Institute of Energetic Materials

Faculty of Chemical Technology
University of Pardubice

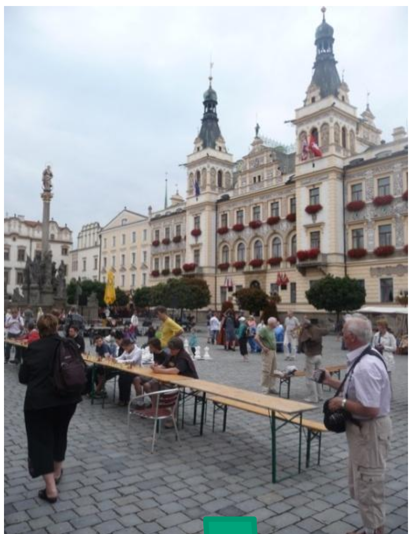
Jiří Pachmáň

Outline

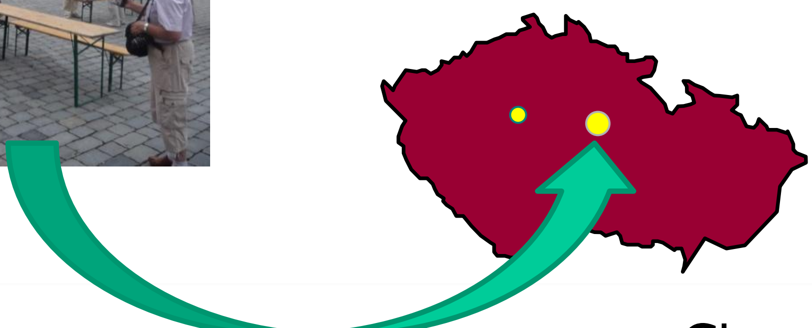
- who we are
- what we doing / not doing
- some thoughts on the general questions
- summary

Institute of Energetic Materials

Pardubice



Institute of Energetic Materials



Chemistry Department

- not a government lab
- not a military

People at the IEM

• Profesor	1	+ 2 external Professors
• Assoc. Professors	2	+ 2 external Assoc. Professors
• Assist. Professors	6	
• Sci. Workers	3	
• Goup of veterans	3	

- 5-10 PhD students (internal, external)
- 5-10 undergraduates

Distance learning programs
(Theory and Technology of Explosives, Rock Blasting)

- teachers
- 20-30 students

Research and Education at the IEM

- Synthetic chemistry
- Detonics
  - theory
  - applications
  - testing
- Safety Engineering

- Education in explosives starts after students obtain Bc. (after 3 years of general chemistry)
- Bc. + 2 years for MSc.
- MSc. + 4-5years for PhD.

Research and Education at the IEM

- Chemical technology
  - chemistry and technology of individual explosive substances
  - analytical chemistry of explosives
- Technology of explosives
  - military & industrial explosives
  - propellants
  - primers & initiators, pyrotechnic products
- Physics of explosion
  - theory of explosives
  - theory of explosion effects
  - technology & safety of blasting
  - construction of weapons and ammunition
- Safety engineering
  - risk analysis
  - consequence modelling
  - prevention and investigation of accidents

NTREM 2011

New Trends in Research of Energetic Materials

Institute of Energetic Materials is organizing Seminar NTREM

- meant especially for younger presenters
- submitted for 2011 - 37 presentations, 80 posters

www.ntrem.com

Central European Journal of Energetic Materials

- Co-founders of CEJEM in 1994
- *CEJEM, ISSN 1733-7178*
- sponsored by Polish Ministry of Science and Information Technologies
- Published by Institute of Industrial Organic Chemistry, Warsaw

where we do it

Facilities for studies of Explosives

Facilities at IEM

- fully equiped chemical laboratories
  + supporting laboratories (NMR, LC/MS, Raman, XRD, etc. at main campus)
- sensitivity testing laboratories
- detonation chamber
- sand pit

Facilities used by IEM

- large scale test sites
- pilot plant synthesis facility at of VÚPCH (research brand of Explosia Co.)

Chemical Laboratories at IEM

- 3 synthetic laboratories
- 1 analytical laboratory
- 1 primary explosives laboratory
- 2 technological laboratories

EXPLOSIA

Pilot plant at Explosia

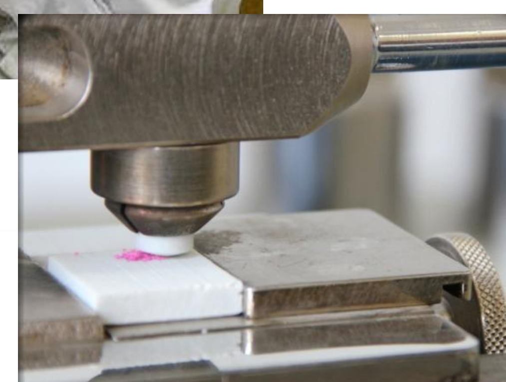
- transformation of new synthesis from laboratory to pilot plant
- explosives, dangerous compounds 5-150 kg (11-330 lbs)
- equipment: double-wall glass, stainless and enamel vessels
  volume: 20-1200 liters (5-300 gallons)
- temperature:
  cooling by brine (-17°C),
  heating by steam (up to 140°C) or by hot water.

- synthesis of energetic materials- pilot plant scale
- crystallization of energetic materials
- phlegmatization (desensitization) of energetic materials

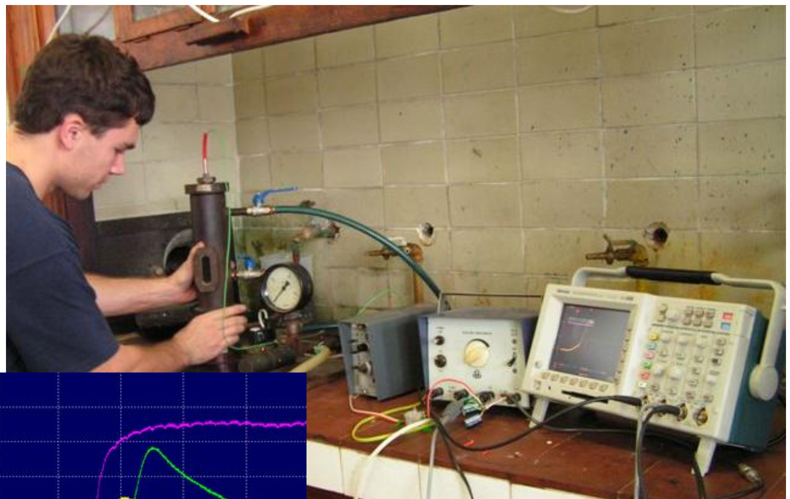
Sensitivity Laboratories at IEM

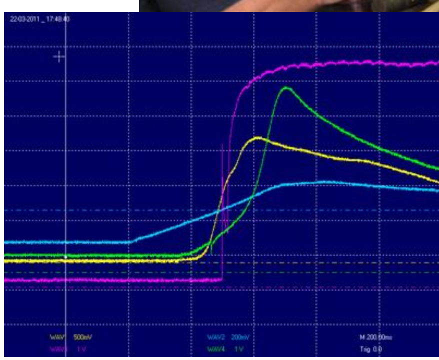
Impact (BAM)

Large Scale Friction (BAM)



Sensitivity testing at IEM





Combustible dust testing
(Hartman pipe)

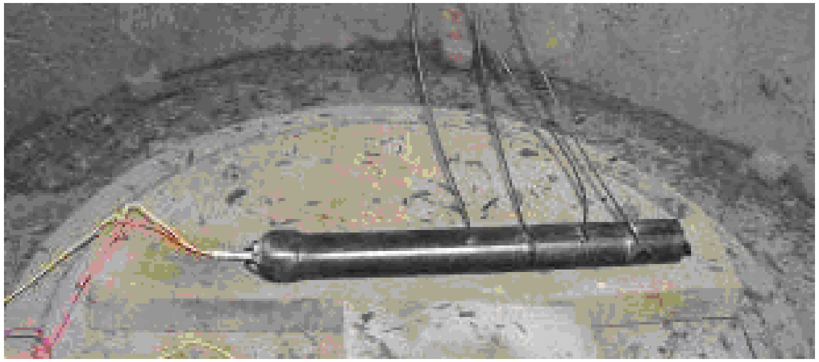
Electrostatic discharge testing

- direct
- dumped

Test sites

- for obtaining well defined experimental data
- published data unfortunately often do not contain failed results or „not so good looking“ results
- real experiments quite often give surprising results

- testing from small to a large scale
- well defined conditions
- hands-on experience



Detonation Chamber KV-2 at IEM

- „in door“ testing
- confinement possible

Sand pit at IEM

- open air testing
- without confinement




Off campus site – a bit larger

ANFO project

- test polygon Polička
  Czech Republic

Off campus site – reasonably large

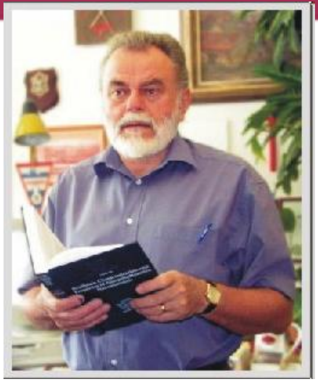
ČVUT project
Resistant Concrete

- test polygon Boletice
  Czech Republic

Off campus site – large

- test polygon Záhorie Slovak Republic
- pictures by prof. Lefebvre tests 2009

who does what



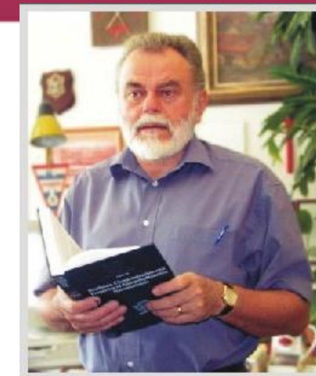
prof. Svatopluk Zeman

Initiation Reactivity, Synthesis, Technology

Initiation reactivity – relations

- heat, electric spark, impact and shock sensitivities vs. ^{15}N and ^{13}C NMR chemical shifts, to charges at nitrogen atoms and to net charges of nitro groups
- relationships between the individual types of sensitivities with respect to reaction centers in molecules
- chemical mechanism of initiation of explosive mixtures (W/O emulsions, mixtures with organic peroxides)
- study of friction sensitivity, its relation to impact sensitivity, thermal reactivity, detonation parameters and to the DFT surface electrostatic potentials in nitramines

Summarized in monograph of Klapoetke T. (Ed), *High Energy Density Materials*, Series: Structure & Bonding, 125, Springer, New York, 2007, pp. 195-271.

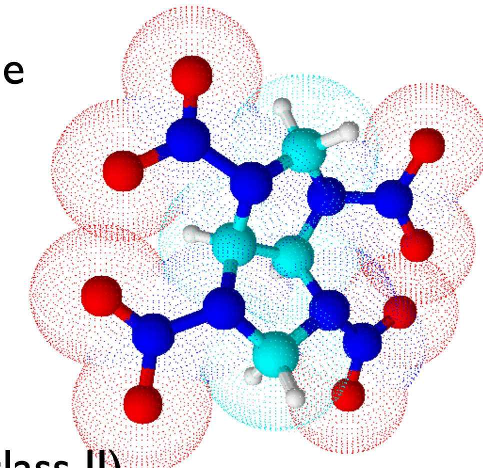


prof. Svatopluk Zeman

Initiation Reactivity, Synthesis, Technology

Attractive cyclic nitramines

- *cis*-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-d]imidazole (bicyclo-HMX, BCHMX)
- RS-CL20 (Reduced Sensitivity) with a increased purity and decreased impact sensitivity - 10.0-10.8 J



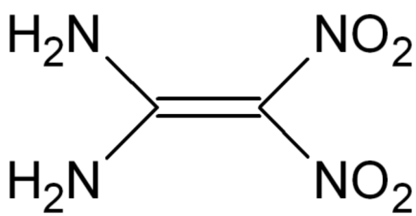
Explosive mixtures

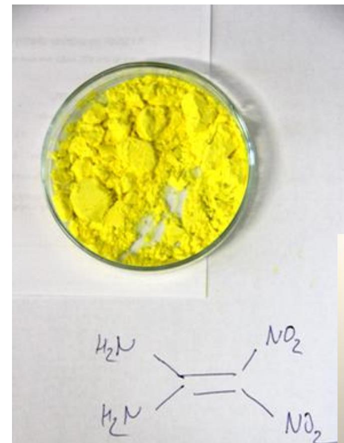
- development of W/O emulsion explosive for mines (class II)
- utilization of demilitarized explosives as fortification additives of the W/O emulsion explosives
- PBXs on the basis of attractive cyclic nitramines (RDX, HMX, BCHMX and CL20)

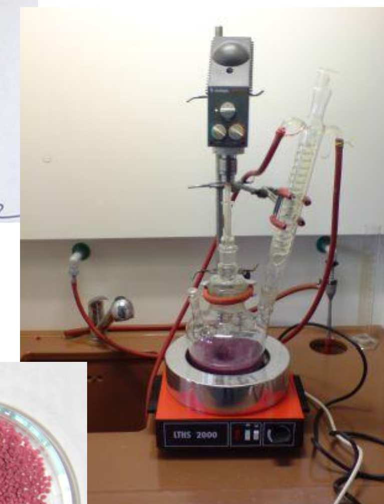
Zdeněk Jalový, PhD

Synthesis of Explosives

Energetic materials with low sensitivity







Fuels for pyrotechnics of inflating vehicle occupant safety systems

Zdeněk Jalový, PhD
Synthesis of Explosives

Syntheses of energetic materials, precursors, intermediates & by-products for:

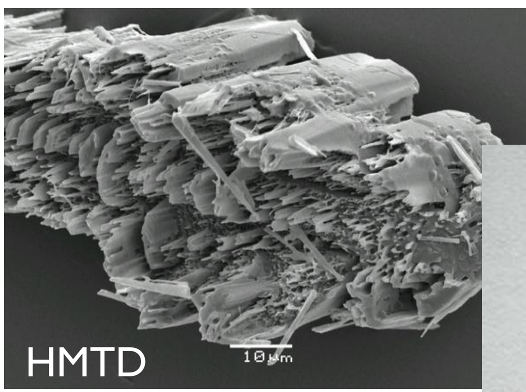
- forensic purposes
- projects connected with decontamination of water and soils after explosives planting
- industrial companies

Robert Matyáš, PhD

Synthesis of Explosives

Improvised explosives

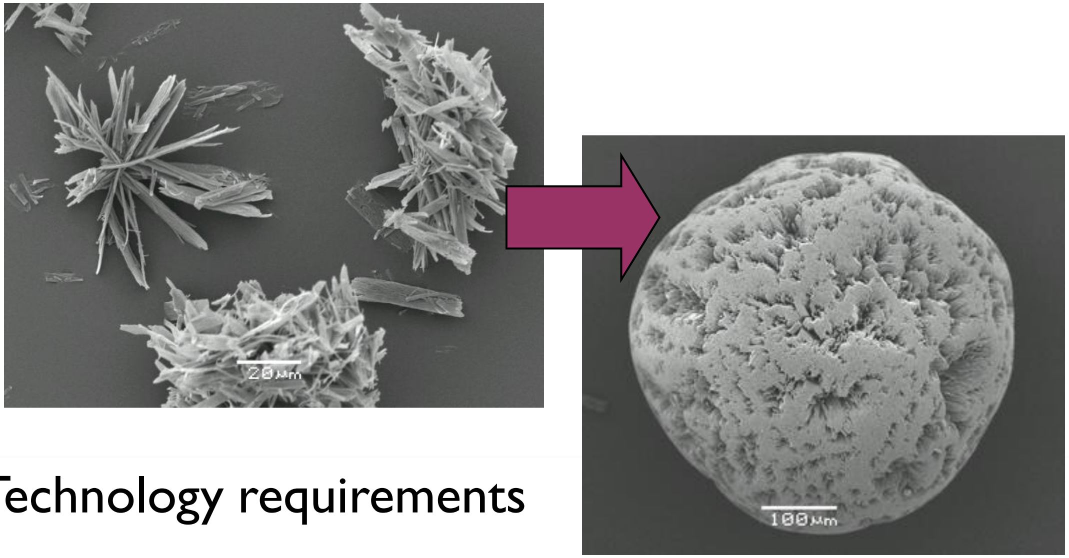
- precursors of improvised explosives
- organic peroxides (TATP)
- nitrate esters



Robert Matyáš, PhD
Synthesis of Explosives

Primary explosives

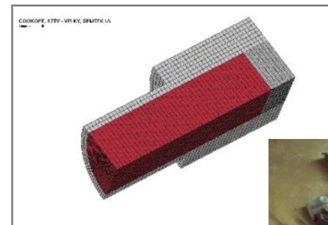
- sensitivity of primary explosives
- green primary explosives



Technology requirements

Jakub Šelešovský, PhD

Detonics, Numerical Modeling

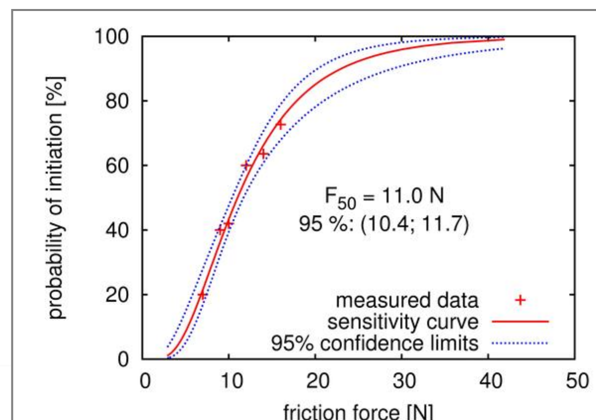


Thermal loading of explosives

- heat transfer in EM
- thermal decomposition of EM
- slow cookoff test- experimental- simulation

Sensitivity of EM

- impact, friction, gap test, ESD
- usage of various statistic methods
    - Bruceton
    - probit analysis
    - Neyer-D-optimal test



Jakub Šelešovský, PhD

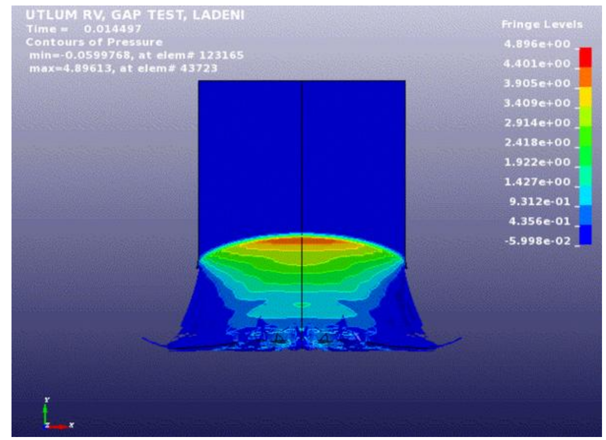
Detonics, Numerical Modeling

Numerical simulations

Finite Element Modeling (FEM)

LS-DYNA

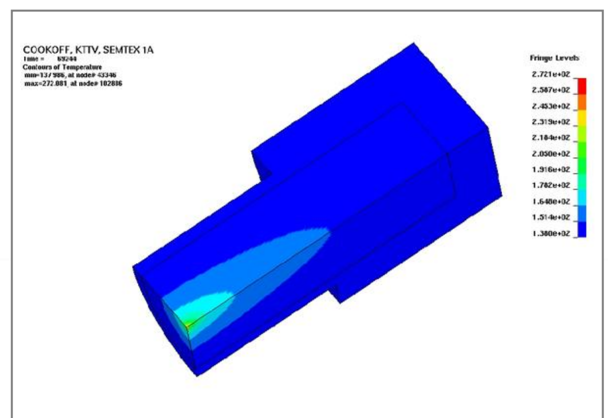
- shock waves
- heat transfer



Finite Difference Modelling (FDM)

GNU Octave

- heat transfer

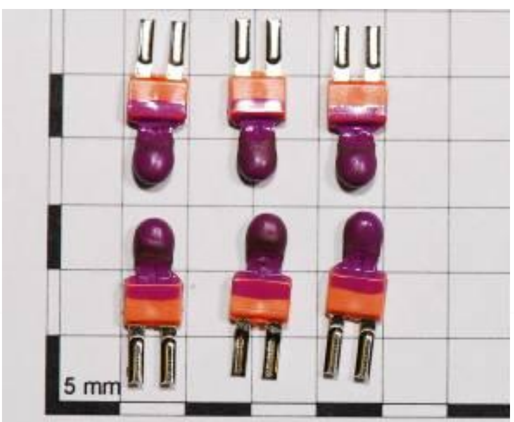


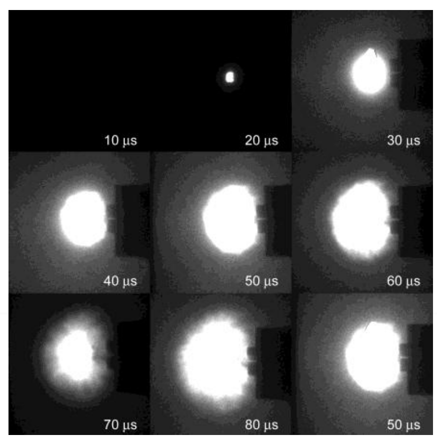
Vojtěch Pelikán, PhD

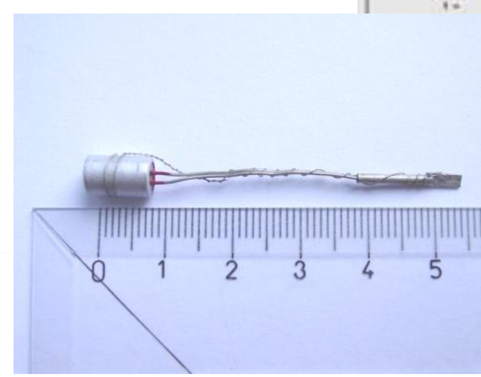
Initiators, Pyrotechnics, Explosives Testing

Initiators

- New compositions for bridge wire fuseheads
- EED’s performance, optimization and examination
- Improvised initiators
  seminars for Police and Military EOD teams







Vojtěch Pelikán, PhD

Initiators, Pyrotechnics, Explosives Testing

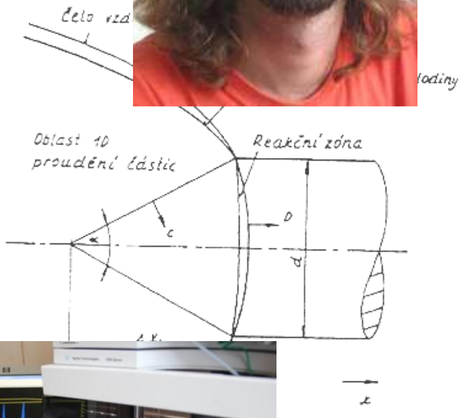
Pyrotechnics

- Development and improvement of pyrotechnic ammunition for industry
- ESD sensitivity of pyrotechnics compositions

Testing of explosives

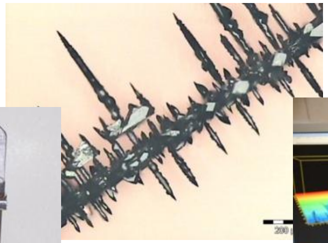
- ESD sensitivity and development of ESD testing methods and testers
- Air shock wave measurement in confined vessels
- New testing methods for EM's

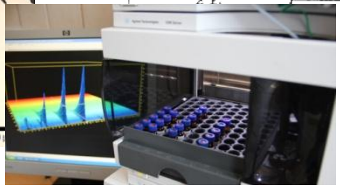
Jiří Pachmáň, PhD
Analysis, Explosives Testing, Theory

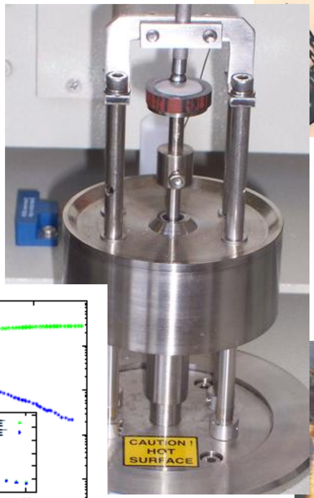


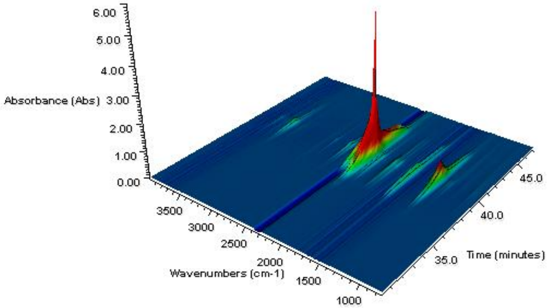
Material Characterization

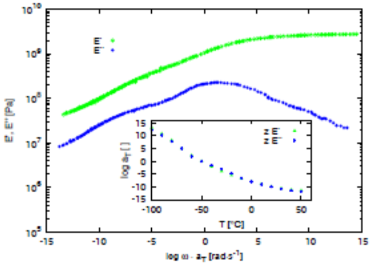
- chromatography, spectroscopy
- thermal analysis, decomposition
- mechanical analysis
- shelf life, aging

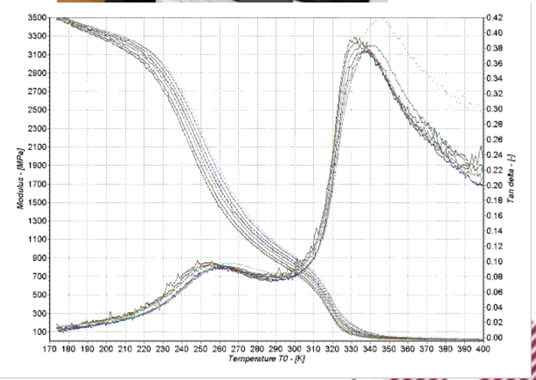












Jiří Pachmáň, PhD
Analysis, Explosives Testing, Theory

Explosives Testing

- basic detonation parameters
- blast waves in air, shock waves
- explosion effects

Marcela Jungová, PhD

Rock Blasting, Explosives Testing

Explosives testing

- friction sensitivity, its relation to impact sensitivity, thermal reactivity, detonation parameters
- explosive strength, impact sensitivity of PBXs on the basis of attractive cyclic nitramines (RDX, HMX, BCHMX and CL20)

Demil applications for rock blasting

- utilization of demilitarized explosives as fortification additives of the W/O emulsion explosives

Marcela Jungová, PhD
Detonics, Explosives Testing

Initiation capability of detonators

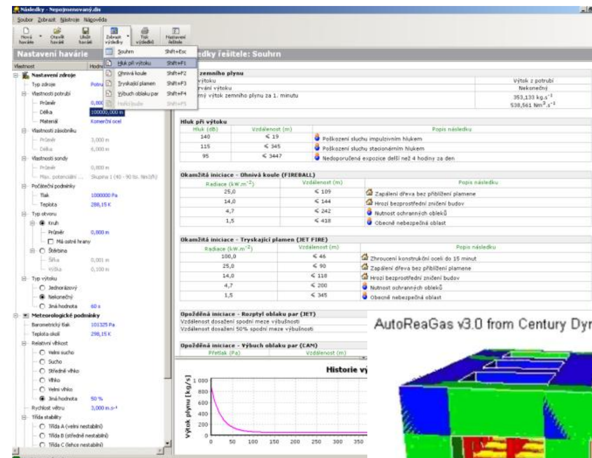
Theoretical Applied Physics of Explosion
Laboratory training in Physics of Explosion

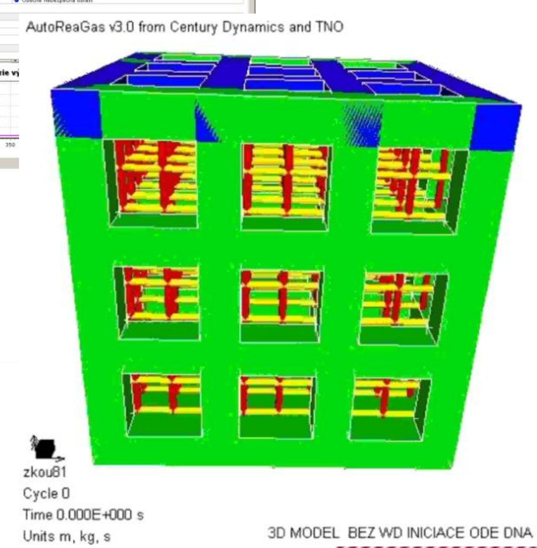
assoc. prof Břetislav Janovský

Safety Engineering

Consequence analysis calculation:

- Source term
  - Outflow and evaporation
- Dispersion
- Fire
  - Pool, jet and fireball
- Explosion
  - Calculation and measurement of gas, dust and physical explosion



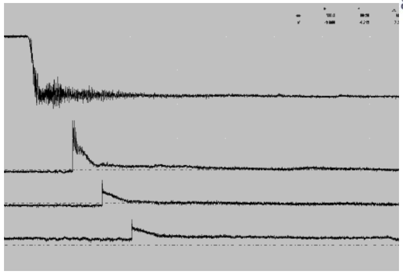


assoc. prof Břetislav Janovský

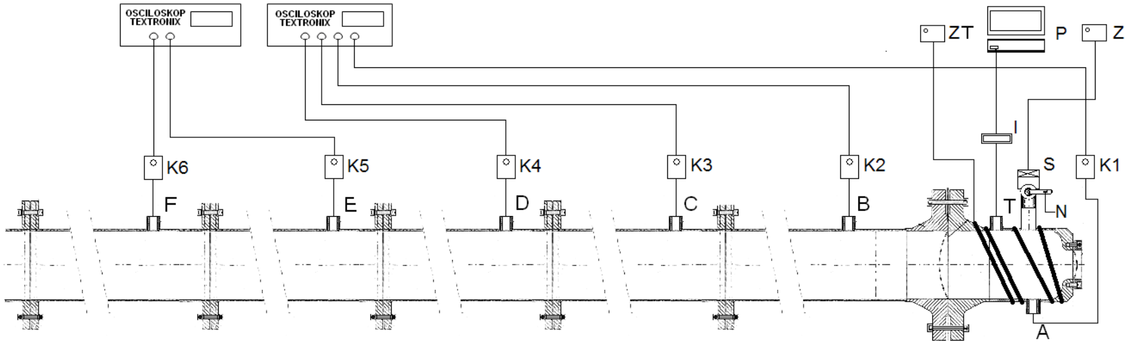
Safety Engineering

BLEVE

- Calculation of:
  - Overpressure generated
  - Heat radiation caused by fireball



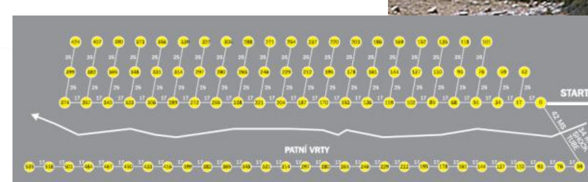
- Experiments in 1-D geometry



Miloš Ferjenčík, PhD
Safety Engineering

Learning from incidents –
methods for cause analysis of undesirable events
Analyses of real undesirable events
Fundamentals of safety - approach to safety teaching
Simplified analyses of risk
Application of risk analysis in explosive sector
Participation in European projects EUExCert and ESSEEM

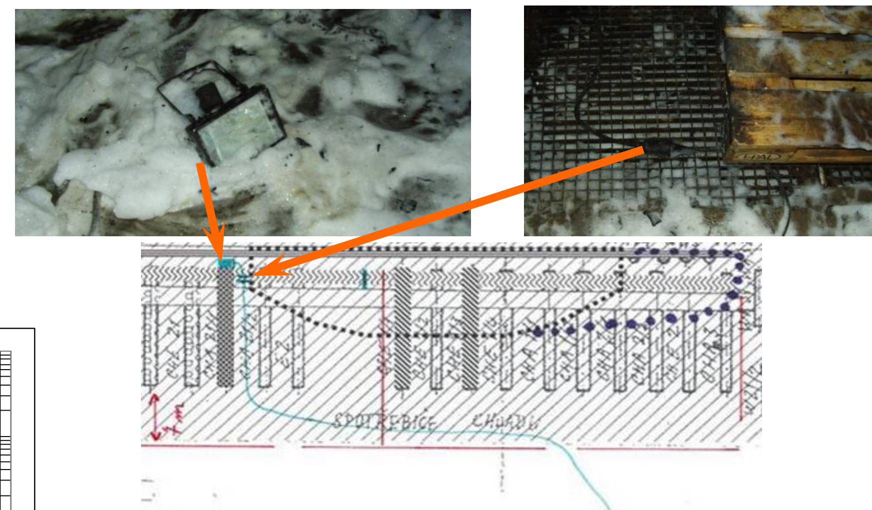
EU ExCert
Certifying Expertise in European Explosives Sector

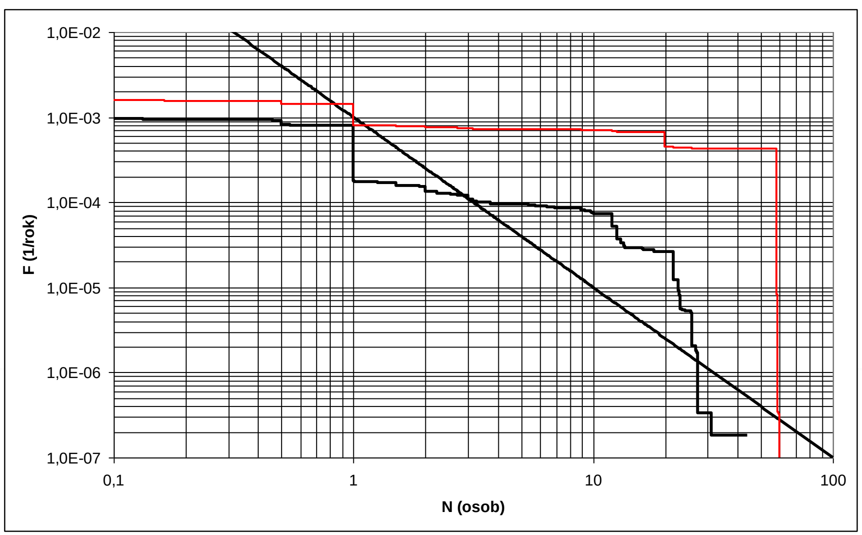


Miloš Ferjenčík, PhD
Safety Engineering

Teaching

- Safety of industrial processes
- Safety engineering 1
- Safety engineering 2



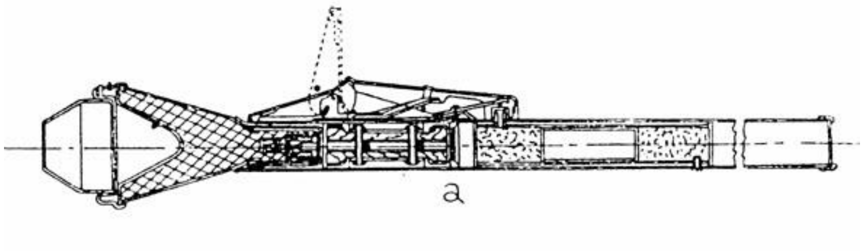


Matice rizika scénářů nehod		následky			
		nízké I	střední II	vysoké III	extrémní IV
četnosti	1,E+00 - 1,E+01				
	1,E-01 - 1,E+00				
	1,E-02 - 1,E-01				
	1,E-03 - 1,E-02				
	1,E-04 - 1,E-03				41a-K
	1,E-05 - 1,E-04				29-A; 29-B; 45a-O
Četnosti nad horní mezí					
Četnosti pod dolní mezí				38a-B; 45-M; 50a-P; 50b-Q	29a-C; 32a-B; 38b-B; 40a-J

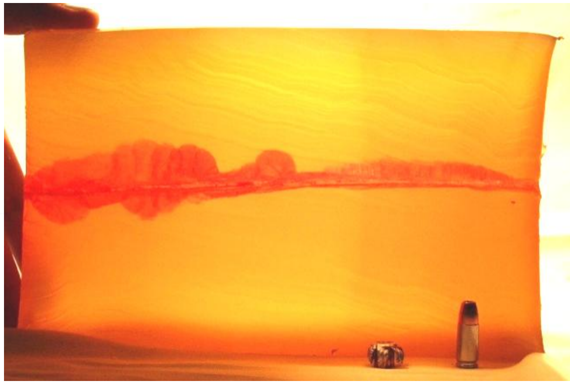
assoc. prof. Ludvík JUŘÍČEK

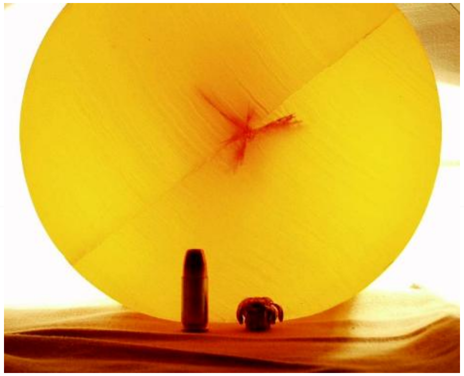
Ballistics, Forensic Expert

Basics of Munitions Construction



Theoretical Wound Ballistics

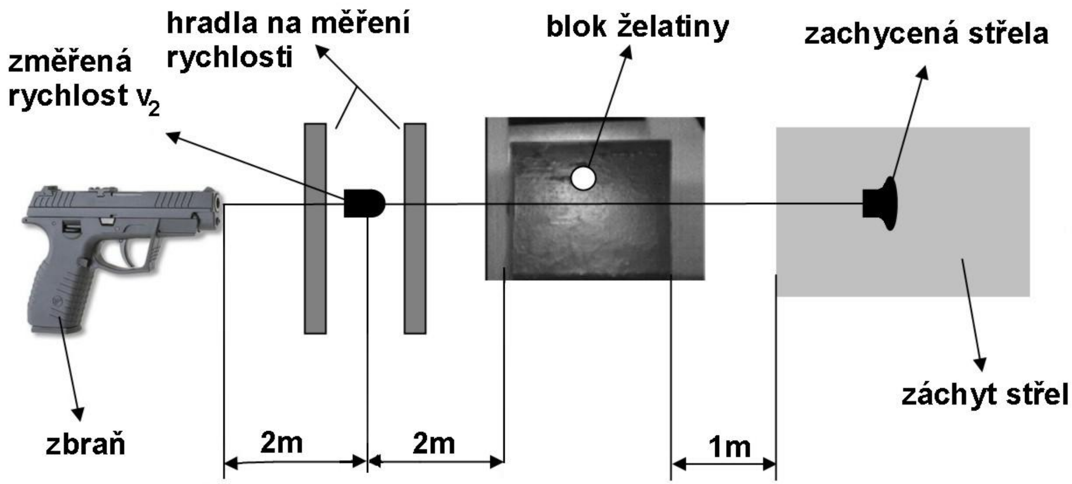


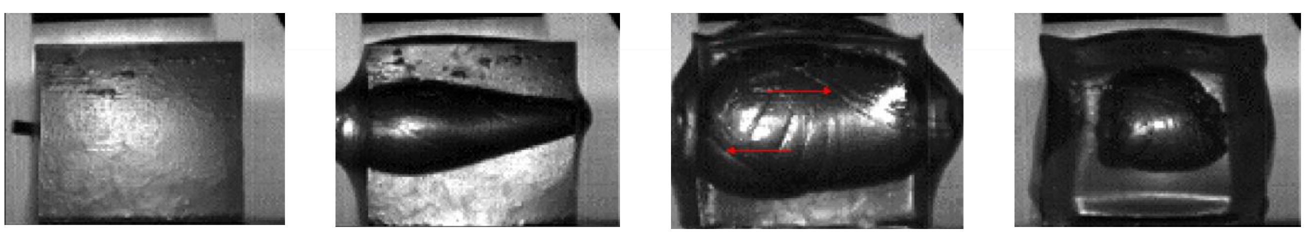


assoc. prof. Ludvík JUŘÍČEK

Ballistics, Forensic Expert

Experimental Wound Ballistics





The general questions to address

1. Critical issues synthesis, scale-up, fielding

- Critical issues
  - in laboratory – none
    pressure, temperatures, atmospheres, exotic materials, catalysis, equipment (all can be solved)
  - scale-up – economy, toxicology, waste, 1 step process
  - full scale – can not comment on technical aspects, limitation in:
    - traditionalism (unknown dangers in new tech., digital balance)
    - local legislative regulation

- PRICE - the most critical criteria
  - use of existing technology (e.g. casting below 100°C)
  - minimal number of risky operations (e.g. grinding)

1. Critical issues synthesis, scale-up, fielding

- Criteria
  - what are energetic materials?
  - application in mind from the early beginning
  - not spending time on unrealistic criteria

- Right balance of properties

- Differentiating research
  1. finding applications for substances (basic research, academia)
  2. finding substances for applications (applied research, industry, military)

II. Technical limitations for new ingredients in munitions

- I can not competently comment on this topic

III. Failed Candidates Re-evaluation

- Curtius initial work on azides in Spandau in Prussia 1893, accidents stopped further work till 1907, even later in twenties - strong disbelief due to high sensitivity. Today LA represents most often used detonant.
- DDNP 1858 Griess, seemed to be too weak, inferior to MF and later to LA. Today it is back.
- GNGT to most just sensitizer, to some fully functional primary
- picric acid
- SA extremely sensitive, after WWII production of spherical with lower sensitivity
- Cyanuric triazide in NOL-130G , melting point 94°C
- NTO 1905, patented as „3-nitro-1,2,4-triazol-5-one, A less sensitive explosive“ in 1988

IV. Emerging Technologies

- I can not competently comment on this topic

V. Efficient Candidate Screening

- set exact and meaningful criteria
  - hard (unchangeable) - physical & chemical properties
  - soft (modifiable) - synthetic route, cost, environmental issues, unavailable starting materials
- from application targeted research exclude candidates after finding problem in hard criteria if design modification is not possible (leave the substances to academics)
- reading even the old stuff and talking to the veterans
- experience
- trends (extrapolations)

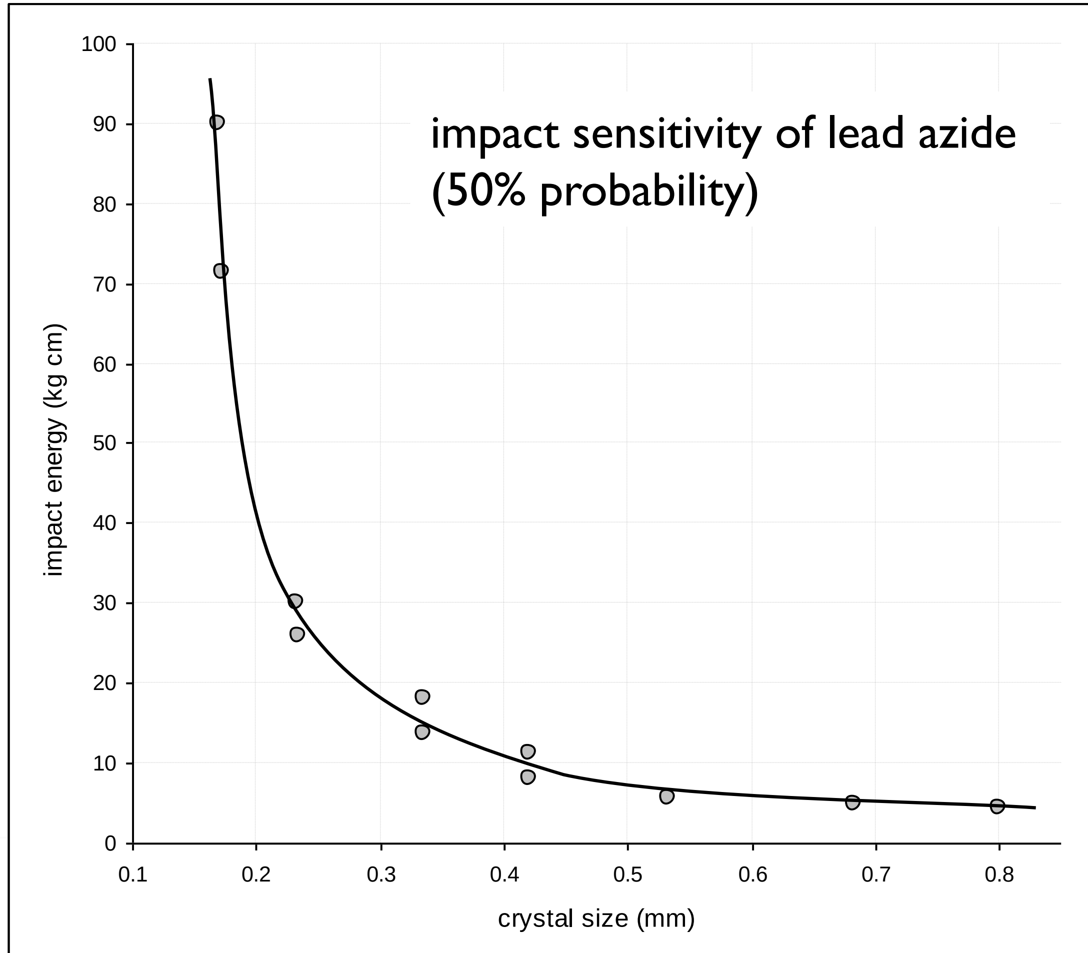
VI. Small Scale Testing

- investment in rapid characterization
  - sensitivity – H50 vs. H10, H100 – small number of trials is misleading
  - thermal behavior – relatively well understood process
  - shelf life – define critical process, invest to mechanical properties and aging
  - compatibility – chemical vs. physical
  - mapping small scale to a large scale – cook off
- invest into experimental studied directed towards explanation of the mechanisms of critical processes (does NOT have to be chemistry)

VI. Small Scale Testing

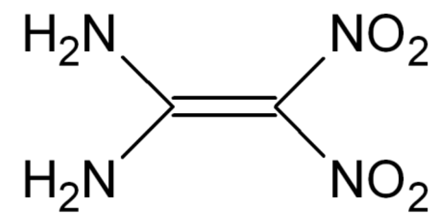
3M
- material
- machine
- methodology

different conditions:
H0 = 10kg / 1m



Bowden F. P. and Singh K.: "Size effects in the initiation and growth of explosion", *Nature*, **172**, 378-380 (1953)

VII. Interesting Candidates



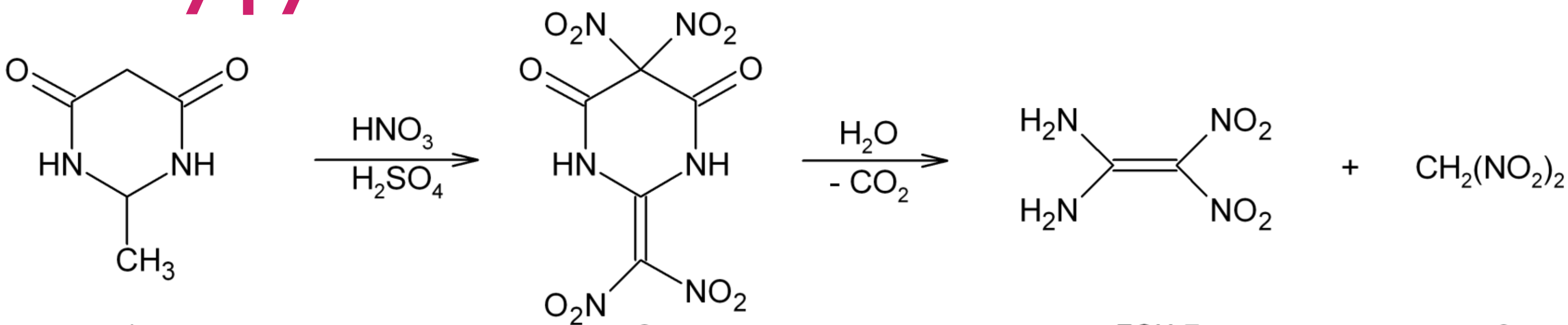
- example 2,2-Dinitroethene-1,1-diamine (FOX-7)

Property	FOX-7	RDX
M_w (g.mol^{-1})	$C_2H_4N_4O_4$	$C_3H_6N_6O_6$
Density (g.mol^{-1})	1.88	1.82
Oxygen balance (to CO_2, %)	-21.6	-21.6
Decomposition (ARC, onset, °C)	219-223	195-199
Detonation velocity (exp., m.s^{-1})	8870	8930
Detonation pressure (calc., GPa)	33.96	34.23
Impact (Dropweight test, BAM 2kg, cm)	126	38
Friction (kp)	>350	120

Two synthetic methods suitable for scale-up

*Bellamy, A. In *Structure and Bonding*; Mingos, D.M.P.; Klapötke, T.M, Eds.; Springer-Verlag: Berlin, 2007, pp. 1-33 and references cited therein.

Process starting from 4,6-dihydroxy-2-methylpyrimidine *



1 2 FOX-7 3

Advantages

- Starting material commercially available.
- One or two step synthesis, yield 70-80%.

Disadvantages

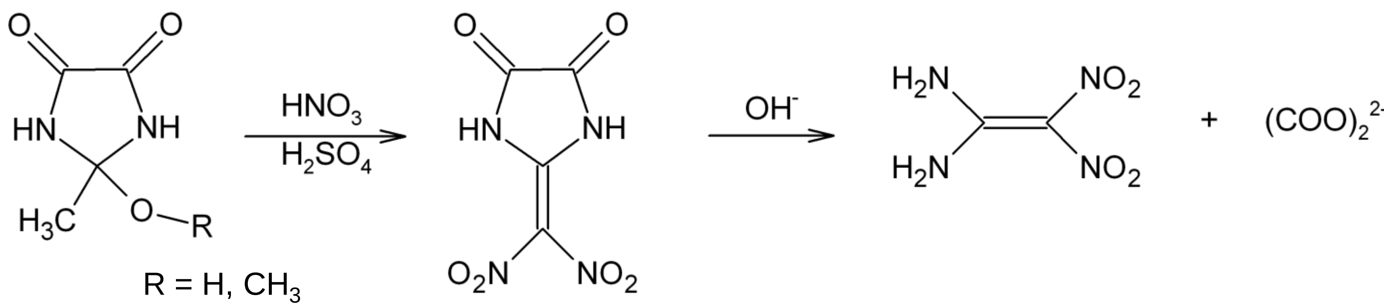
-Handling of sensitive intermediate **2**.

-Formation of dinitromerthane **3** – poisonous and extremely instable compound.

-Production of dilute sulfuric acid which is difficult to recycle.

*(a) Astrat'ev, A. A.; Dasko, D. V.; Mershin, A. Y.; Stepanov, A. I.; Urazgil'deev, N. A. *Russ. J. Org. Chem.* **2001,** *37*, 729-733. *(b) Latypov, N. V.; Johansson, M.; Holmgren, E.; Sizova, E. V.; Sizov, V. V.; Bellamy, A. J. *Org. Process Res. Dev.* **2006,** *11*, 56.

2. Process starting from methylimidazolidinediones*



R = H, CH_3

4

5

FOX-7

Advantages

-Dinitromethane does not form

-Intermediate **5** has acceptable stability

Disadvantages

-Starting material is not commercially available

-Lower overall yield with comparison to process from 4,6-dihydroxy-2-methylpyrimidine

* (a) Latypov, N. V.; Bergman, J.; Langlet, A.; Wellmar, U.; Bemm, U. *Tetrahedron* **1998,** *54*, 11525-11536. *(b) Jalový, Z.; Mareček, P.; Dudek, K.; Fohl, O.; Latypov, N. V.; Ek, S.; Johansson, M. *Conference proceedings* New Trends in Research of Energetic Materials 8, 2005, Pardubice, Czech Republic, pp 579-583.

FOX-7 from five member heterocycles

Results until now

- the process is scalable
- Scale-up in kilogram amounts in Explosia (Czech Republic) and FOI (Sweden) in 2007-2008 within EDA project
- No special equipment necessary (no high pressures, no special solvents)

The research continues, but at the moment is not covered by any project.

Summary – FOX-7

- detonation properties slightly lower to RDX
- thermal stability slightly higher than RDX
- sensitivity substantialy lower than RDX
- synthesis not complicated, but necessary to change some features in procedure in order to reduce the production cost and improve technology to large scales

VIII. Energy Content vs. Sensitivity

- Understanding the mechanism of initiation
- Understanding what is measured by sensitivity tests (at the bottom level, not the engineering one)

- experimentalists – run tests under perfectly defined conditions (e.g. impact)
- theoreticians – rely only on well defined data (do not select data to fit the idea)

- prof. Zeman correlations

IX. Eliminating deleterious effects of EM

X. Predictive capability for synthesis

- I can not competently comment on this topic

Conclusion

- golden rule for structure vs. properties does not seem to be available
- there is no substitute for experience yet
- „I have been preparing primary explosives for more then 30 years now and I still can not say from the structure if it will be a detonant or not.“

a friend

Jirka N.