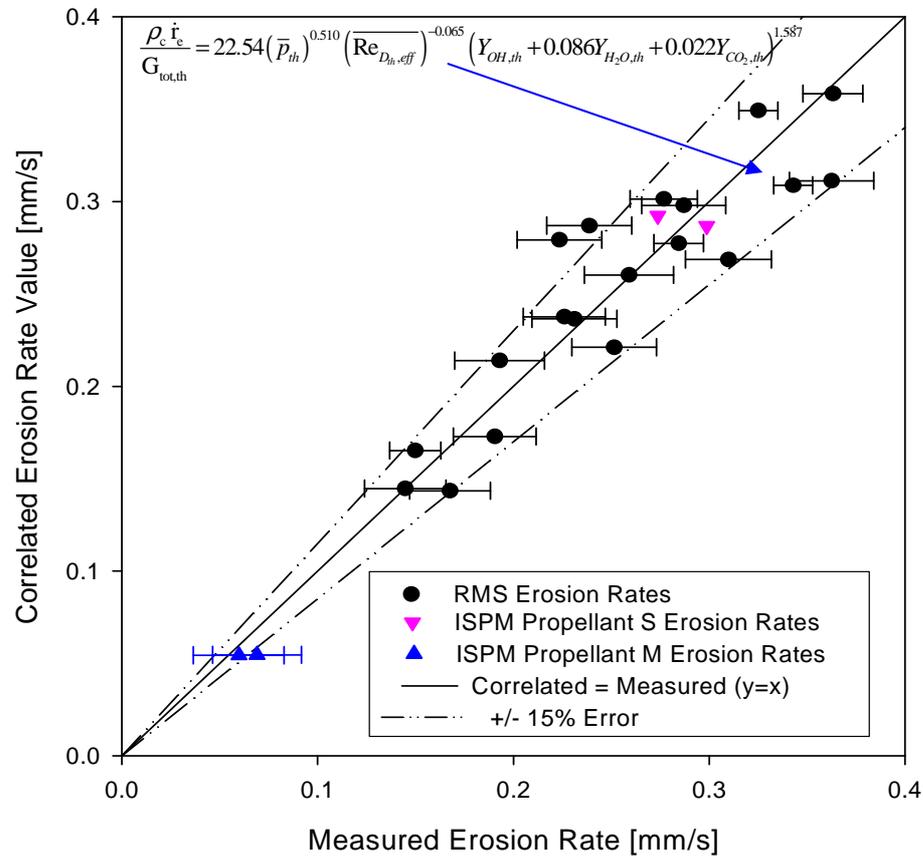


Figure 1: Comparison of calculated throat erosion rates from correlation and measured nozzle-throat erosion rates.

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# Poster Presentations

November 4, 2009 (14:45 – 17:25)

Snapshot Presentations in Roof Terrace Room: 14:45 – 15:45

Posters presented in Room 2.65-2.66: 16:05 – 17:00

Co-Chairs: Dr. Deon van Zyl & Prof. Hansie Knoetze

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## Fast Adsorptive-Photocatalytic Air Decontamination from Chemical Agents with Nanosize Aerosols Generated by Combustion or Explosion

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### ABSTRACT

Recent increases of risks to civil populations due to man-caused and terrorist activities urge the development of novel methods of immediate response. The present work proposes and evaluates a novel method based on an agile generation of high density nano-sized aerosols that capture agents over their surface with partial destruction and subsequently decompose them into inorganic products under mild ultraviolet irradiation (UVA). After precipitation, a powder of aerosol particles can be cleaned with a usual vacuum cleaner.

This concept of air decontamination rests on very small diffusion distances and times in dense aerosols, e.g. diffusion time of a molecule of the chemical agent simulant dimethyl methylphosphonate (DMMP) to an aerosol particle below 10 ms in an aerosol with a concentration of  $10^6 \text{ cm}^{-3}$ . Upon adsorption over TiO<sub>2</sub> and other oxide surfaces, chemical agents' molecules undergo a hydrolysis that makes them less volatile. The irreversible and complete destruction of chemical agents is obtained in photocatalytic oxidation. The resultant powder contains only inorganic compounds that can be disposed of, after a pH adjustment, with municipal waste.

Experiments were performed with titanium and iron oxide nano-powders aerosolized with the developed sonic aerosol generator. Decontamination of air by 95+% in a 0.1 m<sup>3</sup> research chamber from DMMP and insecticide diisopropyl phosphonofluoridate (DIPF) was obtained within 3 minutes from the start of the aerosol release. Complete destruction under UVA irradiation of absorbed organic species took several hours.

Toxic effects were checked by mice exposure to DIPF vapors with and without TiO<sub>2</sub> aerosol decontamination. Without TiO<sub>2</sub> aerosol, the mice showed signs of acute neurotoxic poisoning that would inevitably have led to death if the exposure had not been stopped. With TiO<sub>2</sub> aerosol decontamination of DIPF, the mice demonstrated normal behavior during and after the experiment.

As compared with similar technologies which can be used only indoors or as decontaminating coatings, our new technology is a unique one because mobile and stationary complexes can be applied for deactivation of much larger volumes of atmospheric air, while a deactivating substance based on nano-sized TiO<sub>2</sub> is produced not only in stationary aerosol generators (powder fire extinguishers) but also by combusting or exploding special pyrotechnic mixes or "soft" explosives (nitrosemicarbozide) after they have been delivered to any area in the atmosphere within 10 km range. This makes it possible to use traditional ammunition for fast delivery of deactivating mixtures to a contaminated area in the atmosphere and to enhance deactivation at any time of day or night and in all weather conditions.

The work was supported by ISTC grant 3305 and partially by NATO SFP grant 981461.

## **EXTRUDED THERMOPLASTIC ELASTOMER COMPOSITE PROPELLANT FOR IR DECOY FLARE APPLICATIONS**

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### **ABSTRACT**

Composite propellant is usually manufactured according to a process wherein a liquid polymer such as hydroxyl-terminated polybutadiene (HTPB) is mixed with an oxidiser such as ammonium perchlorate (AP). The liquid polymer in the mixture is then cross-linked with a suitable cross-linking agent and before final curing takes place, the propellant is cast into the required grain geometry. This results in the production of a rigid thermoset rubber, filled with oxidiser particles.

In the case of thermoplastic elastomer propellant, a solid polymer (thermoplastic elastomer - TPE) instead of a liquid polymer is used. The use of a TPE binder in composite propellant results in a propellant that has the properties of a thermosetting rubber (such as HTPB) but, unlike thermosetting rubbers, can be processed in a manner similar to thermoplastics. The latter becomes soft at elevated temperatures and can thus be extruded in similar fashion as double-base propellant, the latter being an example of a thermoplastic material.

Standard mixers and extrusion presses as it is used for the manufacture of double-base propellants were used to manufacture TPE propellant formulations and grains.

Various TPE elastomers from different suppliers were used in the study. The mechanical properties of propellant with a solids loading ranging from 76% to 86% were determined and values for tensile strength as high as 3.8 MPa and values for elongation as high as 70 % were observed. The mechanical properties for TPE propellant were unaffected when subjected to an accelerated ageing program at a temperature of 60°C for 12 months. The burning rate for the TPE propellants was in the range of 0.6 – 1.7 mm/s at atmospheric pressure.

Since this propellant manufacturing process is highly suitable for the series production of IR decoy flares, the intensity ratio for some of the TPE propellants were determined. The maximum value that was observed was 9.2. These preliminary results indicate that these TPE propellant formulations have the potential to be used in IR decoy flare applications.

## MUNITIONS SAFETY INFORMATION ANALYSIS CENTER

Bernard C. Halls  
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### ABSTRACT

The Munitions Safety Information Analysis Center (MSIAC) provides information and advice to its member nations and also works within NATO to provide information and support in developing munition safety standards and documentation. Its core element was the introduction of reduced sensitivity and reduced accidental reaction from munitions. The term “Insensitive Munitions” (IM) is used to indicate when munitions exhibit reduced vulnerability when measured against the pass levels in (NATO - Standardization Agreement) STANAG 4439. This task continues and is a core part of reducing the risk to personnel, assets and capability. A considerable piece of work has recently been concluded and published, which was the updating of STANAG 4439 and a considerable enhancement of AOP 39. An ongoing task is the review of Response Descriptors which has led to the proposal of significant changes to the criteria for assessing the response to the 6 standardized aggressions. There are currently proposals to modify some of the IM test STANAG, which MSIAC will offer support to the various subcommittees involved.

MSIAC has arranged many workshops over the years that bring together a wide range of international experts to work together to provide viable, cost effective solutions to high-risk, or low-risk, but high-consequence munitions. MSIAC is currently updating its tools and databases and has migrated some to online applications, which can be accessed through our restricted access web pages. The current work with storage transport and testing, and expert working groups is ongoing. MSIAC is also working towards a large workshop on IM shortfalls in technology to be held in 2010. A summary of the topics identified for this workshop will be provided.

MSIAC has recently developed a product which brings together the considerable plethora of national, NATO, and International standards which are used in the development of the design requirements, testing, and assessment of all the elements of a munition system. This library has been brought together and is being maintained for official use by MSIAC and NATO countries. It will save time and ensure that the latest standard is available to the user.

A key area of MSIACs work is providing data and analysis to customers who have asked specific technical questions. The questions range significantly from providing small-scale testing results to reviewing whole areas of technology and help in formulating national IM policy.

There have been many initiatives which result in the sharing of data that leads to tried and tested design concepts and practical solutions. MSIAC has assisted nations in developing IM policy in line with NATO STANAG 4439 requirements leading towards a commonality in testing and acceptance of other nations’ testing and sharing of results. A suite of tools and data are available to help munition designers save money and time. These tools are also useful to the authorities who need to assess the safety of munition design, transport and storage. This paper will review the work of MSIAC and give an introduction into the tools and data available to MSIAC Nations.

## **NANO-ENERGETICS FOR INSENSITIVE BOOSTER EXPLOSIVES**

Anthony Di Stasio, Sanjeev Singh, Philip Samuels, and Victor Stepanov  
*US Army ARDEC, USA*

### **ABSTRACT**

Recent developments in the realm of Insensitive Explosives have, for the first time, allowed warheads using HE to pass all IM testing. With this great advancement comes certain drawbacks. Due to the obvious insensitivity of these new main fills, a very powerful booster explosive is needed to set them off, either in the form of a fuze booster or a Supplemental Charge. These powerful booster explosives, by nature are too sensitive and must be addressed. Using nano-RDX powders allows for the energy associated with nitramines to be utilized, but with only a minimum drawback in IM response.

ARDEC wishes to demonstrate that nano-based energetics can be used to detonate IM explosives, as well as mitigate shock threats. The goal of this effort is to use a nano-sized nitramine based explosive in the form of a 22g booster to detonate IM explosives. The project is constrained by the current geometry of the mortar explosive train. No modification to the current train (larger booster for the fuze) can be made. The second part is to demonstrate insensitivity through shock mitigation. We plan to show that by using nano-RDX and nano-based explosive formulations, one can show reliable initiation of the most insensitive main fills, as well as IM properties above and beyond the most state-of-the-art booster formulations.

## **FORMULATION AND DEVELOPMENT OF AN EXPLOSIVE THAT ALLOWS CONVENTIONAL 155mm PROJECTILES TO ACHIEVE IM STATUS**

Sanjeev Singh<sup>1</sup>, Philip Samuels<sup>1</sup>, Anthony Di Stasio<sup>1</sup>, Barry Fishburn<sup>2</sup>, and Paul Vinh<sup>1</sup>

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<sup>2</sup>*Janets Consulting, USA*

### **ABSTRACT**

An intensive effort is being made to develop a cost effective, IM compliant 155mm bursting projectile. Understandably, the desire is for performance and cost comparable to the current projectile, but, in addition, the ability to pass most, if not all, IM tests.

The Energetics & Warheads Division at ARDEC worked to develop an explosive formulation for this purpose which achieved good success at fulfilling all the goals, including passing IM tests. Achieving success in Sympathetic Detonation and Shaped Charge Jet was especially noteworthy. The formulation can be melt cast loaded in existing production facilities and uses readily available ingredients.

The formulation to be discussed utilizes a TNT melt phase component that is desensitized using a method identified at ARDEC in the late 1980's. Further shock desensitization was achieved by seeding the melt phase with NTO. It has an energy output similar to TNT and there is no performance degradation due to adding the TNT desensitizing ingredients that occurs, in fact, the detonation pressure actually improves. A method used to adjust shock sensitivity to the value needed to pass SD by varying the fractions of the ingredients will be discussed. Laboratory characterization of the explosive will be presented.

IM tests, sometimes with slight, cost reducing modifications from the STANAG's, were performed with the formulation loaded into M795 projectiles, a large 155mm bursting projectile having about 12 kg of explosive. The results will be presented.

## **IM COMP A5 REPLACEMENT**

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### **ABSTRACT**

There is a need for current munitions to be more compliant with the requirements of insensitive munitions (IM). The High Velocity HEDP 40mm grenade (M430A1) is a munition moving towards a transition period where multiple IM technologies are under consideration for integration into the round, including an explosive replacement. The current explosive in the M430A1 is Comp A5, which is a powerful pressed explosive consisting of 98.5 - 99% RDX. The explosive replacement will have to meet the performance requirements set forth by PM-CAS and reduce the sensitivity to penetrating threats (bullets and fragments).

The IM explosive replacement formulation will consist of high explosives and/or energetic binders in conjunction with insensitive binders. A wide range of formulations will be analyzed via thermochemical calculations to determine if the predicted energetic output is within the requirements/specifications for the explosive. Several candidates will be selected and put through safety analysis, the explosive development process, and characterization of their sensitivities and performance. . After characterization is completed, down-selected candidates will be subject to engineering IM tests: Bullet and Fragment impact in Statistical Analysis Bodies for Ranking Explosives (SABRE).

The main objective of the IM explosive Comp A5 replacement is to improve the sensitivity against penetrating threats. Other efforts in the M430A1 project plan are being undertaken to reduce other threats to achieve IM compliance. The main technical challenge facing the explosive replacement program is achieving the performance necessary in a melt cast explosive. The proposed solution will be a melt cast explosive (belt-flaked) that will be pressed to theoretical maximum density for all characterization and end item tests.

## **IM H6 REPLACEMENT**

Amy Chau, Sanjeev Singh, Philip Samuels, and Anthony Di Stasio  
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### **ABSTRACT**

There is a need for current munitions to be more insensitive munitions (IM) compliant. The 40 lb Cratering Charge (M039) is a munition moving towards a transition period where IM technologies, specifically an explosive replacement, are under consideration for integration into the munition system. The current explosive in the M039 is H6 which has a relatively low detonating velocity and the capability of generating higher pressures. This makes it a suitable explosive for cratering and ditching operations. The explosive replacement will have to meet the baseline performance requirements and have reduced sensitivity to penetrating threats (by bullets and fragments) and cook-off (slow and fast).

The IM explosive replacement formulation will consist of high explosives and energetic binders in conjunction with insensitive materials. A wide range of formulations will be analyzed via thermo-chemical calculations to determine if the predicted energy output meets the requirements of the legacy explosive. Several candidates will be selected and analyzed for safety, shock sensitivity and performance. Down-selected candidates will be subject to IM Bullet and Fragment Impact tests in Statistical Analysis Bodies for Ranking Explosives (SABRE).

The objectives of the IM H6 replacement program are to improve the sensitivity against penetrating and cook-off threats, while maintaining the performance characteristics of the legacy explosive. The main technical challenge facing the explosive replacement program is achieving the performance characteristics with a melt cast explosive.

## **STANAG 4170 QUALIFICATION OF INSENSITIVE PBX FORMULATIONS**

Melinda Diedericks  
*Rheinmetall Denel Munition, South Africa*

### **ABSTRACT**

An overview is presented on STANAG 4170 qualification of three pressable plastic-bonded explosives (PBX) developed by Rheinmetall Denel Munition (RDM) in collaboration with Ammscor and manufactured by RDM at their Somerset West site. RXHR X is a RDX-based low sensitivity pressable PBX to be used as a main charge filling in Insensitive Munition (IM) artillery, whereas HXHR Y and HXHR Z are HMX-based low sensitivity pressable PBXs to be used as IM booster explosives.

Since pass/fail criteria do not apply, these explosives were evaluated relative to a known in-service explosive with proven safety characteristics used as pressable main charge and booster explosives. RDX/Wax 91/9, also pressed in high setback ammunition, was identified as reference explosive. Test results for two PBXs qualified at an earlier date are included. SPX-1 is a RDX-based low sensitivity pressable PBX manufactured by RDM with technology sourced from Chemring Nobel and pressed as main charge filling in IM artillery. DPX-2, is a HMX-based low sensitivity pressable PBX from Chemring Nobel, used as booster explosive in IM.

Thermal properties were evaluated by standard tests of vacuum thermal stability, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The responsiveness of the explosives were evaluated by ignition temperature and fast and slow cook-off tube tests; sensitivity properties by electrostatic discharge, impact, friction, and shock sensitivity tests, and mechanical and rheological properties evaluated by thermo mechanical analysis (TMA), dynamic mechanical analysis (DMA), and compressive strength tests. Detonation velocity was used to evaluate the explosives' performance.

## **INSENSITIVE COMPOSITE PROPELLANTS BASED ON A HTPE BINDER SYSTEM**

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### **ABSTRACT**

Apart from higher energetic propellants, the technology field receiving most attention worldwide is Insensitive Munitions (IM). There is concern about the catastrophic responses produced by many propulsion systems when they are subjected to the thermal and ballistic impact hazards. Tactical rocket motors are usually loaded with propellants based on ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB) binders. These propellants have been optimised to obtain high energy and density and have excellent mechanical properties and processing properties. However, without active or passive mitigation systems, most of these rocket motors fail the slow cook-off test.

A new generation of insensitive composite propellants was developed by various companies. These propellants are based on alternative binders such as hydroxyl-terminated polyether (HTPE) or hydroxyl-terminated polycaprolactone (HTCE). According to ATK, HTPE propellants have comparable performance to HTPB propellants, but pass the slow and fast cook-off tests. Also, these propellants have ballistic, mechanical and ageing properties similar or superior to HTPB-based propellants and are suitable for use in tactical rocket motors.

In this paper, some of the work that was conducted over several years on insensitive composite propellant technology by Rheinmetall Denel Munition will be presented. Initially, a commercial grade HTPE polymer was used, but later the military grade polymer, TPEG, was acquired. Formulating insensitive composite propellants based on the HTPE binder system and which also contain energetic additives like AP, BuNENA and ammonium nitrate (AN) presented several challenges. Successful processing and cross-linking of the HTPE propellant was the first objective. The effect of different curing agents on the mechanical properties was also quantified.

The slow cook-off behaviour of these propellants was studied in a slow cook-off visualisation (SCV) test. The effect of variables such as BuNENA concentration, AN type and concentration were determined during these tests. These variables had a pronounced effect on the cook-off temperature and also on the physical behaviour of the propellant.

# CONTROL RADICAL POLYMERIZATION TECHNIQUES FOR SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS

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## ABSTRACT

Incidents in different parts of the world related to ammunitions use, transport, and storage have encouraged most of national defense force and ammunition industry to comply with IM policy. High performance, low sensitivity, environmental acceptance, and low costs are examples of main requirements for energetic materials used in IM. Polymeric materials are considered as one of the practical ways for the implementation of insensitive munitions, which is associated with high flexibility in synthesis, modification, and availability of raw materials.

Most energetic binders uses glycidyl azide polymer (GAP), which is usually converted to a cross-linked binder by reaction of the terminal hydroxyls with isocyanate monomers via the formation of urethane linkages. The drawbacks of this technique are limited recyclability, void formation, and inhomogeneous cross-link distribution. It is possible that other polymerization techniques could overcome some of these limitations and be cost effective. Examples for such polymerization techniques examined with energetic binders are Redox initiation, nitroxide-mediated process, and dithiocarbamate iniferter. This paper reviews the most common control radical polymerization techniques reported in synthesis of energetic thermoplastic elastomers and provides a comparison between them in different aspects like polymerization conditions, initiation groups, and final binder properties. Also, utilization of dithiocarbamate iniferter as controlled radical polymerization of vinyl monomers (styrene and Methyl methacrylate) to yield energetic themoplastic elastomers will be described in more detail.

## SEMI-ANALYTICAL MODEL FOR SUBSONIC TAILPIPE: EFFECTS ON SRM PERFORMANCE

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### ABSTRACT

A review of the one-dimensional steady-state equations was performed for the flow in a subsonic blast tube/tail pipe of a rocket motor. From the assumption of constant diameter and only frictional losses, the analytical model that was derived from these equations is discussed.

In spite of the complex set of chemical reactions between the combustion products from the motor chamber and the ablative liner, char-layer formation and wall roughness variation, a simplified, semi-analytical model regarding internal ballistic effects was developed and is presented.

The trend of Tailpipes leads to overestimating the characteristic velocity ( $C^*$ ) of the propellant and underestimating the thrust coefficient ( $C_F$ ), due to new stagnation conditions. Even for bell-shaped nozzles, the raw data after static firing tests have shown an appreciable loss in their performance. Some considerations have to be taken in account to compensate these perturbations, without jeopardizing the overall performance.

The findings of this study are validated with data from a real low-smoke propellant solid rocket motor.

**Keywords:** *Tailpipe, Blast Tube, Internal Ballistics, Solid Rocket Motor*

## THE SCALING OF PEAK OVER-PRESSURE OF SMALL SPHERICAL CHARGES

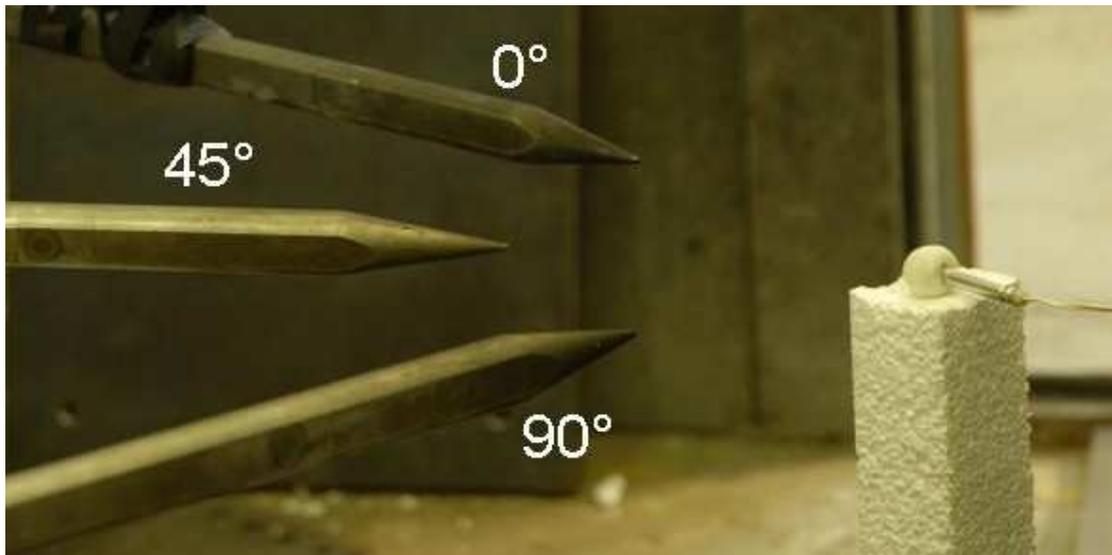
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### ABSTRACT

Small and spherical explosive charges are used frequently in research to analyse concepts and formulate test objectives. The underlying assumption is that these small-scale tests can be related to larger scales by scaling such as geometric similarity or others. In the test results reported below, this underlying principle of scaling is analysed in terms of small charges. Three small geometrically similar spherical charges were detonated freely in air. The side-on, over-pressure at scaled distances was measured and compared with respect to scaling and the distribution of the expanding gases. Computational analyses show good agreement with the experimental results.

Three spherical charges with mass 4g, 16.4g and 32g PE4 (an explosive similar to C4) were detonated as close as possible to the centre. Three probes with pressure transducers were positioned around each charge (see Fig. 1 for the 4g charge). One probe pointed directly towards the curved surface of the charge ( $0^\circ$ ), another one pointed at  $45^\circ$ , and another at  $90^\circ$ .



**Figure 1: The 4g PE4 spherical explosive charge and pressure probes**

The parameters of the test setup are given in Table 1. The mass, radius of the charges, and the stand-off distances (SOD) for the pressure transducers are all related by scaling the model set-up by the results from prototype 1.6 or 2.

**Table 1: The set-up parameters for the tests**

	Model	Prototype 1.6	Prototype 2
PE4 Mass (g)	4.0	16.4	32.0
Radius (mm)	8.42	13.47	16.84
Pressure probe SOD (mm)	300	450	600

Five detonations per charge were performed and the average peak over-pressures at the scaled distances are shown in Table 2.

**Table 2: The average peak over-pressure associated with the spherical charges**

	Peak over pressure (kPa)			SOD (mm)
	0 °	45 °	90 °	
4g PE4 (Model)	225	191	275	300
16.4g PE4 (Prototype 1.6)	306	231	221	480
32g PE4 (Prototype 2)	232	260	231	600

Due to geometric similarity, the sizes of the peak over-pressure should be identical for the various directions of measurement. There is, however, some variance as is evident for the 16.4g PE4 charge. The peak over-pressure in the 0° direction is 26% larger than for the model 4g PE4 problem. Also, due to the spherical shape of the charge, it is expected that there should be little difference between the various measurements. As is evident from the results, there are some deviations.

The experimental and computational analyses of these tests are discussed in the paper. The time of arrival, impulse density, and positive duration of the over-pressure time histories will also be discussed.

# COMBUSTION OF ALANE-BASED SOLID FUELS

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## ABSTRACT

Hybrid rocket motors have been the subject of study for many years due to their inherent advantages over other types of rocket propulsion, namely safety. One major drawback associated with hybrid motors is the typically low regression rates associated with the solid fuels. There have been numerous studies involving the addition of metals on both the micron and nano-scale in order to increase the regression rates and the energy density of the propellant system. The addition of aluminum nanoparticles has been shown to increase solid fuel regression rates<sup>1</sup> and solid propellants<sup>2</sup>. The increase in regression rate is generally attributed to an increase in energy release closer to the fuel/propellant surface which is partially a result of the lower observed ignition temperature<sup>3</sup> on aluminum nanoparticles in comparison to their micron-sized counterparts. More recently, it was found that micron-sized aluminum hydride, or alane, ignites at temperatures similar to that of nanoaluminum.<sup>4</sup> Aside, from having a low ignition temperature, alane is an interesting candidate as a fuel supplement in propulsion systems due to its ability to increase performance. For example, a hybrid rocket using a fuel of HTPB and alane can expect to see an increase of 8-10 seconds in specific impulse over a similar HTPB aluminum fuel when using oxygen as the oxidizer. At the same time the alane fuel has a lower adiabatic flame temperature than the aluminized fuel helping to reduce thermal loads on the propulsion system. This can further propagate into improving performance by increasing the mass fraction.

In this study solid fuel combustion behavior between solid fuels loaded with micron-sized aluminum, nanoaluminum, and aluminum hydride with loadings of 10, 20, and 40% by mass are compared directly using pure oxygen as the oxidizer. Deluca *et. al.*<sup>5</sup> performed test using 5.6 and 11.2% alane in the HTPB binder and 50/50 O<sub>2</sub>/N<sub>2</sub> mixture as the oxidizer. An opposed flow burner was used to screen the various fuels at various oxidizer flow rates. Gaseous oxygen and nitrous oxide were the oxidizers considered in this study. Regression rates were gathered over oxidizer flow rates ranging from 1 – 6 LPM. Finally, a lab-scale hybrid rocket motor was used to compare the combustion performance of the fuels relative to each other. Data included were thrust, pressure, regression rate, and mass burning rate.

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## SHOCK WAVE SENSITIVITY OF NITROMETHANE MIXTURES WITH NON-EXPLOSIVES LIQUIDS

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### ABSTRACT

Using a slit photo-registration for initiation process observation, shock wave explosive generators were selected in compliance with the scheme active charge (booster) – inert barrier (attenuator) – mixture under study to provide limit actions to excite detonation in binary mixtures of nitromethane (NM) with methanol (M) and nitrobenzene (NB). Streak camera photographs register initiation stages typical for liquid explosives: preliminary luminescence connected to expansion of detonation in shock-compressed substance; narrow zone of bright luminescence caused by overdriven effect; the detonation withdrawal from overdriven regime.

The measurement of the initiation shock wave parameters has been conducted on an electromagnetic installation. To determine the particle velocity,  $u$ , and front velocity,  $D$ , the stepped gages from aluminum foil were used. In this case the gage was placed at the interface attenuator (teflon) – liquid under study (in glass confinement of 70mm diameter). The pressure has been calculated using formula  $P = \rho_0 u D$ .

For minimum pressures that initiate (i) detonation (thermal explosion) and for maximum pressures that do not (n) initiate the processes, the following dependences on diluent content were established:

- $P_i = (7.90 - 2.0 \alpha)$  GPa,  $P_n = (7.70 - 2.0 \alpha)$  GPa for NM/M mixture with methanol's part weight  $\alpha = 0.2, 0.25, 0.30, 0.35, 0.38$  and  $0.40$ ;
- $P_i = (8.05 + 2.0 \alpha)$  GPa,  $P_n = (7.75 + 2.0 \alpha)$  GPa for NM/NB mixture,  $\alpha = 0.25, 0.32, 0.39$  and  $0.43$ ).

Note that in both cases the last values of  $\alpha$  correspond to mixtures that are undetonable in real conditions. A relatively small decrease in the pressures,  $P_{i-n}$ , with the increase in methanol content does not mean that NM/M mixture becomes more sensitive. The nitromethane dilution with non-explosive liquids only reduces mixture sensitivity. This assertion is confirmed by the necessity of more intense shock wave actions, i.e. of stronger shock wave explosive generators. The negative slope of the linear dependences,  $P_{i-n}$ , is connected with the decrease of NM/M mixtures initial density because of the increase of methanol content due to the fact that methanol density ( $\rho_0 = 0.79 \text{ g/cm}^3$ ) is noticeably less than nitromethane density ( $\rho_0 = 1.14 \text{ g/cm}^3$ ).

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## THE COMPARATIVE ANALYSIS OF NONSTATIONARY BURNING RATE OF SOLID PROPELLANTS

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### ABSTRACT

Results of measurements of non-stationary burning rate of homogeneous solid propellants are presented at a drastic pressure decay in a combustion chamber obtained by two independent methods – a method of high-speed filming and a method based on the solution of inverse internal ballistic problem. The comparative analysis of the received results has confirmed the V.N. Marshakova–K.I. Sinaeva hypothesis about the heat source pulsing mechanism of condensed systems combustion and also has shown that the considered methods are complementary.

Reliable methods for the creation of measurements for non-stationary burning rate (NBR) of solid propellants (SP) is of interest not only by way of the further development of the non-stationary combustion theory [1, 2], but also for designing solid-propellant rocket motors and gas generators with precise guidelines.

The combustion process of a solid propellant under drastic pressure decay in a combustion chamber designed for measurement of NBR represents strong practical interest (with applications in: cutoff drafts of impellent installation, slaking of propellant, etc.) and also plays the important role in testing the validity of physical and mathematical models for simulating the non-stationary combustion processes of the condensed systems [1–4]. In known variants of this method, the hypothesis of quasi-steady flame was used when an additional nozzle was introduced to decrease the chamber pressure and the subsequent slaking of the burning rate of the propellant [5]. In the present work, a new method of measurement for NBR [6] is offered.

The scheme of experimental installation is presented on figure 1. The test rig consists of a steel combustion chamber (1) with the investigated sample of solid propellant (2) supplied by basic (3) and additional (4) nozzles. Additional nozzle (4) is opened during combustion and has a star-shaped plug (5) made of gunpowder. Diameters of basic (3) and additional (4) nozzles depend upon the selected pressure levels between  $p_0 = (3 \text{ to } 10)$  MPa and the rate of pressure decay  $dp/dt = (-50 \text{ to } -800)$  MPa/s. On the viewing port surface of the combustion chamber, the transparent window (6) of quartz glass with a thickness of 20 mm was used. The regression process of the propellant was recorded by means of a high-speed movie camera (7) and an external lighting system (8) was installed. The sample of solid propellant (2) is pasted by special burning material on an internal surface of quartz window (6). Such technology prevents the occurrence of meniscus on the border glass–sample and also rigidly fixes the sample to the window in order to reduce the sample deformation to a minimum during the sharp pressure decay. The investigated sample (2) in the form of a semi-circle in diameter 100 mm and height (20 to 30) mm is retained to the window by the linoleum dissolved initially in acetone on perimeter in such a manner that it burns two sides – top surface (9) and exposed lateral surface (10) (see figure 1). For reduction of thermal streams in the walls of the steel

combustion chamber, inside of chamber textolite loose leaves by thickness of 5 mm are densely established.

Filming of burning surface was conducted by high-speed movie camera SKS-1M with rate up to 2000 pps. Film processing (figure 2) was performed using a microscope (IMI-100) with electronic-digital indication of coordinates  $x$  and  $y$  a burning surface. At that some coordinates  $x_i$  with an identical interval  $\Delta x$  got out for which processing of each staff (figure 1) with the purpose of instant value definition of linear burning rate was spent. Values of coordinate  $y$  were measured with use of two reference points (14) (figure 1) and the time interval between the next staff was fixed on a film by means of a time marker.

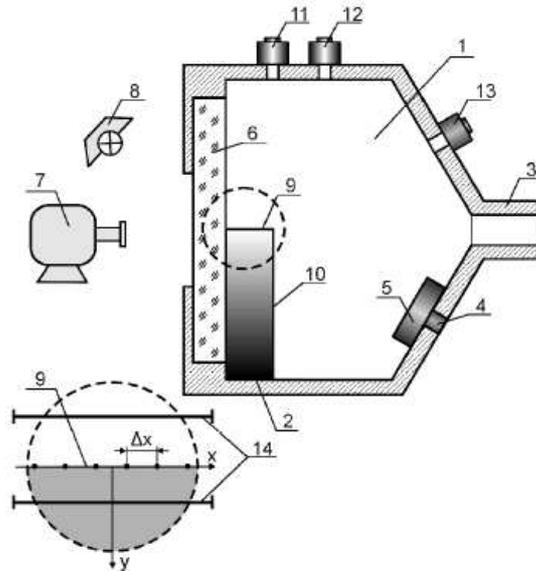


Figure 1: The scheme of experimental installation: 1 – the combustion chamber; 2 – the solid propellant sample; 3, 4 – the basic and additional nozzles; 5 – a burning down fuse; 6 – a quartz window; 7 – a movie camera; 8 – system of illumination; 9, 10 – burning sides of sample; 11, 12 – gauges of pressure and temperatures; 13 – an igniter; 14 – reference points

At the realization of the method based on statement and decision of inverse problem internal ballistics (IPIB-method), non-stationary burning rate  $u(t)$  during transient was defined on the measured curve of pressure  $p(t)$  in the combustion chamber. The system of the equations expressing laws of preservation for averaged on volume of the combustion chamber of parameters [5, 7] was considered(?):

$$\begin{aligned} \frac{d}{dt}(\rho V) &= S \rho_m u - G, \\ \frac{d}{dt} \left( \frac{pV}{k-1} \right) &= c_p T_p S \rho_m u - \frac{k}{k-1} \frac{p}{\rho} G, \\ p &= \rho R T. \end{aligned} \quad (1)$$

The mass second charge of combustion products (for supercritical conditions of the flow) paid off under the formula

$$G = (\varphi_1 F_1 + \varphi_2 F_2) \cdot \sqrt{k p \rho \left( \frac{2}{k+1} \right)^{\frac{k+1}{k-1}}} \quad (2)$$

Here  $r$ ,  $k$ ,  $cp$ ,  $R$ ,  $T$  – density, a parameter of an adiabatic curve, a specific isobaric thermal capacity, a gas constant and temperature of combustion products;  $\varphi_1$ ,  $\varphi_2$ ,  $F_1$ ,  $F_2$  – factors of the charge and the area of critical sections of the basic and additional nozzles;  $S$ ,  $T_p$  – the area of a combustion surface and temperature of solid propellant.

The decision of inverse problem of internal ballistics assumed identification of burning rate function on the set experimental curve  $p_e(t)$  by the method of direct search [8]. Thus dependence  $p_e(t)$  is broken on  $n$  time intervals  $\Delta t_i$  ( $i = 1, \dots, n$ ). On each interval,  $\Delta t_i$ , the system of the equations (1) is consistently solved at a variation of size of burning rate and there is a calculation value  $p(t)$ . For known on the given interval of time  $\Delta t_i$ , experimental  $p_e(t)$  and calculation  $p(t)$  values of pressure (figure 2) are a functional minimum

$$J = \int_{t_i}^{t_i + \Delta t_i} |p(t) - p_e(t)| dt \quad (3)$$

The decision is spent by direct search method for the varied parameter  $u_{i+1}$  on the value of burning rate  $u_i$  certain on the previous step. Thus, used in (1) dependence for burning rate it is defined for the given interval of time by linear interpolation:

$$u(t) = u_i + \frac{u_{i+1} - u_i}{\Delta t_i} (t - t_i), \quad t_i \leq t \leq t_{i+1} \quad (4)$$

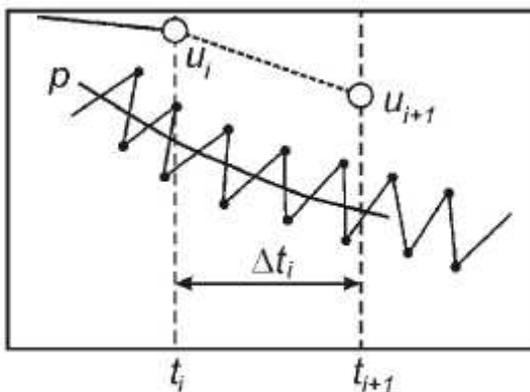


Figure 2: The calculation scheme of functional  $J$  on an interval  $\Delta t_i$

The estimation of errors and borders of applicability of the IPIB-method was spent by the decision of a modelling problem and comparison of measurement results of NBR by two independent methods of carrying out of experiments in identical conditions.

Experiments were spent at constant value of a combustion surface of propellant  $S = 78.5 \text{ sm}^2$ ; varied size of initial pressure in the chamber in a range (of?)  $p_0 = (2.5 / 11) \text{ MPa}$  and the maximal speed of pressure decay in a range  $\max dp/dt = (50 / 765) \text{ MPa/s}$ . Speed of pressure

decay varied change of the area of critical section of the additional nozzle  $F_2$ , and volume of combustion chamber  $V$ , and paid off by means of numerical differentiation of the measured curve dependence of pressure from time  $p(t)$ .

Results of NBR measurements during pressure decay received by the IPIB-method are presented on figure 3. Values of burning rate  $u$ , and pressure  $p$ , are carried to corresponding initial values  $u_0$ ,  $p_0$  (before the beginning of pressure decay). Here dependences quasi-stationary of burning rate  $u_{qst}$ , the speeds of burning calculated on the power law for considered solid propellant are resulted.

For homogeneous solid propellant the possible factor influencing on slaking the heat source pulsing mode of combustion and dispersion with regulation of size of a return thermal stream in the condensed phase is (?). According to this hypothesis [9], the combustion surface consists of the separate centers of burning which during each moment of time burn with essentially differing burning rates. The burning rate of the separate center varies in time and the centers burn out with the certain periodicity for the set pressure.

Presence of several modes of homogeneous propellants non-stationary combustion at pressure decay confirms V.N. Marshakova–K.I. Sinaeva hypothesis. In particular in the field of process parameters typical for a mode «slaking–reignition» depending on ratio of quantity of the centers with different burning rate before pressure decay, during recession of pressure there occurs a slaking in a greater or smaller part of combustion surface. But owing to the kept centers of burning, later some period of delay occurs reignition of all propellant surfaces (?).

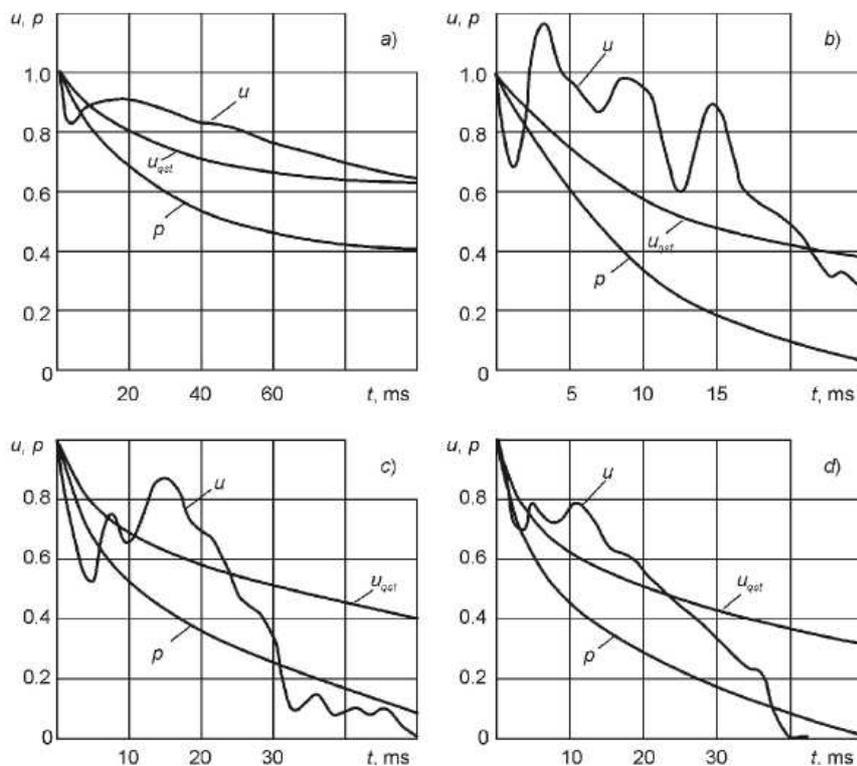


Figure 3: Measurements results of NBR of homogeneous solid propellant by the IPIB-method:

$$a - p_0 = 10.7 \text{ MPa}, \left| \frac{dp}{dt} \right|_{\max} = 250 \text{ MPa/s}; b - p_0 = 2.9 \text{ MPa}, \left| \frac{dp}{dt} \right|_{\max} = 295 \text{ MPa/s};$$

$$c - p_0 = 6.07 \text{ MPa}, \left| \frac{dp}{dt} \right|_{\max} = 430 \text{ MPa/s (slaking-reignition)};$$

$$d - p_0 = 7.87 \text{ MPa}, \left| \frac{dp}{dt} \right|_{\max} = 765 \text{ MPa/s (slaking)}$$

Comparison of NBR measurements results of homogeneous solid propellants at drastic pressure decay by the IPIB-method and a method of high-speed filming has shown that these methods yield following close enough results.

- Oscillation regimes of change  $u(t)$  the big amplitude for speed of pressure decay  $\left| \frac{dp}{dt} \right|_{\max} \sim 200 \text{ MPa/s}$  and  $p_0 \sim (2 \div 3) \text{ MPa}$ .
- Substantial growth  $u(t)$  in comparison with  $u_{gst}(t)$  during the separate moments of time at  $\left| \frac{dp}{dt} \right|_{\max} > 400 \text{ MPa/s}$ .
- Absolute damping occurs at achievement  $p \sim 0.1p_0$  and  $\left| \frac{dp}{dt} \right|_{\max} \sim 520 \text{ MPa/s}$  in a range  $p_0 = (5.5 \div 8.0) \text{ MPa}$ .

For a range of pressure  $p_0 = (5.5 \div 8.0) \text{ MPa}$  critical value of slaking parameter  $B_{sp} = p_0^{-1} \left| \frac{dp}{dt} \right|_{\max} = (80 \div 100) \text{ c}^{-1}$ .

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## An Infrared and X-ray Diagnostic Study on the Combustion of Solid Propellants

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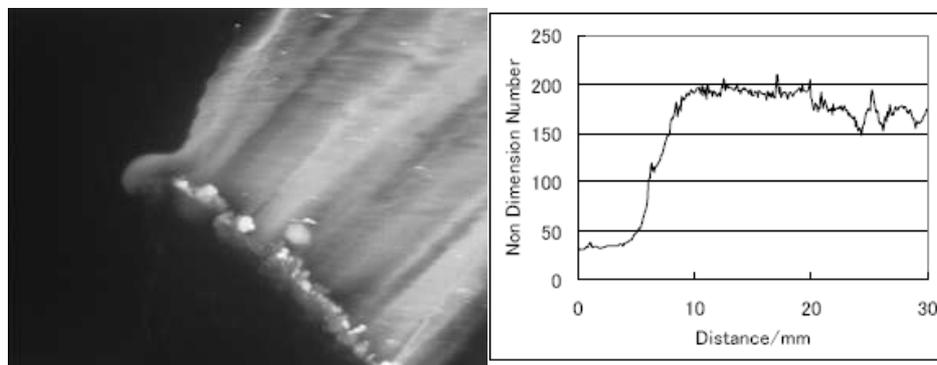
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### Extended Abstract

It is important to understand the combustion phenomenon of solid propellants for the improvement of performance and reliability of solid rocket motors. Efforts have been paid to enhance the spatial resolution of X-ray imaging devices and the distribution of burning rate along a burning surface was successfully obtained. The temporal change of the combustion wave propagation at a deficit in a propellant grain was analyzed in detail using this method. The distance needed for the recovery of a flat burning surface was measured as a function of pressure, which would be useful for the definition of the deficit regulation for the solid propellant grain.

Infrared technology has also been applied to the study of the solid propellant combustion. Infrared intensity does not correspond to temperature, linearly; however, the maximum intensity may indicate the maximum temperature. Thus, it may be possible to determine the position of flame using the infrared data. Further, thermocouple measurement is one-dimensional; however, this technique allows for two-dimensional measurement, which provides information about the flame zone in a combustor. Figure 1(a) shows the direct infrared image of burning composite propellant at 0.1MPa. The burning surface is recognized where aluminum particles are departing, and hot gas streams from the burning surface are also observed. Non-dimensional infrared intensity along the dotted line in Figure 1(a) is shown in Figure 1(b). The location of the burning surface may be defined as the point where the intensity increases abruptly and the intensity reaches its maximum approximately 5mm from the burning surface. This shows the standoff distance of the flame is about 5mm at 0.1MPa.

Burning surface regression at non-flat surfaces was observed using both of these two methods simultaneously. Results correlate the local burning rate and the spatial structure of the flame and will be discussed.



(a)IR image

(b)IR intensity distribution

**Fig.1 IR observation of composite propellant at 0.1MPa**

## DETONATION CHARACTERISTICS OF NITROMETHANE DILUTED WITH NON-EXPLOSIVE LIQUIDS

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### ABSTRACT

Binary mixtures of nitromethane (NM) as detonable energy-containing liquids with non-explosive liquids - methanol (M) and nitrobenzene (NB) have been investigated. The liquids are of different molecular structure and also vary in their initial density. For determining the set of detonation parameters as completely as possible, the electromagnetic method of particle velocity profile  $u(t)$  registration was utilized.

In comparison with the number of investigations in which the electromagnetic method was purposefully used in solid explosives, a number of such experiments in liquid explosives are rather small. Particularly there were apprehensions that the interaction between detonation front and a gage metal surface in homogeneous matter would be able to influence the energy-release process and was the reason for the distortion of  $u(t)$  oscillograms from the point of view of their correspondence to the true detonation wave profile. In this work, the gages from aluminum foils of different thickness were used. Stainless steel confinements with diameter of 50mm and thickness of 3mm provided stable (without failure) propagation of the detonation process in all mixtures under study.

In all mixtures, the typical detonation wave spike predicted by hydrodynamic Zeldovich – Neumann – Doering theory was registered in  $u(t)$  oscillograms. It allows for the identification of the Chapman - Jouguete (CJ) state and the determination of an almost complete set of detonation characteristics for nitromethane diluted with methanol of 10, 20, 25, 30, 35 % and nitrobenzene of 15, 25, 30, 36, 39 % (weight percentage). Experimental results on detonation velocity were fitted adequately by linear dependences  $D = (6.25 - 3.39 \alpha)$  km/s for NM/M and  $D = (6.26 - 1.92 \alpha)$  km/s for NM/NB mixtures ( $\alpha$  – weigh portion of diluent). Corresponding dependencies for pressures of explosive products at CJ state are  $P(\alpha) = (11,26 - 20,0 \alpha + 21,0 \alpha^2)$  GPa and  $P(\alpha) = (10,33 - 3,60 \alpha)$  GPa. Duration of chemical reaction in detonation front rises with dilution for both mixtures and is within the range of 0.13 – 0.30  $\mu$ s.

It is a well known fact that a liquid explosive dilution with non-explosive liquid results in a reduction of the detonation velocity (parameters), and the mixture, as a result, becomes undetonable at real conditions. This situation is quite predictable from the energetic point of view and can be considered as the detonation limit on concentration (DLC) by analogy with gas mixtures. A knowledge of  $P(\alpha)$  dependence is a precondition for determining the true DLC that corresponds to concentration of non-explosive diluent, above which the mixture is not able to detonate in principle.

It should be noted that in the investigated mixtures, a pulsating front of detonation has been observed, i.e. the detonation front is not smooth. There are also other disagreements with one-dimensional detonation theory.

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# LOX VAPORIZATION TECHNIQUES FOR SWIRLING-OXIDIZER-FLOW-TYPE HYBRID ROCKET ENGINES

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## ABSTRACT

### *Background and purpose*

Applying swirl to gaseous oxygen flow through a fuel grain head of a hybrid rocket engine is useful to improve the poor combustion property of hybrid rockets. This effect was confirmed by the result that the swirling gaseous oxygen flow increased the overall fuel regression rates of the engine (propellant: GO<sub>2</sub>/PMMA) up to about 3 times [1]. Using this type of engine, we succeeded in the first launch of a small hybrid rocket in Japan [1]. In order to put the engine into practical applications, the use of LOX is indispensable for increasing the capacity of oxidizer for hybrid rockets. However, when swirling LOX was injected directly into the combustion chamber, the engine performance became lower than that of swirling GOX. Thus, vaporizing LOX before injection into the combustion chamber is required for practical swirling-oxidizer-flow-type hybrid rocket engines to attain sufficient performance. We proposed two methods to vaporize LOX; one is through a heat exchanger using a regenerative-cooling LOX-vaporization nozzle, and the other is through the combustion heat of a solid fuel in LOX. We are planning to launch a small sounding rocket up to about 25 km using this type of hybrid rocket engine with a thrust of 1500 N and a burning time of 30 sec. For the project described in this paper, we made a small LOX-vaporization nozzle and conducted combustion tests. In addition, the feasibility of a LOX-vaporization burner using combustion of a solid fuel in LOX was examined from the viewpoint of thermal energy management of the propulsion system. PMMA was selected as a solid fuel by a preliminary combustion test in LOX.

### *Design and experiment of LOX-vaporization nozzle*

The design point of the engine is as follows: propellant = LOX/polypropylene, combustion chamber pressure = 4 MPa, oxygen mass flow rate = 388 g/s. In order to design the nozzle, we analyzed thermal conditions of a regenerative cooling-channel wall of the nozzle using LOX as a coolant. The analysis indicated that LOX can be gasified at the exit of the cooling-channels with a thin channel depth smaller than 1.0 mm. The maximum temperature of the channel wall is much lower than the melting point of the copper used as the wall material. As the channel becomes more shallow, the channel wall temperature becomes lower, and the oxygen temperature at the flow outlet becomes higher. Based on these results, the regenerative-cooling LOX-vaporization nozzle with 30 rectangular channels, each 1.0-mm deep, as shown in Figure 1(a) was initially produced for the 1500N-thrust hybrid rocket engine. The vaporization tests showed that LOX could be vaporized safely through the nozzle. Burning tests using the vaporized oxygen through the nozzle showed that reliable and rapid ignition and stable combustion without combustion oscillation were achieved as shown in Figure 1(b). However, it was found that the wall temperature of the nozzle exceeded the strength limit temperature of 800 K for burning durations longer than 8 sec. To decrease the wall temperature, the 0.5mm-depth channel with a 1500N-thrust LOX-vaporization nozzle was newly designed and is currently under construction.

### Feasibility of LOX-vaporization burner

For this hybrid rocket engine, the amount of heat needed to vaporize LOX at 90 K and to increase the temperature of vaporized oxygen up to 200 K at 5 MPa was estimated to be 110.5 kJ/s. This value of heat is obtained by burning PMMA in LOX; the amount of PMMA is at most 3% of the mass of the rocket's fuel propellant. The trade-off consideration between the LOX-vaporization burner and the LOX-vaporization nozzle suggested that the burner had the advantage of a simple, compact structure, as compared with the nozzle. The preliminary experiment showed that PMMA could burn steadily and safely in LOX and vaporize a large amount of LOX.

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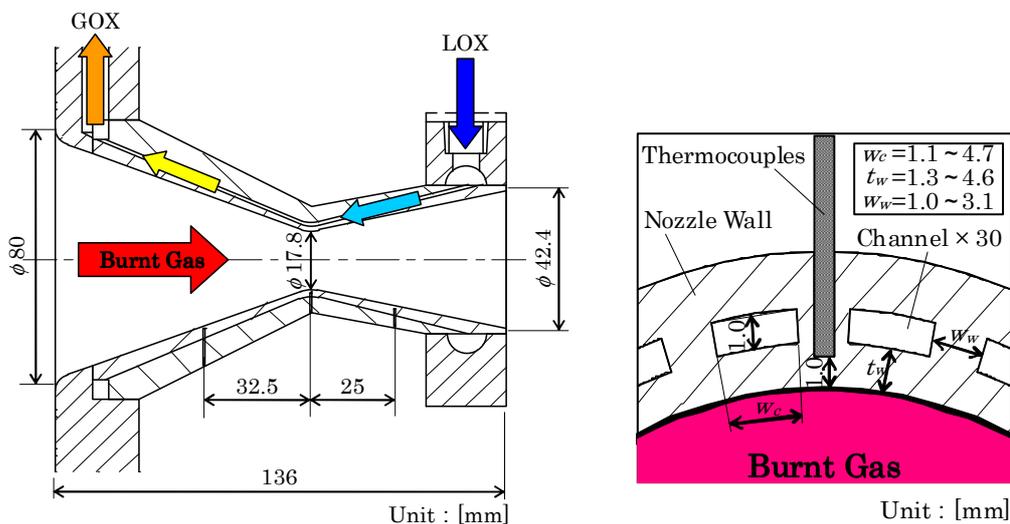


Fig.1(a) 1500N LOX-Vaporization Nozzle (Channel Depth 1mm) and Cross Section (Vertical to the Flow )

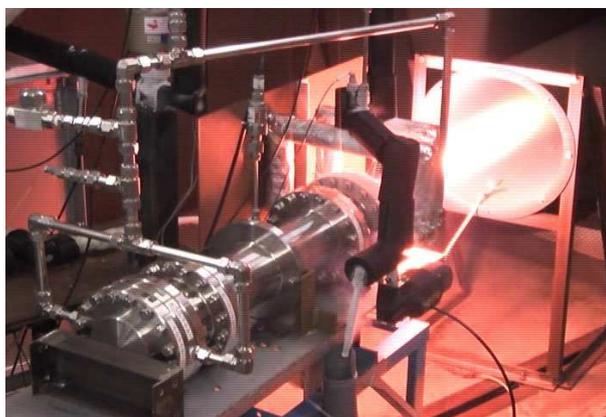


Figure 1(b): Burning Test Behavior using 1500N LOX-Vaporization Nozzle

# CHARACTERIZATION OF CARBON FIBER REINFORCED COMPOSITES USED IN ROCKET MOTORS

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## ABSTRACT

The main objective of this research work was to obtain two formulations of ablative composites. The first formulation (Composite I) was manufactured with phenolic matrix reinforced with chopped carbon fiber. The second formulation (Composite II) was manufactured with phenolic epoxy matrix reinforced with chopped carbon fiber.

The composites were obtained by the hot pressing technique.

These composites are also known as ablative structural composites, for applications in atmospherically severe conditions according to the high-temperature, hot gaseous products flow generated from the burning of solid propellants.

Another purpose of this work was to conduct the physical and chemical characterization of the matrix, the reinforcements and the composites.

After the characterization, a nozzle divergent of each formulation was manufactured and its performance was measured through the static test in a training rocket motor.

The composites samples exhibit densities range from 1.45 to 1.47 g/cm<sup>3</sup>. In Thermal-Dynamic-Mechanical properties, the Elastic Module (E') of 1.14 GPa to 2.50 GPa and Viscous Dissipation Module (E'') of 60.2 MPa to 163.0 MPa, were obtained depending upon the temperature range.

The Glass Transition Temperature (T<sub>g</sub>) measurements obtained by Differential Scanning Colorimetry (DSC) were 95 and 92°C, and the values for linear thermal dilation were 449.85x10<sup>-7</sup>/°C and 76.36x10<sup>-7</sup>/°C respectively.

The composite specific heat (C<sub>p</sub>) was from 0.319 J/g/°C to 1.254 J/g/°C, according to range into -80.0 to 40.6°C.

The mechanical properties obtained for both composites formulations exhibited similar values.

The ablation performance for the Composite I formulation was superior to the Composite II formulation, which was confirmed by the static test in training rocket motor.

The Thermal Conductivity values were from 39.1 to 48.0 W/mK, according to range into 50.0 to 450.0°C.

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