Abstracts of the 16th Seminar on

New Trends in Research of Energetic Materials

NTREM

Pardubice, April 10–12, 2013

University of Pardubice, Faculty of Chemical Technology
Institute of Energetic Materials

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Held at the University of Pardubice

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Intended as a meeting of students, postgraduate students, university teachers, and young research and development workers, concerned from the whole world.

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Preface

This sixteenth seminar NTREM takes place in the year of 60th anniversary of the beginning of education in the field of science and technology of explosives at the University of Pardubice; the education was rehoused on September 1953 from the Institute of Chemical Technology in Prague where it was practised from 1920 with interruption during the time of the WWII. The first seminar was carried as an internal meeting of the Research Institute of Industrial Chemistry (from Explosia Co.) and hence the meeting as we know it today is actually the fifteenth one organized by our institute. These past fifteen years have shown that the seminars not only serve for the exchange of professional information but also fulfill the original idea and help creating a pleasant meeting where young specialists from different countries have the opportunity to meet and gain personal contacts and develop further cooperation.

One of the decisive factors enabling realisation of these seminars has been the financial assistance of well-wishers of this activity. Traditionally, the seminars were sponsored by number of institutions. We are grateful that their interest continues and that Austin Detonator Vsetín, Indet Safety Systems (*a member of Nippon Kayaku Group*) Vsetín, Faculty of Chemical Technology of the University of Pardubice, Explosia Co. Pardubice, and OZM Reasearch Hrochův Týnec decided to support us this year again. There are also new supporters of the seminar including the Ministry of Defence of Great Britain (Defence Science & Technology Laboratory), Sevenoaks, Institute of Shock Physics at London Imperial College, Bofors Test Center, Sweden and Nicolet, Prague. The efficient help in ensuring smooth and successful course of the meeting obtained from all these institutions is gratefully acknowledged. We greatly appreciate that thanks to this support all the specifics of the seminar can be preserved.

Finally, I wish to thank the members of the Scientific Committee, the authors of all the seminar papers and, last but not least, you, the participants of this seminar, for its continued success. I hope our seminar will contribute in creating links among young students, junior researchers, university teachers and other specialists working in the field of teaching, research, development, processing, analysing and application of all kinds of energetic materials at our University.

Allow me to use this opportunity for inviting you in the name of my co-workers and myself: We are looking forward to meet you at the sixteenth seminar in the second half of April 2014 at the Aula Magna of our University.

Pardubice, March 10th, 2013

Svatopluk Zeman

Rheology of HTPB propellant: effect of particle size distribution of ammonium per chlorate and its influence on properties of composite propellant

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Keywords: rheo-kinetics; particle size; distribution; composite propellant; viscosity build up; ammonium perchlorate.

In this paper, the cure kinetics of composite slurries based on hydroxyl-terminated poly butadiene (HTPB) and iso-phorone diisocyanate (IPDI) has been evaluated experimentally using viscosity build up method. Propellant compositions contain solid loading from 84 to 92 per cent and their two main ingredients are ammonium per chlorate and aluminum powder. This work investigates the effect of particle size distribution and shape of oxidizer on propellant slurry. Results are presented that show how broader distributions can create difficulties in process abilities and its effect on quality of composite propellant. The reaction rate constants for viscosity build up method at various shear rates (rpm) were evaluated for the same loading but different particle size distributions. The large amount of small size particles can influence the reaction rate constants at the same shear rate. The batch containing large quantities of small particles and broad distributions caused problems during curing. The particle distribution was measured using laser diffraction technique i.e. Malvern Mastersizer. The data indicates that as the quantity of smaller size particles increases the propellant slurry viscosity and burn rate changes. It has been observed that the blending of AP particles before addition to binder can reduce the variations within the batches caused due to these small particles.

Theoritical and experimental investigation of reduced smoke composite propellants

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Keywords: Reduced smoke propellant; Scavenger; non-chlorine and neutralized propellant ; Smoke density.

Tactical and technical demands of modern types of composite solid propellants focused recently on decreasing both the primary smoke concentration (by minimizing the amount of solid particle as metal oxides and carbon soot) and the secondary smoke concentration (by minimizing the amount of gaseous hydrogen chloride in the exhaust plume). In this work, different compositions of reduced smoke composite propellant formulations were theoretically investigated using ICT thermodynamic program to select the propellant formulations of reduced both primary and secondary smoke that are candidate for the experimental investigation. Scavenger, non-chlorine and neutralized composite propellant formulations were prepared. Explosive and ballistic parameters were experimentally determined for the prepared samples. The densities of primary and secondary smoke were monitored in the combustion exhaust by high speed camera and thermal camera. A smoke filter device was used for measuring the primary smoke concentration while a portable gas analyzer in gas tunnel was used for determining the secondary smoke concentration. Neutralized propellant which uses magnesium instead of aluminum as a metallic fuel and HMX with ammonium perchlorate as an oxidizer secured acceptable performance characteristics as well as about 64% decrease of primary smoke concentration without secondary smoke compared with conventional aluminized composite propellants.

Progress in the development of high energy dense oxidizers based on CHNO(F)-compounds

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Keywords: high energy dense oxidizer; polynitro compounds; sensitivities; specific impulse.

Here we report about the synthesis of 15 selected compounds with positive oxygen balances Ω as potential high energy dense oxidizers. We focused mainly on carbonate derivatives, carbamates, nitrocarbamates, nitramines and tetrazoles in combination with the fluorodinitromethyl and trinitromethyl moieties. The prepared materials were characterized thoroughly using vibrational analysis (IR and Raman), multinuclear NMR spectroscopy, mass spectrometry, elemental analysis as well as DSC measurements and single crystal X-ray diffraction. In addition, the perfor-mances regarding the specific impulse Is were estimated by calculation using the EXPLO5 computer code, with heats of formation calculated at the CBS-4M level of theory, and room temperature densities obtained from pycnometer measurements. The sensitivities towards impact and friction were determined according to BAM standard methods, as well as a small scale electrostatic discharge test (OZM).

The Prout-Tompkins description of autocatalytic reactions - Problems and the Solutions

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Keywords: Reaction kinetics; autocatalytic description; Prout-Tompkins model; simplified autocatalytic description; improved Prout-Tompkins equation.

The work with high explosives, in general with materials with higher energy content, leads very quickly to the need for autocatalytic description of decomposition data. The autocatalytic behaviour shows a sigmoid change of the conversion. However, not every sigmoid change is caused by autocatalysis. There are several types of autocatalytic equations – one is the Prout-Tompkins (PT) equation. The Prout-Tompkins equation is a reaction kinetic model belonging to a series of models with a single reaction rate constant, which are favourably used in the field of reaction kinetic based thermal analyses. The PT equation was developed and published in the 1940s by E.G. Prout and F.C. Tompkins, which tried to describe reaction kinetically their observations on the thermal decomposition of potassium permanganate [1]. They recognized the autocatalytical behaviour of this decomposition and developed step by step the full autocatalytic description of the type, which is used in general today [2]. But in spite of using the full description with two reaction rate constants, they simplified the expression and kept only the autocatalytic part of the complete equation by arguing that this part is much faster than the primary or intrinsic part and determines nearly totally the conversion of the substance. This can be right, depending on the system considered. But this simplification has resulted in a lot of application problems and also in problems to formulate the model in a correct way. In this paper the problem is analysed and the viable solution will be given, which is called the improved Prout-Tompkins model. Further a lot of papers and applications can be found in literatures, which are a commingling of several concepts. These are presented also to dissolve the commingling and to foster the proper application.Please fill in (or paste) your abstract here. Use about 300 words.

Understanding the effects of blast on biological systems

Chiara Bo, Nicolas Newell, Thuy-Tien Ngoc, Ben Butler, James Wilgeroth, Jens Blazer, Spyros Masouros, Anthony Bull, Sara Rankin, Katherine Brown, William G. Proud, Andrew Philips, Alun Williams

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Keywords: blast effects; biology; biofidelic; modelling.

A signature of current conflicts is the use of buried improvised explosive devices to cause injury to military personnel and damage to their vehicles. Explosive devices also cause injuries to non-military populations and mines in former zones of conflict also cause on-going casualties. The nature and placement of the explosive charge has a marked effect on the loading experienced. In all situations damage to tissues occurs when the energy and loading rate exceeds that which the human body can support. Currently, it is difficult to isolate the various time-dependant effects of blast injury because of the complexities of the rapid initial accelerations, the loading geometries, and the heterogeneous nature of the tissues that can be damaged. In this paper a series of experimental scenarios are discussed which are used to isolate the rate-dependencies of the blast-loading process. This is followed by presentation of initial results and an outline of the ways in which one may study how explosive energy interacts with biological systems. Several principle conclusions emerge: the strain-rate behaviour of cells and tissues displays marked rate dependence; and differential cellular damage can be observed in complex tissues.

Influence of pulsed electric fields in the shock and shock-wave sensitivity of some condensed explosives

Valery Borisenok, Vasheslav Bragunetz, Vladimir Simakov, Alexander Mikhailov, Anna Sirotkina

Sarov Physics-Technical Institute-Branch of the National Research Nuclear University
Russian Federal Nuclear Center

Keywords: condensed explosive; electric field; the shock and shock-wave sensitivity; electric model of detonation.

Some aspects of the "electric" model of detonation and results of pulse electric field on sensitivity of superfine PETN and shock-wave sensitivity of flexible HMX are presented.

The influence of aluminum particle size on combustion parameters of model compositions with nitramines

Anatoly Bragin, Konstantin Monogarov, Yuri Frolov, Nikita Muravyev, Aleksey Zhigach, Ilya Leipunsky, Michael Kuskov, Elena Afanasenkova, Nadejda Berezkina

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Keywords: HMX; ADN; aluminium nanoparticles; flow-levitation method.

Abstract: Nitramines HMX and ADN are widely used in modern solid propellants as well as aluminium powder. The size of the aluminium particles affects propellant combustion parameters, such as burning rate and pressure exponent in burning rate dependency. This work investigates the effect of various aluminium particles (micro-, nano-, and ultrafine-sized) on the combustion of model binary compositions, i.e., HMX/Al and ADN/Al. Aluminium nanoparticles with two types of functional coatings were synthesized by the flow-levitation method with hexamethyl-disilazane (trimethyl-siloxane) and thin oxide coatings. Some nanocomposites were fabricated during nanoparicle synthesis in one technological step, i.e., suspension atomization drying. To mix aluminium nanoparticles and particles of nitramine (i) dry mixing and (ii) method of sonification in liquid were applied. Scanning electron microscopy is used to characterize the mixing quality and homogeneity rate. Results reveal the optimal combustion parameters (highest burning rate and lowest pressure exponent) for Al/HMX compositions with nanosized aluminium with thin oxide coating. Keywords: HMX; ADN; Aluminium nanoparticles; flow-levitation method

A novel energetic material, from theory to practice

Christopher H. Braithwaite, Phillip D. Church, Robert Claridge, Phillip R. Ottley, Ian M. Lewtas, Nigel Harrison, Peter J. Gould, Andrew P. Jardine

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Keywords: Powdered metals; novel materials.

The use of a novel energetic material is profiled, from the underpinning physics, through small scale testing to a systems implementation. This represents an informative progression and demonstrates the importance of both understanding the basics and maintaining an idea of the final goal of research.

Approaches to the prediction of the non-ideal detonation characteristics of condensed phase explosives

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Keywords: non-ideal detonation; steady state detonation modeling; heterogeneous explosives; blasting.

The detonation characteristics of classes of energetic media that include both heterogene-ous secondary and tertiary explosives cannot be readily predicted purely with thermo-mechanical theory. The detonation physics of these media show a dependency both on charge diameter and confinement and this manifests itself in curved shock fronts, limiting critical diameters and detonation velocities significantly less than Chapman Jouguet esti-mates. A variety of approaches have been taken in the past to predict non-ideal detonation behaviour ranging from computationally expensive direct numerical simulations, detona-tion shock dynamics and cruder estimates based on slightly divergent flow. In this paper we report a method based on a streamline analysis for steady state detonations in rate sticks that allows fast computations but with little loss of accuracy compared with a full numerical simulation.

Determination of diphenylamine on initial thermal decomposition of single based propellant by using HFC

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Keywords: single based propellant; thermal decomposition; HFC.

In the present study were examined nitrocellulose propellant, which were obtained in different processes of removed the volatiles compounds. The volatiles compounds (water, ether diethyl and ethyl alcohol) were introduced in process of formation a powder dough. Studies was performed using a heat flow calorimeter (HFC) in temperature 90°C. For analysis were used a dependence on normalized heat versus time. It has been shown that in the first stage, the heating effect is controlled by the reaction of diphenylamine. The dependence between constant of generated heat and concentration of DPA were determined. The obtained results indicate that the water content have the more destabilizing effect than ethyl alcohol. The proposed method allows for assessment of the safety risks associated with the rate of reaction DPA and decomposition products of propellant, which have properties of catalytic decomposition.

Igniter examination utilising a modified closed vessel

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Keywords: igniter; closed vessel.

Ignition systems used in torpedo systems are typically made up of a combination of a propellant start grain and an igniter. The igniter contains a fuze head, a pyrotechnic composition and gunpowder pellets. In manufacture, ballistic assessment of the start grain and the igniter is carried out on the pair. However, until recently no tool allowed the assessment of this specific igniter. Assessment of the igniter design identified several potential fail modes. On ageing, deterioration of the fuze head or air/moisture degradation of the pyrotechnic and gunpowder compositions may lead to a misfire. It was felt that in order to assess the igniter performance throughout the life of the weapon a tool for the examination of the igniter was needed.

In this paper we will describe a method developed for the examination of the igniter in isolation by use of a modified a closed vessel (RARDE 80cc vessel) to accept the complete igniter assembly. Firing programmes using aged and out of service items were developed. Once the firing parameters were established, in-service igniters were fired and a satisfactory firing profile was compiled. This firing profile allowed assessment of the performance of the igniter during annual routine surveillance. Parameters such as time to ignition, rate of pressure increase and total pressure are used to assess performance. The initial fears that air/ moisture degradation of the pyrotechnic composition that would prevent the igniter from functioning for the required service life have not been realised. During routine surveillance, this tool has has demonstrated that the pyrotechnic and gunpowder compositions have not been adversely affected to the levels initially thought and this has increased confidence that the igniters in storage and service will be suitable for service in the future.

New polynitro alkylamino furazans

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Keywords: EM synthesis; heterocycles; 2,2,2-trinitroethyl; 2-fluoro-2,2-dinitroethyl.

New energetic compounds have been synthesized which consist of 1,2,5-oxadiazoles substituted with polynitro alkyl amines. The 2,2,2-trinitroethylamino- containing compounds are 3-(4-((2,2,2-trinitroethyl)amino)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5-amine (LLM-199), N4,N4”-bis(2,2,2-trinitroethyl)-[3,3’:4’,3”-ter(1,2,5-oxadiazole)]-4,4”-diamine (LLM-204), and 4”-nitro-N-(2,2,2-trinitroethyl)-[3,3’:4’,3”-ter(1’,2’,5’-oxadiazol)]-4-amine (LLM-206). N3,N4-bis(2-fluoro-2,2-dinitroethyl)-1,2,5-oxadiazole-3,4-diamine (LLM-208) replaces a nitro group with a fluorine atom. These new materials have been treated with acetyl nitrate to afford the acyclic nitramines N,N’-([3,3’:4’,3”-ter(1,2,5-oxadiazole)]-4,4”-diyl)bis(N-(2,2,2-trinitroethyl)nitramide) (LLM-211) and N,N’-(1,2,5-oxadiazole-3,4-diyl)bis(N-(2-fluoro-2,2-dinitroethyl)nitramide) (LLM-209). New materials have been subjected to small-scale safety testing and their responses to impact, friction, and electrostatic discharge have been measured along with thermal stability testing (CRT). Chemical structures have been determined by spectroscopy and single crystal x-ray diffraction. Syntheses up to the 10 gram scale have been carried out and material detonation properties and Isp have been predicted relative to HMX. The syntheses, reactivity and relative thermal stability of these new compounds are discussed.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-ABS-608693

Novel energetic hexaazaisowurtzitane derivatives bearing nitro and azido

Kai Dong, Yuan Wang, Xubin Gong, Jing Zhang, Chenghui Sun, Si-Ping Pang

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Keywords: hexaazaisowurtzitane derivatives; synthesis; characterization.

Novel hexaazaisowurtzitane-based energetic derivatives bearing both nitro and azido group, 2,6,8,12-tetranitro-4,10-bis(azidoformoxyl)-hexaazaisowurtzitane(TNBAFIW) and 2,4,6,8,12-pentanitro-10-azidoformoxyl-hexaazaisowurtzitane(PNAFIW), have been synthesized and well characterized by IR and NMR(1H,13C) spectroscopy, Mass spectrum(MS) and differential scanning calorimetry (DSC). Their key properties such as melting and decomposition temperatures, densities, detonation pressures (P) and velocities (D) were measured or calculated, which indicated a good combination of moderate detonation performance and high stability.

The synthesis and characterization of 1-hydroxy-5-aminotetrazole and highly energetic azo-bis(1-hydroxy-tetrazole) and their ionic derivatives

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Keywords: tetrazoles; N-oxides; explosives; crystal structures; performance.

In this contribution we report on the synthesis and characterization of energetic materials based on 1-hydroxy-5-aminotetrazole (1, which is obtained by the reaction of cyanogen bromide and hydroxyl amine. Oxidation with potassium permanganate yielded dipotassium 5,5´-azo-bis(tetrazole-1-oxide) which is stable up to temperatures of 280 °C. Protonation yielded highly energetic 5,5´ azo-bis(1-hydroxytetrazole) (2). This compound was reacted with several nitrogen-rich bases such as ammonia, hydrazine, hydroxylamine, and triaminoguanidine etc. to form energetic ionic derivatives with excellent properties as additives for explosive and propellant formulations. All derivatives were characterized by low temperature X-ray diffraction, NMR and vibrational spectroscopy, elemental analysis and differential scanning calorimetry. Heats of formation were calculated by CBS-4M electronic enthalpies. Detonation and propulsion data were computed by the EXPLO5 code. In addition, all sensitivities towards impact (BAM drophammer), friction (BAM friction tester) and electrostatic discharge (OZM electrostatic discharge tester) were determined. Keywords: explosives; tetrazole-oxides; crystal structures; energetic materials

Boron combustion in propulsion systems

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Keywords: boron; combustion; ramjet; high energy fuel.

Boron exhibits outstanding theoretical heat of combustion when burning with air, about 40% higher on a gravimetric (mass) basis and about 3 times higher on a volumetric basis than hydrocarbon fuels. Hence, it is particularly attractive for air breathing propulsion systems such as ramjet engines. Boron theoretical energetic contribution in rocket propulsion is not as dramatic. In fact, it is inferior to that of aluminum additives. This paper will focus on the use of boron in air-breathing systems. Realization of the theoretical heat of combustion of boron is very difficult because of a number of reasons, including need to achieve very high temperature to sustain combustion in order to evaporate the protective boron oxide layer forming on the particle surface, "trap" of energy in products formed in less energetic reactions, loss of energy in gas-phase boron oxide, and blocking of reaction due to saturation of boron oxide vapors. These aspects are elaborated in the article.

Realization of power pulse illuminations in aeroballistic and hydrodynamic researches

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Keywords: shock waves; generator of shock wave; shadowgraph; shock-compressed xenon; brightness temperature.

Description of classical Voitenko compressor by means of which it is possible to achieve high experimental brightness temperatures correspond to shock-compressed gas temperatures is given. Analytic model of the explosive gasdynamic compressor on the basis of which its small-size version has been developed is presented. The phenomenon of the brightness temperature saturation is discussed. A possibility to obtain the radiation flux correspond to real temperatures behind strong shock in gases is shown. The method described allows one to realize a powerful short light source for s serious of applied purposes, for example, in obtaining data in aeroballistic and hydrodynamic experiments.

Shadowgraph technique and optical initiation for study of solitary longitudinal waves

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Keywords: soliton; shadowgraph; optical initiation; pyrotechnic photosensitive composition.

The problems related to propagation of longitudinal non-linear strain waves in elastic rods and their further reflections are described. We present an improved method for simultaneous generating solitons in several samples using multipoint optical initiation by a non-coherent light source. Recording the waves by means of shadow methods is discussed.

Strength and fracture of energetic materials under shock wave loading

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Keywords: energetic material; shock wave loading; spall fracture; strength; durability.

Various energetic materials are widely used in weapon and aerospace structures since they allow realizing the rapid release of a large amount of energy for a short time. Such energy materials as explosive formulations and propellants can also partially carry out a role of structural materials taking up certain static and dynamic mechanical loads. A detailed knowledge of their relevant mechanical properties is necessary to predict the behavior of structural components under such loads. For the structures exposed to the action of shock wave loading, an important mechanical property is the resistance of a material to spall fracture that is defined by the spall strength and the limiting spall durability to complete fracture. The quantity of published works dealt with determination of spall fracture conditions for energetic materials is rather restricted. In this paper a quite complete overview of works fulfilled on this theme by the author and some other researchers is presented. They are first of all results obtained on spall fracture of a number of explosive formulations on the basis of RDX, HMX and PETN. In this case the samples in the form of disks of various thicknesses were loaded by impact of steel and aluminum plates. The character and level of samples fracture were estimated visually, and the conditions of shock wave loading were determined as a result of elastoplastic calculations. The equations of state and elastoplastic properties of formulations were determined using experimental results on recording the process of shock wave loading in samples. Thus the dependences of the spall durability as the critical negative pressure resulting in complete spallation on the velocity and thickness of an impacting plate and the thickness and initial state of a sample were obtained. The influence of preliminary normalization of samples and reinforcing of formulations with fibrous filler on spall fracture conditions was revealed. Results on temperature effect in spallation of several explosive formulations were obtained too. Moreover, the results on determination of the spall strength as the critical tension stress resulting in initial spallation were considered for several explosive formulations and propellants. For all the materials being heterogeneous by structure, the considerable difference in values of critical loads corresponding to initial and complete spallation was noted. The kinetic continuous models of spall fracture making it possible to explain this distinction are presented. Some common tendencies characteristic for all considered energetic materials are revealed.

Biodegradation of nitroglycerine and ethylene glycol dinitrate by free and immobilized cells

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Institute of Chemical Technology in Prague
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Keywords: nitroglycerine; ethylene glycol dinitrate; biodegradation; mixed culture; free and immobilized cells; packed bed reactor.

Aerobic biodegradation of nitroglycerin (NGL) and ethylene glycol dinitrate (EGDN) individually, and in the mixture by free cells was investigated using batch cultivations. A mixed culture isolated from soil and sediments of a long-term contaminated area of the Explosia Pardubice plant was used as a catalyst. Effects of pH, temperature and additional energy sources e.g., pyruvate, glucose and glycerol, on a degradation ability were tested. Also a preliminary degradation of NGL in a packed-bed reactor with immobilized cells was carried out. NGL was found to be degraded by our mixed culture, but EGDN just in a presence of a cosubstrate. Cells were able to degrade NGL, with maximal degradation rate of 60.9±4.1 $mg.g_w^{-1}.h^{-1}$ at the starting concentration of 30 $mg.L^{-1}$. Exceeding this concentration resulted in an inhibitory effect on the cells. A presence of EGDN in a mixture with NGL had negative impact on the NGL degradation rate. EGDN was not degraded at all, but in a presence of pyruvate or glycerol as the cosubstrate. A presence of the cosubstrates (100 $mg.L^{-1}$) increased the degradation rate of NGL of 17 % with pyruvate and of 11 % with glycerol. An addition of glucose caused a drop of NGL degradation rate of 4 %. However, presence of higher concentrations of all cosubstrates of 500 $mg.L^{-1}$ had a negative effect on a degradation of NGL. NGL also was efficiently degraded in a continuously operated packed bed reactor with hydraulic retention time of 90 min.

Silicon based energetic materials

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Keywords: porous silicon; energetic material.

In the past few years, experiments carried out in the US, Germany, and others have indicated feasibility for an energetic reaction of nanoporous silicon impregnated with an oxidizer. Nanoporous silicon is an inert material that can be fabricated by anodization of silicon in a highly concentrated hydrofluoric acid solution. The inert nanoporous silicon structure can be transformed into an energetic material by impregnation of a dissolved oxidizer into the nanopores. The process creates a mixture of a fuel (silicon) and an oxidizer in an almost molecular level, due to the unique nanoporous structure of the silicon. This type of energetic material has unique advantages for multiple possible applications. Most importantly, the fabrication process of the nanoporous silicon based energetic material is compatible with MEMS fabrication techniques, enabling manufacturing of the energetic material as an integral element of a MEMS system.

In our research, nanoporous silicon was fabricated by electrochemical etching using different electric current densities. The nanoporous structure was characterized via HRSEM and nitrogen porosimetry. The specific surface area, pore size, porosity and pore depth were greatly affected by the electric current density applied. Most significantly, the pore depth increased by a factor of three, when increasing current density from 20 mA/cm2 to 80 mA/cm2. The nanoporous silicon samples were impregnated with sodium perchlorate oxidizer dissolved in methanol. The impregnation method was optimized to achieve a filling factor as high as 42%. Feasibility proof for an energetic reaction of nanoporous silicon samples impregnated with sodium perchlorate oxidizer was demonstrated by a thermal analysis (DSC) and by ignition of the samples on a hot plate. The DSC plots of the impregnated samples showed two unique exothermic reaction peaks corresponding to the energetic reaction of nanoporous silicon with the oxidizer. All samples were instantly ignited on a hot plated a-priori heated to temperatures above 300°C.

Changes of chemical and mechanical properties of double base propellants over artificial ageing

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Keywords: double base propellant; artificial ageing; nitrocellulose; mechanical properties; weight average molar mass; size-exclusion chromatography.

Solid propellants are the part of an armament that is most liable to ageing processes. The most remarkable factor of ageing of double-base propellants (DB propellants) is temperature whereas increase of temperature by 10 °C causes around 2.9 times increase of the rate of chemical decomposition and the main role in the ageing act nitrocellulose (NC). Over ageing are not only split off radicals NO2 even at room temperature due to low activation energy of O-NO2 bond, but also cut chains of NC which means reducing of average molar mass. The lowering of average molar mass of linear polymer leads to lowering mechanical strength and to changes in other mechanical properties. The paper shows results of an experiment that was performed on propellants consisting of nitrocellulose, nitroglycerine and dinitrotoluene (DNT) and its alternative with replaced DNT by other plasticizer. Grains of propellants were artificially aged at 65 °C and 80 °C for a period corresponding to 5, 10, 15 and 20 years of storage at 25°C. Molar mass distributions of samples NC were determined by size-exclusion chromatography. Mechanical properties of DB propellant were investigated by dynamical mechanical analyses and uniaxial compression and tensile tests. From the results we obtained the value of activation energies of scission of NC chain in investigated temperature interval for two types of DB propellant. It is 85 kJ.mol-1 and 105 kJ.mol-1. We also analysed relationship between changes of average molar mass and surveyed mechanical properties.

Preparation and characterization of n-butyl-N-azidoethyl nitramine

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Keywords: azidonitramine; plasticizer; azidation; phase transfer catalyst; ultrasound.

The paper is focused on n-butyl-N-azidoethyl nitramine (BAENA), potential energetic plasticizer for gun or rocket propellants. Three alternative synthetic methods, azidation in polar aprotic solvent, azidation in presence of phase transfer catalyst and azidation supported by ultrasound, were compared in view of usefulness and product quality. Analysis of the product was conducted with the help of thin layer chromatography, high performance liquid chromatography and infrared spectroscopy. Chemical and physical characteristics of BAENA related to its potential use were determined.

Dinitroguanidine and some its derivatives as compounds of solid composite propellants

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Keywords: solid composite propellants; dinitroguanidine; oxidizers; binders; specific impulse.

During a few last decades lot of new energetic compounds have been synthesizing, but most of them have been considered as explosives only, not as compounds for solid composite propellants (SCP). A rather narrow set of compounds has been used as main compounds of SCP, i.e. AP, HMX, ADN, finally CL-20. As energetic potential of SCP basing on these compounds is almost limited, one should study the possibilities to find principally new effective compounds that are not synthesized yet, as well as we has to reconsider all listing of known substances to find those that may be useful as effective compounds. The paper is considered to energetic abilities of dinitroguanidine (DNGu) and some of its salts (hydrazonium and hydroxylammonium). DNGu is a rather accessible substance with zero enthalpy of formation. Energetic parameters of DNGu have been studied by applying DNGu not only as the main oxidizer, but as component of binary oxidizer in mixture with another one having higher α value (by the same manner as HMX is applying in mixture with AP). Being considered as the main oxidizer DNGu is compared with AP and ADN, while being considered as the second oxidizer DNGu is compared with HMX. Three kinds of binder have been considered, and aluminum and its hydride have been considered as energetic compounds. It was shown that in metal-free formulations DNGu shows energetic potential higher than AP does and almost equal to ADN. In formulations with aluminum hydride and active binder DNGu shows higher potential than AP and a bit lower than ADN do. As second oxidizer DNGu is a bit less energetic than HMX. Monohydrazonium and monohydroxylammonia salts of DNGu are not effective as main oxidizers and they are less effective than HMX as the second compounds of binary oxidizer.

New methods for the synthesis of 5-nitrotetrazole-2-N-oxides

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Keywords: synthesis; nitrotetrazole; N-oxidation.

Two efficient procedures for the preparations of 5-nitrotetrazole-2-N-oxide salts were presented. 5-Nitrotetrazole-2-N-oxide anion can be prepared through 5-nitrotetrazole salts by the oxidization of Oxone and H2O2 at different temperature. The last approach provides convenient green access to 5-nitrotetrazole-2-N-oxides, which are difficult to prepare using existing synthetic strategies. Sodium 5-nitrotetrazole-2-N-oxide monohydrate and sodium 5-Nitrotetrazole-2-N-oxide dihydrate crystallize in the Orthorhombic space P2(1)2(1)2(1) group and the Monoclinic space P2(1)/n group, respectively, as determined by single-crystal X-ray diffraction. Their densities are 1.897, and 1.993 g•cm-3, respectively, much higher than that of sodium 5-nitrotetrazole dihydrate (1.731 g•cm-3). Moreover, the N→O bonds of the two structures are entirely different.

Self-synchronization of the magneto-dipole micro/nano- structures in the reactionary zones and concept of the smart solid micro-propulsion system

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Keywords: reactionary zones; liquid-viscous layer; magneto-dipole micro-structures; collective interaction; self-organization & self-synchronization; unsteady combustion.

For more than ten years, solid micro-propulsion has been an active world-wide field of research. In the combustion chambers of the solid micro-propulsion systems of the small-sized orbital maneuvering vehicles, the scale factor has the significant influence. In this connection, the micro/nano- structures arising in the energetic material reactionary zones has a large influence on physical and chemical processes and on controllability of ignition and combustion processes. The analysis of experimental data shows that in a number of cases, the macro-scale phenomena at the energetic material combustion are result of self-synchronization of the magneto-dipole micro/nano- structures in the reactionary zones. In the paper the new hypothesis of excitation of some combustion instabilities, that are connected with self-synchronization of the magneto-dipole micro-structures in the reactionary zones is suggested. This hypothesis is supported by the experimental data provided by Jap-anese research team. This data has been obtained during study of oscillation and synchronization in the simple experimental system, containing a set of paraffin candles. Discovered in the 17th century by Christian Huygens, self-synchronization was observed in physics, chemistry, biology and even social behaviour, and found practical applications in engineering. This phenomenon are universal and can be understood within a common framework based on modern nonlinear dynamics. The new possibilities for effective control by ignition and combustion processes opens in connection with possibility of initiation of self-organizing of the reactionary zone by use of the electric fields and the electric discharges. Self-organizing of the reactionary zones is essentially new level of self-organizing which is determined by achievement of critical spacial concentration of the micro/nano- structures. In particular, application of an electric field, changes the burning surface roughness, i.e. modifies the process of excitation of the micro/nano- structures in the reactionary zones. The new concept of the smart solid micro-propulsion system includes inte-gration of the propellant reactionary zones both into the control system by combustion mode, and into the general control system of the small-sized orbital maneuvering vehicle.

Study of surface treatment for improvement in the interaction of RDX with TNT through ETPE pre-coating

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Keywords: interaction; surface-treatment; ETPE; RDX; TNT; SEM; XPS.

To improve the interaction of cyclotrimethylenetrinitramine (RDX) with 2,4,6-trinitrotoluene (TNT) in TNT-based explosive formulations, an energetic thermoplastic elastomer (ETPE) bearing trinitrobenzene similar to TNT was chosen to coat RDX by combining the solvent- nonsolvent and the aqueous suspension-melting method, based on its solubility in ethyl acetate. Scanning electron microscope (SEM), X-ray photoelectron spectrometry (XPS) and Optical microscope (OM) were employed to characterize the samples. The impact sensitivity, friction sensitivity, and the thermal stability of unprocessed and coated RDX were investigated. Results indicated that when melted the PVTG with other two binders, it was interestingly found that F2314 enhanced the coating degree of PVTG but Estane decreased the coating effect. There was a gain in friction insensitivity and impact insensitivity in RDX with PVTG/F2314 coated material due to its better coating degree. However, there is merely a small increase in exotherm and thermal decomposition temperature in the coated materials.This study could be useful for design and preparation of new ETPEs applied in PBX or melt-cast explosives.

Thermal decomposition mechanism of ammonium dinitramide using pyrolysate analyses

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Keywords: ammonium dinitramide; solid propellant; thermal decomposition mechanism.

Ammonium dinitramide (ADN) is one of the promising new solid propellant oxidizers because its oxygen balance and energy content are high, and ADN does not contain halogen atoms. One of the characteristics needed for solid propellants is chemical stability. For practical use of ADN as solid propellants, it is necessary to clarify aging behavior; decomposition mechanism, kinetics and performance decrease. In this study, to get a better information about thermal decomposition mechanism of ADN, its exothermal behavior and thermal decomposition products during constant rate heating were measured simultaneously using combined instruments. The results of these analyses showed that the decomposition of ADN occurs via multiple stages in the condensed phase.

Reactive nanolaminates with tailored energy yield

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Keywords: thermite; multi-layers.

Multi-layer nano metal-oxide/metal thin films have the potential to augment and improve existing energetic materials used in the military and industry. Here we report on a series of reactive oxygen exchange nanolaminates between an oxygen source, CuO, and a reactive metal oxygen sink where the propensity for energy release is tailored by material selection and by multilayer geometry. These results suggest it is possible to create a class of energetic materials whose yield can be tailored for specific applications. In one set of experiments we demonstrate that by considering anion transport in the terminal oxide, we can produce multilayers that are unstable at room temperature, or those which require substantial thermal energy to ignite. We first explored this terminal phase hypothesis by comparing CuO-metal laminates with the reactive metals: Mg, Zr, and Al. The nanolaminates were exposed to rapid furnace anneals and subsequent x-ray diffraction to identify the onsets of oxygen exchange. Zr-CuO laminates were the least stable, owing to the fast oxygen transport through the ZrO2 terminal oxide, while CuO-Al laminates were the most stable, owing to the excellent diffusion barrier properties associated with Al2O3. CuO-Mg exhibited intermediate stability.. In a second set of experiments we explore how geometry can be used to regulate the exothermic exchange reactions. For the reactive laminate systems of CuO-Al, CuO-Zr, and CuO-Mg, we prepared sets of multilayers of constant total thickness, but where the individual layer thicknesses are varied such that the number of metal oxide interfaces range from1 to 7. Using ex-situ x-ray diffraction and rapid furnace anneals, we identify that the minimum temperature needed to initiate the reaction drops in all cases on the order of 200°C as the number of interfaces increases. Calorimetry data for these samples show multiple exotherms that exhibit thickness-dependent temperatures. The exotherms can be attributed to the oxygen exchange from CuO and Cu2O to the reactive metal. The magnitude of the Cu2O exotherm and its temperature are strongly dependent upon the number of interfaces. Finally, we demonstrate that an applied voltage can be used to joule heat the electrically conductive laminate constituent and initiate the exothermic oxygen exchange. In all cases, small applied voltages could initiate the reaction. X-ray diffraction and optical images reveal that such reactions occur homogeneously over sample areas greater than 20 cm2.

Impact of ageing on the loss factor of composite rocket propellants and interpretation of changes considering post-curing

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Keywords: ageing; composite rocket propellants; dynamic mechanical analysis; modelling of loss factor; non-destructive monitoring of ageing; curing study.

Accelerated ageing of HTPB-based composite rocket propellants (CRP) changes the me-chanical properties like Young's modulus, tensile strength and the glass-to-rubber transi-tion region. The methodology introduced by Bohn and Cerri [1, 2, 7] of studying the loss factor by DMA (dynamic mechanical analysis) as function of measurement temperature is used to analyse micro-molecular effects due to ageing. Base of the methodology is to fit experimental loss factor curves with so named exponentially modified Gauss (EMG) dis-tribution functions in order to separate the regions with different molecular mobility, as mobility unrestricted binder, the increasing cross-linking in the binder matrix, and the mo-bility hindrance in the polymer shell around the filler particles. The data base was in-creased by manufacturing and testing several further CRP. The typical ageing trend has been found again. The analysed propellants show at least two typical obvious glass transi-tion regions and one more or less hidden transition region. By modelling the loss factor curve, it is possible to localize such transition regions, where ageing shows the main im-pact on the mechanical behaviour of the material. DMA technology is also used to analyse post-curing effects. The HTPB-based formulations were cured by isophorone-diisocyanate which has two NCO groups of different reactivity. It is normally not possible to complete curing during the mostly used curing conditions of 3 to 6 days at 60°C. Post-curing is in-evitable during the in-service times. One objective of this work is the separation of post-curing from ageing using the results of curing studies obtained by microcalorimetry and by pressure courses in closed pressure cells. This separation is necessary to validate the methodology of non-destructive monitoring of the ageing of rocket motors by measuring bondline stresses with special sensors embedded in the rocket motor. Keywords: Ageing of composite rocket propellants; dynamic mechanical analysis; model-ling of loss factor; non-destructive monitoring of ageing; curing study;

Aging study and structural analysis of solid fuel loaded in composite casing under operating pressure and vertical storage condition for service-life prediction

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Keywords: solid fuel; viscoealsticity; aging; storage slump; service-life.

Composite material casing is frequently used for various size solid fuel systems particularly for reducing inert mass. A composite shell is observed to exhibit a higher order strain and deformation as compared to steel casing under same pressure loading. Structural integrity analysis of the solid fuel encased in a composite shell under applied loading conditions is necessary for the system's operational and service life assessment. This work presents prediction of deformation strain and stress of HTPB based solid fuel structure encased in composite shell under operating pressure and due to environmental aging during vertical storage condition. Furthermore, the same naturally aged solid fuel structure is compared with the unaged one under similar loading conditions for aging effects study. Viscoelastic mechanical properties of the unaged and aged solid fuel are determined by DMA and used for finite element analysis. Simplified orthotropic fitting properties of com-posite casing were assumed such that the predicted deformation from finite element analysis and that from a series of hydrotests were comparable. Based on this, finite element analysis for structural integrity of the solid fuel structure was performed. The solid fuel has axisymmetric cylindrical geometry satisfying all the ballistic mission requirements making it suitable to consider longitudinal cross-section of the solid fuel geometry for analysis. Long term vertical storage thermo-mechanical degradation was analyzed considering the storage environment thermal effects juxtaposed with 1-g vertical load on the solid fuel. Inner bore strain and outer bore bond-line stress on the solid fuel structure were evaluated as degradation indicators. Magnitude of the stresses at various times was considered to calculate the cumulative stress and hence the overall damage induced in the solid fuel structure. Linear damage rate is calculated from these results, which is used to predict the service life of the system.

Production of activated metal powders as potential energetic materials

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Keywords: metal powders; ignition.

There is an interest in low cost technologies as well as higher performance novel energetic materials, in particular synthesis of energetic ingredients for application to explosives, propellants and pyrotechnics. Some examples of areas of interest include nano-sized energetic metals and activated metal powders. There are many advantages in incorporating activated metal powders, including nano-size metal powders, into fuels, propellants, and pyrotechnic compositions such as: shorter ignition delay and burn times, and enhanced heat-transfer rates from the surface area. This paper presents some results regarding processing and characterization of activated and nano-size metal powders. One possible approach to the development of activated metal powders consists of a modification of the surface layer of the metal to improve its reactivity. Coating of aluminum particles by nickel and iron has been suggested for enhancement of oxidation and ignition of aluminum powder in air. Investigations of the behavior of the coated Al particles during their heating in air were carried out. Experiments demonstrated better ignitability of the coated Al particles in comparison with regular Al particles. It has also been demonstrated that during ignition in air the coated aluminum particles exhibit reduced agglomeration in comparison with regular Al particles. Other possibility to get the high-reactivity metal powders is to increase their specific reaction surface. Nanosize metal powders with particle smaller than 0.1 μm may be good candidates as fuel components because of their high reactivity and short ignition time due to the large reaction surface. In this work a specific technology was used for the production of nanosize metal powders. Study of the ignition behavior of these powders revealed their very high reactivity and shorter ignition times in comparison with corresponding coarser (>1 μm) metal powders. The other approach is production of the porous metal powders with a large surface of reaction. 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 m2/g). Study of the ignition behavior of the highly-porous aluminum powders with mean particle size of 10 and 25 μm revealed their very high reactivity and short ignition time, comparable with that of nano-scale aluminum powders.

Reflected and negative phase airblast energy measurements

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Keywords: airblast; energy; reflected; negative phase; surface burst.

The total energy contained in the positive phase of propagating airblast waves has recently been established as a measurable parameter by analyzing field test Pressure versus time curves. Airblast energy data from free- air and surface explosions are now readily obtainable. The airblast energies observed compare favorably with the total detonation energy. Due to energy losses, the data demonstrate that the airblast energy decays with increasing distance from the explosion. When a high characteristic impedance surface such as a concrete wall is loaded by airblast, we have the status of a reflected wave. Utilizing similar procedures as used in the free-air and surface burst energy determinations, one thus obtains the energy based on the reflected airblast wave. The reflected airblast parameters measured vary over the surface of such a wall depending on the location of the measurement point relative to the ground and sides. Similarly, we present the energy of the negative phase of free air, surface burst and reflected airblast waves.

Mechanical properties study of toughened and modified melt-cast TNT based explosive formulations for anti-cracks and brittleness

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Keywords: TNT; melt-cast explosive; composition B; crack; brittleness; toughness.

Melt-cast explosives often have poor mechanical properties and exhibit cracks, exudation, voids or brittleness. Especially, the exhibition of brittleness and cracks can affect the mechanical and detonation properties of melt-cast explosives based munitions, and restrain the application in high-performance weapon systems. Thus the defects in TNT based melt-cast explosive are analyzed. The concept of "Toughening and Elasticizing of Melt-cast explosive" may become one of the directions in the study of melt-cast explosive, (i) research on the melt-cast explosives modifier mainly aiming at oil saturation and sensitivity reduction, in which the problem of brittleness and cracks has not been solved yet; (ii) employ toughening techniques of other composites in the melt-casting process of composition B, such as toughening and elasticizing techniques of nanoparticles and polymer materials; (iii)study the mechanical properties after blending and casting through designing and preparing the modifiers comparable to melt-cast explosives, start to establish the model and mechanism of toughening and elasticizing melt-cast explosives. Recent study of our group is introduced. Nanoindentation and scanning electron microscope (SEM) method were employed to analyze the brittleness of TNT, through indentation test of the large crystal of TNT and RDX, mechanical properties such as compressive modulus and stiffiness were calculated from load-deformation curves. The results indicated that indentation hardness and modulus of TNT are lower than RDX, while residual depth and maximum damage boundary of it were larger than RDX. Influence of additives (sulfide nitrile rubber, organic and inorganic fibers, etc.) on tensile strength, fracture strength and compressive intensity of composition B was investigated. It was shown that sulfide nitrile rubber nanoparticles have better effects on enhancing the elastic behavior of composition B, and glass fibers could reinforce the toughness.

Impact sensitivity investigations of individual explosives: Some experimental and calculating approaches

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Keywords: sensitivity; estimation.

Experimental data of impact and friction sensitivities of energetic materials were generalized for more than 140 individual substances from different chemical classes. The results of structure-chemical composition and sensitivity relationships were analyzed and the corresponding equations to calculate the basic characteristics of sensitivity of explosives to different kinds of impact were elaborated. The high accuracy of the developed methodology was achieved in computations of sensitivity parameters.

The 1,3-bis(5-amino-1*H*-tetrazol-1-yl)triaz-1-en-1-ium cation ($C_2H_6N_{13}^+$): A highly nitrogen-rich moiety with a N_{11} chain

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Keywords: N11; energetic; tetrazole; N-azo; nitrogen-rich compound.

A novel high-nitrogen energetic salt containing the longest nitrogen chain (N11), was obtained by N-azo coupling reaction from 1, 5-diaminotetrazole. The rare chain of 11 nitrogen atoms in this compound was confirmed by X-ray crystallography, and the physical and explosive properties of the title compound were characterized.

Identification and effects of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) as an impurity in RDX and HMX

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Keywords: BSX; RDX; Bachmann process; nitration; stability; nitration products.

In the preparation of RDX by the interaction of hexamine or hexaminedinitrate, fuming nitric acid, ammonium nitrate, and acetic anhydride, a low melting linear side product BSX (Figure 1.) formed. The aim of this study is to identify 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) as a side product of RDX synthesized by Bachmann process and to investigate the thermal and spectroscopic differentials on RDX and HMX. BSX was characterized by Fourier Transform Infrared (FTIR), 1H Nuclear Magnetic Resonance (1H-NMR) Spectroscopy techniques, Scanning Electron Microscopy (SEM), XRD and HPLC. Thermal characteristics of BSX were determined by using Differential Scanning Calorimeter (DSC) and Thermogravimetry/Differential Thermal Analyzer (TG/DTA).

Effects of concentration and particle size on thermal explosive characteristics of fireworks

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Keywords: thermal decomposition; self heat rate; heats of reaction.

Fireworks mixtures are susceptible to explosive decompositions. The aim of this paper is to generate thermal decomposition data under adiabatic condition for ground spinner inner mixture composition, one of the sensitive fireworks mixture widely handled in fireworks industry. In this paper three different types of compositions (small, medium and large) which are different in concentration and particle size of aluminum present in ground spinner inner composition were compared. The self heat rate data obtained from Accelerating Rate Calorimeter showed vigor exothermic decomposition for all the mixtures and depended on the concentration and particle size of aluminum (666) and aluminum (999). All the three compositions showed onset of exothermic behavior at 290°C, small with a peak heating rate of 10.99 (°C/min) at 319.5°C ,medium with 20.71 (°C/min) at 329.5°C, and large with 13.83 (°C/min) at 322.2°C. The thermal run-away behavior continued with multiple exothermic activities until 449.05°C, 449.7°C and 344.1°C for small, medium and large ground spinner inner mixture respectively. A maximum of 19 bar pressure was observed for medium ground spinner inner composition. The heats of exothermic decomposition of fireworks mixture were computed.

Application of quantification of uncertainties method in detonation simulation to steven test

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Keywords: numerical simulation on detonations; quantification of uncertainties; steven impact test.

Detonation sensitivity is important index for measuring initial capability high explosive, Steven test is one of the basic tests about gauging and has greatly increased the fundamental knowledge of practical predictions of impact safety hazards. We describe a modified form of Lee-Tarver reactive flow model, Lagrange model and elastic-plasticity hydrodynamics model. It is better suited for test data. Numerical simulation has become an important means in designing detonation systems and the quantification of its uncertainty is also necessary to reliability certification. We try to apply quantification of uncertainty in detonation simulation to Steven impact test for proof feasibility of the quantifying uncertainty framework in practical problem.

The true history of CL-20

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Keywords: CL-20; history.

The true story of the conception of a caged nitramine based on amine/glyoxal chemistry is presented. A discussion of potential improvements to or alternate syntheses of CL-20 along with other potential caged nitramines is also presented.

Investigation into the interaction of dantocol in polymer bonded explosives and bonding agent development

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Keywords: 1,3-bis(2-hydroxyethyl)-5,5-dimethylhydantoin.

The call for increased safety in explosive ordnance has driven the requirement for improved design of Insensitive Munitions (IM). Cast-cured Polymer Bonded Explosives (PBXs) are often used as an approach to achieving IM compliance. Incorporation of bonding agents is often employed to improve adhesion between particulates and the binder system, however the exact mechanism by which this occurs is poorly understood. In the absence of an appropriate bonding agent, the PBX system is susceptible to mechanical failure via dewetting. This degradative process occurs when the adhesion between filler and binder is poor, causing failure under stress and allowing the binder to break free or 'dewet' from the filler surface.

One of the forerunners in bonding agent technology for nitramine based composites is the Hydantoin derivative 1,3-bis(2-hydroxyethyl)-5,5-dimethylhydantoin, known also as Dantocol. This promotes successful interaction between the filler and binder within polymer composites. Investigations revealed non-polar binder matrices applied in this process enable polar Dantocol molecules to adsorb onto the nitramine filler via secondary bonding. Subsequent reaction with the binder system produces primary bonds involving the diisocyanate curative. This reacts with free hydroxyl groups to form urethane linkages, facilitating integration of Dantocol within the binder matrix. The strength of these bonds dictates the mechanical properties of respective systems, through prevention of deformation mechanisms.

Knowledge of surface characteristics and interacting mechanisms was consequently applied to the design of novel bonding agents. Development of bonding agents focussed on improving mechanical properties of PBX's, with flow-on benefits for explosive ordnance. These advances have the potential to eliminate conjecture regarding the selection of bonding agents and provides viable alternatives for inclusion in cast-cured composite energetic materials.

Synthesis and characterization of a novel unsymmetrical azotetrazole compound with N8 structure

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Keywords: tetrazole; azo bonds; N8; N-azo coupling.

A high-nitrogen compound, 5-(dinitromethylene)-1,4-bis((-2,4-dinitrophenyl)diazenyl)-4,5-dihydro-1H-tetrazole, which can be obtained by N-azo coupling reactions from sodium 5-dinitromethyl-1H-tetrazolate with 2,4-dinitrophenyl diazonium salt solution. This type of Nitrogen-Nitrogen bonding formation provides a new pathway for discovery of novel high-nitrogen energetic compounds. The obtained compound was characterized by multinuclear NMR spectroscopy and IR spectroscopy. Its thermal stability properties were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Additionally, its theoretical performance parameters were computed.

Efficient desensitization of high explosives via energetic coating

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Keywords: core-shell structure; CL-20; HMX; TATB; coating; desensitization.

TATB was selected to investigate the energetic coating of CL-20 and HMX after surface modification. The characterization results indicate the compact coating of submicron TATB on the surface of high explosives, with the high coverage degree compared to physical mixed sample and the sample coated by normal TATB with the particle size of about 20 μm. The impact and friction sensitivity test results indicate that the preparation of core-shell composites offers an efficient route for the desensitization of CL-20 and HMX, with the crystal form of CL-20 maintained ε style by XRD analysis.

Radiometric performances of MTV and modified MTV compositions for three different wavelength intervals

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Keywords: MTV decoy flare; IR flares; radiometric property.

IR guided missiles are one of the most powerful weapons to destroy the low flying air-crafts and helicopters. In order to lure away incoming IR guided missiles, the MTV decoy flare is still used as a passive countermeasure. MTV decoy flare is a pyrotechnic composition based on Mg, Teflon and Viton with burning temperature equal to or higher than the engine exhaust. The hottest part of a military aircraft is the hot tail pipe which radiates at 1.7-3 μm wavelength interval. The middle one is the plume which radiates at 3-5 μm wavelength interval. The skin of an aircraft is the coldest part radiating at 8-10 μm wavelength interval. Classical MTV decoy flares protect an aircraft from missiles guided to its hottest part. However, they are inadequate to protect the aircraft against the advanced IR guided missiles which are able to discriminate the different temperatures or different parts of the aircraft. In this study, we use silicium, ferric oxide, calcium carbonate, graphite, boron and carbon nanotube powders as additives to MTV compositions to improve the radiometric performance of classical MTV. And, their radiometric performances are investigated between the wavelength intervals of 1.7-3 (α) μm, 3-5 (β) μm and 8-10 (γ) μm. First of all, the radiometric measurements are done for the compositions having MTV and 2% of one of these additives. It is obtained that the composition with ferric oxide leads to the highest increase in the spectral radiant intensity values for each of the wavelength intervals. Next, the radiometric performances are investigated by increasing the percentage of powders graphite, boron and carbon nanotube. Namely, the compositions of MTV and 1% to 10% of graphite powder are investigated, and the compositions with 2% of graphite results the best performance. Similarly, it is shown that the compositions with 2% of boron and 2% of carbon nanotube result the best performance among the other amounts of corresponding additive.

Synthesis, structure and thermal analysis of 3-hydrazino-4-amino-1,2,4-triazole energetic salts

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Keywords: synthesis; crystal structure; thermal analysis; 3-hydrazino-4-amino-1,2,4-triazole; energetic salts.

As a key research direction of low melting point of explosives and gunpowder, energetic salts have received a worldwide attention. 3-Hydrazino-4-amino-1,2,4-triazole (HATr) is an important high-nitrogen content compound of 73.65% with good stability. This paper has focus on the energetic salts which was built with HATr and picric acid (PA) or 2,4,6-trinitro-resorcinol (TNR). The HATr•PA and HATr•TNR single crystals were grew and their crystal structures were determined at the low temperature. Their crystal both belong to monoclinic system, P21/n space group, with the unit cell parameters of HATr•PA crystal: a=6.8928(17) Å,b=22.670(6) Å,c=8.460(2) Å,β=96.889(4)°,V=1312.41(57) Å3,Z=4. and those of HATr•TNR crystal: a=15.393(3) Å,b=5.267(1) Å, c=19.042(4) Å,β=111.794(3)°,V=1433.48(50) Å3,Z=4. The Thermal analysis characteristics of the two target compounds were investigated with DSC and TG-DTG. In addition, the non-isothermal kinetics, heat of combustion and sensitivity of the target compounds have also been investigated. The results indicated that these two compounds have certain potential application on gunpowder and propellant materials.

Researches on vapor pressure and thermal decomposition of low-melting explosives

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Keywords: low-melting explosives; vapor pressure; isothermal thermogravimetric analysis; thermal decomposition; dynamic pressure measuring thermal analysis.

Thermal decomposition of explosive is very important to evaluate the thermal stability and calculate the reaction kinetics. However, the low-melting explosive tends to volatize at high temperature, which causes the difficulty for the evolved gas analysis. Therefore, the vapor pressures of three low-melting explosives, TNT, DNTF and DNAN, were determined by isothermal thermogravimetric analysis, and the thermal decomposition processes were measured by dynamic pressure measuring thermal analysis. The net evolved gas pressure was obtained by eliminating the vapor pressure from the apparent gas pressure. TNT, DNTF and DNAN are all thermally stable, and DNAN is most stable among them. The kinetics of thermal decomposition was calculated by the universal integral and differential equation methods. The kinetic parameters and reaction mechanism of each sample changed with temperature, which suggested that the multistep reaction occurred during decomposition.

Method study about quantification of uncertainties in numerical simulation

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Keywords: Numerical Simulation; Quantification of Uncertainties.

QMU(Quantification of Margins and Uncertainties)is generically defined as a framework that captures what we do and do not know about the performance of a nuclear weapon in a way that can be used to address risk and risk mitigation. Among other things, QU (quantification of uncertainty) is the key technology when we resolve engineering questions. As to QU it is the most important to understand how the uncertainties occur and develop when simulations are exerted on from benchmark models to new models. Based on the practices of engineering and the technology of verification & validation, a framework of QU is brought forward in the case that simulation is used on detonation system for the sake of scientific prediction.

X-ray structure of the complex of 5-nitrimino-1,4H-1,2,4-triazole and DMSO

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Keywords: nitrimines; 1,2,4-triazoles; X-ray analysis; molecular structure.

The structure of 5-nitrimino-1,4H-1,2,4-triazole (I) has not been determined so far, for it is difficult to obtain its single crystals suitable for X-ray analysis. Compound crystallized from DMSO to give colorless transparent crystals of a complex with DMSO, which seemed to be suitable for X-ray analysis. But this complex is unstable. It decomposes during upon drying in air for a short time. However, we could carry out of X-ray crystallographic analysis of a complex I*DMSO. According to the X-ray diffraction data, the molecule I has the nitrimine structure. The structure of I shows that it is a planar molecule with hydrogen bondings similar to previously studied nitrimino-1,2,4-triazoles.

Synthesis, energetic and some chemical properties of new explosive - 3,4-bis(4-nitrofurazan-3-yl)furazan (BNTF)

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Keywords: 3,4-bis(4-nitrofurazan-3-yl)furoxan; 3,4-bis(4-nitrofurazan-3-yl)furazan; nitrofurazan; furoxan; 1,2,5-oxadiazol.

The results of our studies concerning synthesis, energetic properties and reactivity of 3,4-bis(4-nitrofurazan-3-yl)furazan (BNTF) are discussed. It is shown that BNTF can be prepared by oxidation of the amino groups in 3,4-bis(4-aminofurazan-3-yl)furazan (BATF) by peroxide oxygen. Novel two step synthetic route to BATF including reductive furoxan ring opening in 3,4-bis(4-aminofurazan-3-yl)furoxan (BAFF) to vicinal isonitroso groups and their further intramolecular dehydration to furazan ring is set forth. It is shown that energetic characteristics of BNTF are quite similar to ones of 1,3,3-trinitroazetidine (TNAZ). As opposed to TNAZ BNTF is non-volatile at elevated temperatures. The readiness of both nitro groups of BNTF to substitution by nucleophyles turns it into a valuable building block for a wide range of new 1,2,5-oxadiazole derivatives, including multi-heterocyclic systems.

Low thermal decomposition studies of certain species in Bachmann process

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Keywords: Bachmann process; thermal decomposition; RDX ; HMX; BSX.

Well-known nitramine type of explosives; hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7- tetrazocine (HMX) are produced by Bachmann process, starting with hexamethylenetetramine (HMT) which turns into hexamethylenetetramine dinitrate (HDN). An impurity termed BSX (BS-Bachmannn and Sheehan) forms as a side product while RDX formation occurs. In this low thermal decomposition study, TGA-GC/MS analyses of all these five species have been done as well as characterization of them.

Synthesis and characterization of 2,2,2-trinitroethyl carbamate and 2,2,2-trinitroethyl nitrocarbamate

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Keywords: high energetic oxidizer; 2,2,2-trinitroethanol; bomb calorimetry; energetic properties; crystal structure.

2,2,2-Trinitroethyl carbamate (1) is prepared from 2,2,2-trinitroethyl chloroformate (2). Nitration of 1 with anhydrous nitric acid yielded 2,2,2-trinitroethyl nitrocarbamate (3) [1, 2]. 3 is a potential perchlorate-free high energetic dense oxidizer (HEDO) with a high oxygen balance of Ω(CO2) = +14.9 %. The characterization of 1 and 3 including multinuclear NMR spectroscopy, vibrational analysis (IR, Raman), mass spectroscopy as well as elemental analysis. The thermal stability is studied using differential scanning calorimeter and the energies of formation are calculated on the CBS-4M and other different levels of theory using Gaussian 09 Revision A.02 [3]. The heat of combustion is measured with static bomb combustion calorimeter. Furthermore, X-ray diffraction studies are performed and the crystal structures of 1 and 3 are presented.

Adsorption of military-grade 2,4,6-trinitrotoluene residuals in water using tufa modified with nano copper

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Keywords: TNT; adsorption; tufa; equilibrium isotherms.

2,4,6-trinitrotoluene (TNT) presents major secondary explosive which residuals are found at Serbian military ranges, military factories and demilitarization facilities. Natural mineral tufa is coated with nano copper and used as adsorbent for the removal of TNT from aqueous solution. Various adsorption isotherms and kinetic parameters were computed using batch adsorption experiments in order to determine the adsorption capacity for TNT and to understand the mechanism of adsorption.

Some detonation characteristics of milled double-base gunpowder

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Keywords: detonation; detonation velocity; gunpowder.

The results of experimental detonation velocity for milled double-base gunpowder are presented in this paper. The gunpowder was milled in a mill with wet process. Three different granulations of milled gunpowder were then used for formation of charges with different diameters, which were detonated using a booster made of plastic explosive. Detonation velocities were measured using Explomet-FO® apparatus. Obtained results were then analyzed using a non-linear regression mod-els.

Atomistic simulation study of intermolecular interactions between binders and plasticizers used in propellants and high explosive charges

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Keywords: intermolecular energetic interactions; binder HTPB; binder GAP; plasticizers; atomistic simulation.

The intermolecular energetic interactions between binders, plasticizers and fillers in elas-tomer bonded composite rocket propellants (CRP) and elastomer bonded high explosives charges (HEC)(some of the PBX family) are of great interest to explain the glass to rubber transition and to elucidate the different binder fractions and their specialized hindrances in molecular mobility. In a first step the interactions between binders and plasticizers will be considered. Using the program package Materials StudioTM (MS) version 6 of company Accelrys, Inc. an atomistic simulation of such interactions is possible. An appropriate op-timized unit cell with the MS-tool Forcite was built for each of the considered substances and mixtures of them. The substances used are hydroxyl terminated polybutadiene (HTPB), dioctyl adipate (DOA), 1,2,4-butanetriol trinitrate (BTTN), azido plasticizers and others. For energetic equilibration of the molecules and of the configuration to each other, mo-lecular dynamic simulations were performed in NPT ensembles with a Berendsen barostat to control the pressure and an Andersen thermostat to control the temperature of the sub-stances in the unit cell. The kernel for calculating the molecular interaction energies and also the intramolecular ones is the force filed COMPASSTM in order to get the total energy of the system and the cohesive energy density between the pure substances.

Velocity of detonation of the low density ANFO mixture

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Keywords: velocity of detonation; low density ANFO mixture.

Blasting operations in built-up areas, at short distances from structures, impose new requirements on blasting techniques and properties of explosives in order to mitigate seismic effect of blasting. Explosives for civil uses are mixtures of different chemical composition of explosive and/or non-explosive substances. Chemical and physical properties, along with means of initiation, environment and the terms of application define detonation and blasting parameters of a particular type of the explosive for civil uses. Velocity of detonation is one of the most important measurable characteristics of detonation parameters which indirectly provide information about the liberated energy, and applicability for certain purposes. The level of shock effect of detonated charge on the rock, and therefore the level of seismic effect in the area, depends on the velocity of detonation. Since the velocity of detonation is proportional to the density of an explosive, the described research is carried out in order to determine the borderline density of the mixture of the low density ANFO explosive with expanded polystyrene while achieving stable detonation, and to determine the dependency between the velocity of detonation and the density of mixture.

Sensitivity to impact and detonation parameters for mixtures of okfol-3.5 with nanostructured titanium compounds

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Keywords: sensitivity to impact; parameters of detonation; okfol.

Various metallic additives for increasing the power of high-explosive and throwing action of explosive compounds are introduced typically. The introduction to okfol-3,5 nanostructured titanium compounds on the parameters of detonation and sensitivity to impact are examined.

Calculation of a detonation products composition and optimization of dynamic characteristics of mixed explosives

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Keywords: detonation; conservation laws; detailed equilibrium; relative impulse; optimization.

The mathematical model is proposed for calculation of quasiequilibrium composition of products and relative impulse at a detonation for the multicomponent mixture of explosives. The model consist of system of the equations for variables which describe possible composition and temperature, taking into account conservation laws, partial conditions of detailed equilibrium, semi-empirical functional dependence of energy-release coefficient. The numerical solution of equations allows one to predict a relative impulse at a detonation of a given mixture, and also to state and solve a natural problem of impulse value optimization. Application of proposed mathematical model for optimal composition calculation for standard explosives with atomic structure C,H,N,O,F is considered.

Synthesis of the ionic liquid DETRA-D

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Keywords: synthesis; characterization; sensitivity; DETRA-D.

Ionic liquids are interesting candidates in the development of new energetic materials. One of their favourable properties is their low vapour pressure. Another one is that their melting points can be tailored to the requirements of the desired application. These two factors made us investigate the ionic liquid diethylenetriamine bis-dinitramide (DETRA-D) as a possible replacement for TNT as a melt-cast matrix for explosive charges. Its synthesis, scale-up and thermal characteristics are described in this paper.

Synthesis of nitrofuroxans from acrylic acids

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Keywords: nitrofuroxans; acrylic acids; nitrosation.

Several approaches are used for the furoxan ring formation, principal of them are an oxidation of glyoximes, cyclodimerization of nitrile oxides and dehydration of alpha-nitrooximes. The first method is the most widely known, however it did not practically used for the synthesis of nitrofuroxans, since nitroglyoximes are hardly accessible compounds. In this work new approach to an in situ formation of nitroglyoximes is offered, which is based on an interaction of substituted acrylic acids 1 with nitrosation reagents. This reaction carries out through N_2O_3 addition to double bond of compounds 1 with formation of intermediates 2. Then monooximes 3 are formed as a result of decarboxylation of compounds 2. The monooximes 3 enter in a second nitrosation reaction and formed nitroglyoximes 4 are oxidized into 3-R-4-nitrofuroxans 5 in the reaction conditions. It was found that this reaction can be performed with acrylic acids, containing different substituents R (Alk, Ar). The synthesized nitrofuroxans are of interest as potential components of energetic formulations.

TKX-50 (bishydroxylammonium 5,5'-bis(tetrazolate-1N-oxide))

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Keywords: bishydroxylammonium 5,5'-(tetrazolate-1N-oxide); differential scanning calorimetry; thermogravimetric analysis; heat of decomposition; kinetics; TKX-50.

TKX-50 (bishydroxylammonium 5,5'-bis(tetrazolate-1N-oxide)) is one of the most promising ionic salts as a possible replacement for RDX. The compound can be prepared on a multigram scale by the reaction of 5,5'-(1-hydroxytetrazole) with dimethyl amine to form the bis(dimethylammonium) 5,5'-(tetrazolate-1N-oxide) salt which is then isolated, purified and subsequently reacted in boiling water with two equivalents of hydroxyammonium chloride to form TKX-50, dimethylammonium chloride and HCl. The thermal behavior of TKX-50 (bishydroxylammonium 5,5'-(tetrazolate-1N-oxide)) and the kinetics of its thermal decomposition were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It was found that the thermal decomposition of TKX-50 starts at 210-250°C depending on heating rate, preceded by an endothermic process in the range 132-200oC. By applying multiple heating rate DSC measurements and Ozawa´s iso-conversional model free method the activation energy of 151.90 kJ/mol, and pre-exponential factor of 1.39 • 1016 s-1 were calculated from DSC peak maximum temperature - heating rate relationship. By applying non-isothermal TGA experiments and the Flynn–Wall iso-conversional model free method, it was found that the activation energy changes with conversion and lies between 146 and 181 kJ/mol, while the pre-exponential factor ranges from 9.81 •1011 to 1.79•1016 s-1.

Heats of formation of 2,2-dimethyltriazanium salts: experimental and computational approaches

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Keywords: 2,2-dimethyltriazanium salts; heat of formation; bomb calorimetry; quantum chemical calculations,.

2,2-Dimethyltriazanium salts are nitrogen-rich hydrazine derivatives where a third atom of nitrogen has formally been added to a hydrazine moiety forming a new sigma single bond. In this work, the nitrogen-rich 2,2-dimethyltriazanium cation was paired with a series of energetic anions yielding a new family of salts with prospective energetic interest. After purification and full characterization, the energy of combustion of the 2,2-dimethyltriazanium salts were measured using bomb calorimetry which enabled the experimental determination of their heats of formation. Additionally, several models of chemical quantum methods were tested in order to accurately evaluate the theoretical values of heats of formation. The good match between calculated and experimentally determined values allowed identifying the model in agreement with the experimental values and on the other hand will permit performance assessment in future energetic compounds.

A theoretical study on dendrimeric nitrogen-rich polymers

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Keywords: dendrimer; nitrogen-rich polymers; synthesis; prediction.

Dendrimeric polymers are type of hyperbranched polymers with highly arranged structure and as a result of this, have certain important characteristics such as high solubility in organic solvents, high concentration of final groups, low melt viscosity and high degree of crystallinity. With carefully selected nitrogen-rich monomers, synthesis of dendrimeric polymers could give important energetic materials. Since experiments with these polymers could be expensive, it is highly economical to predict their properties using certain methods and synthesize only those which have adequate detonation or combustion parameters. The aim of this study is to provide a theoretical basis for synthesis of nitrogen-rich dendrimeric polymers in the view of reactants, conditions and reaction parameters (Carothers and Flory gelation theories). Afterwards, detonation, combustion and sensitivity parameters will be predicted by the means of simple but proven methods. Obtained results will be used for evaluation and selection of compound for further experimental research.

The interaction of 2,4,6-trichloro-1,3,5-triazine with trinitromethane salts and adamantyl alkanols

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Keywords: 2,4,6-trichloro-1,3,5-triazine; trinitromethane salts; (1'-adamantyl)methanol, 2-(1'-adamantyl)ethan-1-ol, trinitromethylation-dialkoxylation reaction.

The interaction of 2,4,6-trichloro-1,3,5-triazine with sodium (potassium)trinitromethane salt and (1'-adamantyl)methanol, 2-(1'-adamantyl)ethan-1-ol, bearing a bulky adamantly group in α- and β-positions, which sterically hinders the reaction center of the alcohol, was studied. It is shown that these adamantyl alkanols behave as other unhindered aliphatic alcohols, and the trinitromethylation-dialkoxylation reaction occurs to give 2,4-di((1'-adamantyl)methoxy-6-trinitromethyl-1,3,5-triazine and 2,4,-di(2'-(1"-adamantyl)ethoxy)-6-trinitromethyl-1,3,5-triazine.

Novel bis-trinitromethylation-alkoxylation reaction of 2,4,6-trichloro-1,3,5-triazine

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Keywords: 2,4,6-trichloro-1,3,5-triazine; trinitromethane salts; secondary and tertiary adamantanols; bis-trinitromethylation-alkoxylation reaction.

The reaction of 2,4,6-trichloro-1,3,5-triazine with sodium (potassium) trinitromethane salt and adamantan-1-ol, 3,5-dimethyladamantan-1-ol, adamanthan-2-ol was studied. In this case the reaction center of the alcohols is sterically hindered by a bulky adamantyl group. It is shown that the novel bis-trinitromethylation-alkoxylation reaction takes place to give corresponding 2-adamantyloxy-4,6-bis(trinitromethyl)-1,3,5-triazines.

Decomposition temperatures-flash points relationships for the high explosives

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Keywords: DTA; temperature of intensive decomposition beginning; maximum decomposition temperature; maximum decomposition rate temperature; flash point.

The temperature of intensive decomposition beginning (Tidb), maximum decomposition temperature (Tmax) and maximum decomposition rate temperature (Tw) values were obtained using DTA (heating speed – 8 degrees per minute) method for 23 high explosives. The express-method flash points (Tfp(1)) and 5-second-delay flash points (Tfp(5s)) for the same explosives were found. The linear correlations between Tidb and Tmax; Tmax and Tw; Tfp(1) and Tidb; Tfp(1) and Tmax; Tfp(1) and Tw; Tfp (5s) and Tdb; Tfp(5s) and Tmax; Tfp(5s) and Tw were found.

Free jet testing of a solid fuel ramjet

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Keywords: ramjet; solid fuel ramjet; SFRJ; free-jet.

The solid fuel ramjet (SFRJ) is an air breathing propulsion means aimed at propelling high speed projectiles or missiles (typically in the speed range of Mach 2-5) at a substantially higher specific impulse than rocket motors. This research describes testing of a laboratory-scale SFRJ in a free jet facility which provides a good flight simulation for the entire propulsion system, including inlet, combustion chamber, and exit nozzle. A vitiated air heater capable of providing incoming air stagnation temperature and pressure as high as 800 K and 50 atm, respectively, has been used. A 10 mm air inlet diameter SFRJ motor operating at a simulated flight design point of Mach 2.8 has been tested. PMMA (Plexiglas) with an initial port diameter of 16 mm has been used as the solid fuel, permitting observation of the flame inside the combustion chamber. Ignition characteristics, combustion stability, fuel regression rate, and combustion chamber pressure have been measured.

Explosion action of a thin layer of light-sensitive explosive formulations on barriers

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Keywords: light-sensitive explosive; thin layer; explosion; barrier; impulsive loading.

The explosion of a thin layer of an explosive formulation is used in particular for testing full-scale structures to the action of a short-time intensive mechanical impulse. In one of such methods the sliding detonation in the layer of a plastic explosive formulation disposed on the surface of a structure is used for this purpose. However, two appreciable shortcomings show up in this case. They are the considerable time diversity of impulsive load application to a large surface and the restriction of an applied mechanical impulse with the minimal value of 1 kPa•s. The method of simultaneous initiation of a thin layer of a light-sensitive explosive formulation by an optical radiation pulse is deprived of these shortcomings to a large degree. It is implemented in one of the research laboratories for testing full-scale military aerospace structures. In this case the layer of silver acetylide-nitrate explosive is sprayed on the surface of a structure and impulsive irradiating is created by an intense flash of light. Many light-sensitive explosives have been designed and investigated until recently. The measurements of mechanical impulses imparted to barriers when initiating the layers of various thicknesses were fulfilled for several explosive formulations. Two most sensitive to optical irradiation explosive formulations were considered in the paper, first one on the basis of perchlorate (5-hydrazine-1N-tetrazole)mercury(II)) and second one on the basis of hexamethylene triperoxide diamine. The binding agent in the formulations was the transparent polymer polymethyl vinyltetrazole. Several interconnected problems have been solved. At first, using the known data on properties of the explosives, the explosive characteristics of the formulations were estimated rather correctly. Then a lot of numerical calculations of the explosion action of these formulations on different barriers were carried out. The barriers made of explosive formulations PP-83 and HTC-70 were loaded directly and through a thin copper layer. These calculation results were compared with the experimental data on detonation initiation in the samples of these formulations when being loaded by the impact of thin steel plates. The calculations of explosive loading of different barriers in the wide range of their acoustical impedances were conducted and appropriate dependences were built. The problem of distribution of a mechanical impulse in a two-layer textolite-aluminum barrier with various relations of layers thicknesses was examined too. The influence of several factors on the impulse distribution regularities, including the dynamic strength of layers adhesion, was revealed.

Influence of structure and properties of molecules on impact sensitivity of triazole nitro compounds

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Keywords: heterocyclic nitro compound; triazole; molecule; structure; impact sensitivity.

Many attempts were undertaken to connect properties of explosives with their impact sensitivities. Various structural and physicochemical properties of explosive molecules were used such as oxygen balance, bonding energy of the most weak bond, the length of this bond, electric charge on the most weakened nitro group, electrostatic potential in a weak bond, band-gap energy, ionization potential, quantity and disposition of functional groups and some other. In one of the works the simple approach to prediction of impact sensitivity was offered, which was based only on elemental composition of considered explosives. Afterwards this approach was improved by introducing additional parameters defining the structure of molecules. The author used a combined method utilizing the simple approach marked above and results of fulfilled quantum-chemical calculations for the groups of aromatic and triazole nitro compounds. The results for triazole nitro compounds are presented in the paper. Complete quantum-chemical calculations have been performed for 34 molecules of nitro compounds on the basis of 1,2,3- and 1,2,4-triazoles. The electronic structure of molecules was calculated using the method of density functional theory implemented in the program of quantum-chemical calculations Gaussian 03. The hybrid functional B3LYP and two basis sets of electronic functions, 3-21G and 6-31+G(d), were used. Zero-point energy corrections were taken into account. The first basis set was used for complete comparative calculation and the second one for more interesting cases as, for example, considerable differences in impact sensitivity for isomers containing in their structure 1,2,3-triazole. They are first of all such heterocyclic nitro compounds as 1-picryl-1,2,3-triazole and 2- picryl-1,2,3-triazole, 4-nitro-1-picryl-1,2,3-triazole and 4-nitro-2-picryl-1,2,3-triazole. The potential energy curves were built during tension of the weakest bonds in molecules and the necessary transition states were calculated for determination of the energy barriers of primary decomposition reactions. The influence of structure and location of triazole groups on decomposition energetics was revealed. Thus, in the molecules of nitro compounds on the basis of 1,2,4-triazole the primary decomposition reaction was the removal of a nitro group, and in the molecules on the basis of 1,2,3-triazole the rupture of a N-N bond in the 1,2,3-triazole group became predominant. The rather accurate tendency of the influence of bonding energy on impact sensitivity of examined nitro compounds was marked and the use of the mentioned combined method allowed obtaining an acceptable correlation dependence connecting impact sensitivity of explosives with the structure and decomposition energetics of molecules.

Structure, properties and decomposition mechanism of cyclic formaldehyde, acetaldehyde, acetone and methyl ethyl ketone peroxides molecules

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Keywords: cyclic peroxides; aldehydes and ketones; molecule; structure; decomposition mechanism.

Peroxides in whole and cyclic peroxides in particular are rather actively studied using experimental and theoretical methods. Their explosive properties and first of all high sensitivity to exterior exposure are substantially connected with the primary mechanism of their decomposition, which in most cases represents the rupture of a weak O-O bond. As was shown by the author earlier, other decomposition mechanisms show up in the conditions of electronic excitation and ionization but all of them are however connected with the presence of a peroxide oxygen bond in the molecule. So, for example, it was obtained that in positively charged molecules of diacetone diperoxide and triacetone triperoxide the tension of one of the oxygen bonds resulted in another O-O fragment moved away from the initial molecule and formed an oxygen molecule. The energetic barrier of the decomposition reaction was in this case approximately three times as lower than the energetic barrier for rupturing an oxygen bond in a positively charged hexamethylene triperoxide diamine molecule. Initial ingredients for the synthesis of cyclic peroxides along with hydrogen peroxide are aldehydes and ketones with the simplest structure such as formaldehyde (methanal), acetaldehyde (ethanal), acetone (propanone), methyl ethyl ketone (butanone). Molecules of twelve cyclic peroxides produced on the basis of these substances have been considered in the paper. They are cyclic dimers, trimers and tetramers of formaldehyde peroxide, acetaldehyde peroxide, acetone peroxide and methyl ethyl ketone peroxide. All the main conformation isomers of molecules were considered and the transition states characterizing the energy barriers of isomerization reactions were determined. If for formaldehyde and acetone peroxides the conformation of molecules was conditioned by the direction of O-O bonds, then for acetaldehyde and methyl ethyl ketone peroxides it was also conditioned by the location of methyl and ethyl groups in the molecules. The electronic structure of all examined molecules was calculated using the method of density functional theory implemented in the program of quantum-chemical calculations Gaussian 03. The hybrid functional B3LYP and the basis sets of electronic functions 6-31+G(d) were used. Zero-point energy corrections were calculated for all stationary and transition configurations of molecules. The most stable configurations were used for consideration of the decomposition mechanism of molecules in their ground, exited and electrically charged states. The values of energetic barriers for rupture of O-O bonds were obtained using calculated potential energy curves for O-O bond tension and corresponding transition states.

A theoretical study about the formation mechanisms of some explosives

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Keywords: OH radical addition; imidazole; triazole; NTO; explosive.

The reactions between hydroxyl radical and 2-nitro-1H-imidazole, 5-nitro-1H-imidazole and 3-nitro-4H-1,2,4-triazole have been investigated theoretically by using B3LYP/6-31G(d,p) level of theory. The OH radical additions to double bonds are explored. All systems are optimized in bulk solvent (water). The data presented show that the barriers to reaction are very low: 3-7 kcal/mol indicating fast reactions. Thermodynamically, OH addition to position 2 of structure A leads to the most stable radical product. Main geometrical parameters have been reported for reactants, transition states and radical products together with some energetic data.

Coefficient of friction between PBXs and an aluminium substrate

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Keywords: coefficient of friction; PBX; aluminium.

The static Coefficient of Friction (CoF) was measured for two Polymer Bonded Explosives (PBXs) and two PBX simulants against an aluminum plate of roughness 900 nm. A drag method, using an Instron 5566 electromechanical testing system, was employed; a pulley system transformed vertical motion to horizontal to facilitate testing. Frictional losses in the pulley were accounted for using an experimental approach, which determined the form of the tension calibration curve. White light interferometry was used to image the polymer surfaces (with nm precision) in order to analyze the impact of wear on them and assess its correlation to the CoF. Finally, the variation of the CoF with polymer roughness, aluminum roughness, and the presence of pollution was investigated. Variations in the value of CoF arising from different surface conditions were found to be far more significant than the associated experimental errors.

Synthesis and characterization of a new energetic polyurethane

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Keywords: energetic material; energetic polymer; polyurethane.

A synthesis of a new energetic polyurethane was developed. The point of interest was the introduction of energetic moieties (in this case nitro groups) to polyurethane units. For the synthesis of the described polyurethane hexamethylene diisocyanate and 2,2-dinitro-propane-1,3-diol together with the catalyst dibutyltin dilaurate were used. Multinuclear magnetic resonance studies, vibrational spectroscopy (IR) and elemental analysis were applied to characterize the synthesized polymer. The decomposition temperature of the compound was determined by differential scanning calorimetry. Detonation parameters were calculated using the EXPLO5 software. The used heats of formation values were determined by bomb calorimetric measurements or theoretically calculated using the CBS-4M level of theory. The synthesized polyurethane possesses a decomposition temperature of 142 °C and shows comparable or even better energetic properties compared to the commonly used energetic binder GAP.

Preparation and characterization of 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol and selected energetic salts

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Keywords: primary explosives; secondary explosives; triazoles; tetrazoles; azides.

The novel nitrogen-rich compound 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (1) has been prepared and fully characterized, including multinuclear NMR spectroscopy and single-crystal X-ray diffraction. Additionally several metal and nitrogen-rich salts, including silver (2), copper(I) (3), potassium (4), cesium (5), copper(II) (7), ammonium (8), hydrazinium (9), aminoguanidinium (10), as well as the respective double-salts of 4 and 8, were prepared and also well characterized. Additionally the structures of 5, 6 • 3 H2O and 8 were determined by single-crystal X-ray diffraction. The sensitivities towards impact, friction and electrostatic discharge were determined according to BAM standards, revealing most of the metal salts as highly sensitive and the nitrogen-rich salts as mostly moderately sensitive to insensitive. The metal salts were further tested as primary explosives.

Synthesis and characterization of energetic 5-(1-methylhydrazinyl)-1H-tetrazole copper(II) complexes as laser ignitable explosives

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Keywords: laser ignition; primary explosive; copper(II) complexe; coordination polymer; energetic material.

The synthesis of 5-(1-methylhydrazinyl)-1H-tetrazole (1, HMHT) as monohydrate (1 • H2O), starting from cyanogen bromide and monomethylhydrazine, is described. HMHT is used as a ligand and the preparation of the corresponding copper(II) complexes with perchlorate (2 and 3), nitrate (4, 5 and 6), dinitramide (7) and chloride (8) as anion is presented. The complexes were characterized by infrared spectroscopy, elemental analysis and single crystal X-ray diffraction. Compound 1 can act as bidentate ligand in the neutral form (HMHT) and as μ2- or μ3-bridging ligand in the deprotonated form (MHT). Complex monomers, dimers and polymers are formed depending on the ligand form and the anion. Furthermore, the behaviour of the complexes towards single pulsed laser irradiation at 940 nm was investigated and their thermal and mechanical sensitivities were determined. Especially the [Cu(ClO4)(MHT)(HMHT)]2 (2) and [Cu(ClO4)(MHT)(H2O)]∞ (3) complexes exhibit good properties as primary explosives whereas the corresponding nitrate complexes might serve as colorants in pyrotechnical compositions.

Transformation mechanisms of 2,4-dinitro-2,4-diazopentane in formation and decomposition processes

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Keywords: organic synthesis; decomposition; computer modeling; DFT calculations; 2,4-dinitro-2,4-diazapentane.

On the example of a widely used component of rocket fuels - 2,4-dinitro-2,4-diazapentane (OCPX) - the computer simulation of two opposite processes (formation and decomposition) have been performed. On the base of DFT quantum chemical methods the mechanisms of its formation have been calculated which are in a good agreement with the experimental data. Applying a set of methods of mathematical chemistry and computer modeling the processes of its decomposition have been studied at the different stages of decay, including the deep stages. The common intermediates for both processes have been identified and the calculated limiting stages of the corresponding reactions have been obtained.

The tests of the high-safety electric blasting cap for compliance with the requirements of the Russian state standard

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Keywords: non-primary explosive blasting cap; response time; shaking resistance; temperature resistance; lead plate punching..

The tests of the designed non-primary explosive high-safety blasting cap (BC-HS) for compliance with the requirements of the Russian state standard GOST 9089-75, according to which Russian blasting caps ED-8Zh are produced, were carried out. It is shown that the BC-HS meets the requirements of GOST 9089-75 at all points (response time, shaking resistance, stability at high and low temperatures, the 5-mm lead plate punching).

Photochemical and photothermal dissociation at laser initiation of pentaerythritol tetranitrate

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Keywords: laser initiation; pentaerythritol tetranitrate; explosion; photoinitiation.

The temperature dependence of the efficiency of laser initiation (λ = 1060 nm) of pure PETN with an open and closed surface and PETN with a lightˆscattering additive (0.5% MgO) and an open surface was studied. It was found that the closing of the surface and introduction of lightˆscattering additives leads to a change in the temperature dependence of the initiation threshold. The observed effect is associated with the specificity of the photoinduced fragmentation of PETN molecules in defective areas of the crystal lattice.

Cyclic nitramines: investigation of their electrochemical properties, cytotoxicity and enzymatic reactions

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Keywords: cyclic, bicyclic and cage N-nitramines; synthesis; electrochemistry; peak potential; toxicity; enzyme PETN-reductase; enzymatic reactions.

The environment contamination by explosive nitrocompounds is an important problem. Cyclic nitroamines are one of the major group of such type contaminants. The toxic action and biodegradation of the above compounds are mostly related to their 1e-/2e-(4e-) reduction by flavoenzymes. In order to understand their bioreduction mechanisms and enzyme substrate specificity, as well as to predict the pathways of their biodegrada-tion, one must to characterize their electron-accepting properties. In this work laboratory scale quantities of 10 organic nitroamines were obtained by nitration with dinitrogen pen-toxide in dichloromethane medium (or other convenient nitrating agents). 9 compounds were synthesized in Institute of Biochemistry, the newest compound from this group - BCHMX - was prepared by original innovative methodology in Pardubice University. All those materials were examined by spectroscopic and voltammetry methods. Voltammet-ric reduction peak potentials (Ep,7) varied from -1580 mV to -555 mV vs. Ag/AgCl for NNHT and N,N'-dinitroimidazol-2-one, respectively. Their cytotoxicity for mice spleno-cytes was investigated. N,N'-dinitroimidazol-2-one, N,N'-dinitropiperazine, K-6 (keto-RDX) and RDX were found to be the most toxic nitroamines (CL50 – 45, 47, 67 and 140 microM) whereas compound BCHMX was less toxic (CL50 = 160 microM). Preliminary evaluation of the latter compound for the acute oral toxicity on mice revealed, that BCHMX did not demonstrate any signs of an acute toxicity in oral doses less than 1000 mg/kg. Generally, bicyclic and cage nitroamine HEMs were found to be less cytotoxic (CL50 = 160-350 microM) than mono-cyclic compounds. All 10 nitroamines have been also examined in their enzymatic reduction reactions catalyzed by flavoenzyme PETN-reductase. The obtained apparent second-order rate constants for enzymatic reduction (kcat/Km) of compounds varied between 2.5×10^2 (for HMX) and 1.3×10^3 $M^{-1}s^{-1}$ (for TNAD).

Influence of structure on the thermal decomposition rate of secondary nitramines

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Keywords: kinetics; thermal decomposition; nitramines; mechanism; induction effect.

Kinetics and mechanism of thermal decomposition of secondary nitramines in a liquid phase are investigated and structural-kinetic laws are established. The quantitative description of the reactivity of nitramines depending on the sum of induction constants σ^* is found. Mechanism is suggested which includes the typical oxidation reactions of thermal decomposition of secondary nitramines in nitrogen dioxide and nitrogen oxide, and explains the structure of decomposition products of N-nitro-bis(2-cyanoethyl)amine.

Theoretical insights into the nature of intermolecular interactions in TNT/CL-20 cocrystal and its properties

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Keywords: intermolecular interactions; TNT/CL-20 cocrystal; structure and properties.

Abstract: Intricate non-covalent interactions, such as Van der Waals interactions, hydrogen bonds and steric repulsion stacking interactions, play a key part in governing the structure of a co-crystal. In this paper, the density functional theory (DFT) method at TPSSTPSS/6-311G (d, p) level was performed to reveal the optimized stable molecular geometry and the electronic structure of TNT/CL-20 copolymers. The electron density and its derivatives were utilized to distinguish and highlight the weak interaction region of TNT/CL-20 super-molecules. The main properties of TNT/CL-20 co-crystal consisting of mechanical properties, stability and interaction formats were studied by molecular dynamics methods.

Fig.1 Plots of the electron density and its reduced gradient for TNT/CL-20 co-crystal

The results show that the two components are connected a series of CH hydrogen bonds between nitro group oxygens and aliphatic hydrogens as well as interactions between the electron-deficient ring of TNT and nitro groups of CL-20 (Fig. 1), which agrees with the result of analys for radial distribution function (RDF) obtained by molecular dynamics (MD) simulations. Electrostatic potential, mechanical properties of the titled compound demonstrated the potential of cocrystallization to realize explosive smart materials by comparing with those of TNT and CL-20.

5-Hydrazinotetrazolium 5-nitrotetrazolate

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Keywords: energetic salts; nitrogen content; hydrogen bonding.

5-Hydrazinotetrazolium 5-nitrotetrazolate (HTZ•NT): an energetic nitrogen-rich salt was prepared and fully characterized by 1H, 13C NMR, and IR spectroscopy, differential scanning calorimetry (DSC), and elemental analysis. HTZ•NT crystallizes in the triclinic crystal system in the space group P-1. By including two molecular moieties in the unit cell, the calculated density is 1.711 g•cm-3. The tetrazole of the cation in the molecule exhibits planar and C–N and N–N bond lengths observed between 1.3266 and 1.3499 Å. There are extensive hydrogen bonding interactions between the cation and the anion form a complex 3D network. The heat of formation was calculated with the Gaussian 03 suite of programs. HTZ•NT exhibit promising detonation performances (pressure: 32.5 GPa; velocity: 8885 m•s-1; EXPLO 5.05) that exceed those of conventional TNT. Impact sensitivity was also determined by hammer tests and resulted at 4.3 J. Due to high enthalpy of formation and high nitrogen content, the specific impulse of HTZ•NT as high as 263.1 s. HTZ•NT exhibit reasonable physical properties, such as good thermal (Td = 184.4 °C), reasonable impact sensitivities, and excellent specific impulses, making this salt potential energetic material.

Multilayer graphene make lead styphnate more safer to electrostatic hazard

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Keywords: grapheme; primary explosive; electrostatic hazard; lead styphnate.

Lead styphnate (LS) is a widely used primary explosive, which is very sensitive to electrostatic spark, and frequently results in unexpected troubles. To improve the security of LS, multilayer graphene was used to modify its' anti-electrostatic performance. Products with various contents of multilayer graphene (mass fraction: 0.1 % to 2 %) was prepared. The SEM was used to characterize the morphology of the samples. The electrostatic spark sensitivity and static electricity accumulation of the obtained samples were investigated with a desirable result, which confirmed that multilayer grapheme can make LS more safer to electrostatic hazard.

Reaction delay of brisant powdery energetic materials tested in electrostatic discharge

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Keywords: high sensitivity EM; electrostatic discharge test; activation; flash-light radiation.

The sensitivity of the majority of fine-grain powders, ignition compositions, high explosives and other types of energetic materials (EM) to effects of electrostatic discharge (ESD) is evaluated according to the standardized methodology IEM on the basis of direct monitoring of the activation symptoms or inertness of the substance and simultaneous quantification of the Joulean energy which was released in the medium of tested substance during the discharge. The monitoring of time connections between individual phases of electrostatic discharge and the activation symptoms of the substance tested can make use—inter alia—of the monitoring of accompanying light radiation with the help of light conducting device POF 1 mm and a rapid opto-electronic transmitter. The verification results of applicability of this measuring method to an increase in interpretation comfort of ESD tests are given in the present communication.

Synthesis ,crystal structure and DFT calculation of an cocrystal energetic materials

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Keywords: cocrystal expplosive; crystal structure; DFT.

A novel cocrystal energetic material Monomethy lamine Triethylenediamine hexperchlorate (MT) has been prepared by one step synthesis method which is first used in cocrystal explosives. The structure of MT was characterized by X-ray diffraction which shows the compound crystallizes in the monoclinic system with Pn space group. The first principle ting-binding method within general gradient approximation (GGA) has been used to study the band structure and density of states (DOS).

Munitions neutralisation using EFP-generating devices

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Keywords: EFP; munition; constrained Lagrange in solid; LS-Dyna.

The study of a steel-TNT-steel sandwich explosive behaviour at the impact with an EFP was performed in the view of designing unexploded ordnance (UXO) neutralisation devices. The design of the EFP generation and its impact against the projectile-like configuration has been achieved through LS-DYNA. Two different cases, including copper and aluminium liners, have conducted to results that give valuable data in the view of designing such explosive devices.

Method for obtaining octogen

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Keywords: octogen; HMX.

In this paper, method of synthesis of octogen was presented. This process is complex as it forms a lot of different products, which seems especially disadvantageous when the process is carried out on an industrial scale. Method of octogen production had been developed and implemented.

Energies of isomerization of di(pyridyl)-azofurazans

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Keywords: furazan; calorimetry; enthalpy of formation; sensitivity; heat of explosion.

The method of calorimetry of burning in oxygen atmosphere has been used for measuring of combustion energy for the set of isomers of pyridylazafurazan and on this base the enthalpy of formation for orto-, meta-, and para-isomers has been calculated. As the result, the energies of isomerization for structural isomers have been estimated and the influence of position isomerism on the enthalpy of formation for these compounds has been studied. It was revealed the presence of intermolecular donor-acceptor bonds in meta-isomer of pyridylazofurazan.

Detonation velocity of mixtures based on fine-dispersed ammonium nitrate with aluminum

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Keywords: improvised explosive; ammonium nitrate; detonation velocity.

There were reported at previous NTREM seminars about the results of investigations for failure detonation diameter and detonation velocities of mixtures based on granular and fine-dispersed ammonium nitrate (AN) with different quantities of aluminum powder. Measurements of detonation velocities of mixtures based on fine-dispersed AN with content of Al (CAl=2,5%; CAl=3%; CAl=5%; CAl=7,5%) were carried out in this work. Using the data received in this and previous works were found that maximum of detonation velocity of mixtures based on fine-dispersed AN with aluminum is increasing with decreasing AN particles size and reaching its maximum when approaching to aluminum particles size.

Thermal mechanism limits of laser initiation of energetic materials

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Keywords: laser initiation; hot spot; thermal explosion.

Laser initiation of energetic materials has a potential to shift a paradigm in the development of novel explosive technologies with a stunningly broad range of applications. Once interactions of laser irradiation with energetic materials are better understood, dramatically improved safe explosive devices, intricate high-precision tools in micromedicine, miniaturized cutting and drilling tools, synthesis of new promising materials with tailored properties, and fundamentally new concepts of converting energy become possible. We consider the interplay between optical and thermal energies, analyze the applicability of the thermal mechanism of initiation, and estimate the limits of its efficiency in the process of laser initiation of energetic materials. We propose a simple demonstration of a feasibility of nonthermal selective photoinitiation while challenging the widely popular perception of the thermal nature of laser initiation.

Synthesis and some properties of 4-(4-Amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl-methylene)-2-phenyl-1H-imidazol-5(4H)-one

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Keywords: 4-(4-amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl-methylene)-2-phenyl-1H-imidazol-5(4H)-one; synthesis; structure detestion.

4-(4-Amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl-methylen)-2-phenyl-1(3H)-imidazol-5-one was synthesized in four steps in high yield. The structure of the compound was deduced from its elemental analyses and its IR, 1H and 13C NMR spectra as well as DFT calculations. The acid-base properties were determined by spectroscopic titration, and the corresponding ionization constants were calculated.

Blast wave parameters of small charges: trinitrotoluene (TNT) and urea nitrate (UNi)

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Keywords: trinitrotoluene; urea nitrate; blast wave; shock in air.

Surface blast wave parameters of 50 mm and 55 mm charges of urea nitrate ranging in size from 100 to 1100g were measured at distances from 3m to 10m. The charges were tested in paper tubes and therefore under light confinement. Results obtained for pressed TNT charges of similar size under the same conditions are presented as well.

Assessment of the influence of AlH_3 on chemical composition and thermodynamic parameters of combustion products of solid propellants

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Keywords: Solid propellant; aluminium hydride.

Chemical composition and thermodynamic parameters of combustion products of composite propellants containing aluminium hydride AlH3 are investigated. Propellants based on ammonium chlorate(VII) (NH4ClO4) modified by standard HTPB binder are considered. As the energetic ingredients Al and AlH3 are considered. The analysis is intended to examine the differences that arise by replacing of Al by its hydrate. Chemical composition and thermodynamic parameters of combustion products are evaluated by MWEQ computer program supplied with large species database. By same weight content, replacement of Al by AlH3 results in lowering of the temperature of combustion products. Enhancement of energetic outcome (Qv) as well as rise of amount of gaseous products, per unit volume of the propellant, is observed.

Low sensitivity secondary explosives based on 5,7-dinitrobenzotriazole and 4,6-diamino-5,7-dinitrobenzotriazole

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Keywords: 5,7-dinitrobenzotriazole; 4,6-diamino-5,7-dinitrobenzotriazole; secondary explosives; energetic performance; crystal structure.

Nitrogen-rich salts of 5,7-dinitrobenzotriazole such as guanidinium (3), 1-amino-guanidinium (4), 1,3,5-triaminoguanidinium (5), ammonium (6) and hydroxylammonium (7) salt were prepared by deprotonation or metathesis reaction from the potassium salt (2). Additionally, 5,7-dinitrobenzotriazole was aminated with trimethylhydrazinium iodide in an aprotic medium to afford 4,6-diamino-5,7-dinitrobenzotriazole (8), which could be further deprotonated to the potassium salt (9). 5,7-Dinitrobenzotriazole (1) and its potassium and guanidinium salts were characterized by single crystal X-ray diffraction. All presented energetic compounds were characterized by multinuclear magnetic resonance study (1H, 13C and 14N), vibrational analysis (IR and Raman), mass spectra and elemental analysis. Thermal stabilities were studied using differential scanning calorimetry. Detonation parameters were calculated by using the EXPLO5 computer code based on CBS-4M computed enthalpies of formation by Gaussian 09. The presented compounds show detonation performances comparable to TNT. Low sensitivities and high thermal stabilities make the presented compounds interesting for further investigations and possible applications as insensitive HEDM.

Bond topological and explosives properties of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) energetic molecule : A theoretical study

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Keywords: energetic molecule; Laplacian of electron density; crystal density; impact sensitivity; electrostatic potential.

Crystal density prediction, charge density distribution and explosive properties of 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105) energetic molecule have been carried out computationally using MOLPAK/PMIN software at the density functional (B3LYP/6-31G*) method coupled with AIM theory. The simulated geometrical parameters of LLM-105, such as bond lengths, bond angles and torsion angles are in good agreement with the reported experimental values. The density simulated from the crystal structure simulation is almost match with the experimental density. The Laplacian of the electron density for the nitro group attached C–NO2 and N-oxide bonds are found to the less negative, indicates the charges of these bonds are depleted; hence these are the weakest bonds in the molecule. The simulated molecule chemical energy of explosion (1.249 kcal/g), energy gap (3.537 eV) and oxygen balance (-0.92%) are almost close to the reported experimental values and these values are comparable with TATB and RDX explosives. Further, the electrostatic imbalance parameter of the simulated molecule is 0.240, this indicates, LLM-105 is almost insensitive molecule. The molecular electrostatic potential exhibits large electronegative regions are found near the nitro group C–N and N-oxide bonds.

1,2,4,5-Tetrazinyl derivatives of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one

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Keywords: tetrazine; 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one; nucleophilic substitution; DSC.

Synthesis and characterization of new energetic 1,2,4,5-tetrazines obtained from bis-3,6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine with 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one in presence of bases is described. It has been shown a possibility of synthesis of ener-getic salts with amines by the example of reaction of 4,4'-(1,2,4,5-tetrazine-3,6-diyl)bis(5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) with triaminoguanidinium chloride. Estimation of thermal stability new energetic compounds was conducted by differential scanning calorimetry.

Structures and spectra of some N-nitrozo-N-alkyl hydroxylamine derivatives with the metal ions of different nature

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Keywords: N-nitrozo-N-alkyl hydroxylamine derivatives; structure; electronic absorption spectra.

The feature of chelate-forming derivatives of N-nitrosohydroxylamines is the possibility to form stable complexes with the metallic ions of various natures (for example, Al and Pd). In addition, lots of them are biologically active compounds, known to display carcinogenic, genotoxic, mutagenic and DNA-damaging effects. Previously [1-3] we reported synthesis, some thermal, spectroscopic and crystallographic studies of potassium salts and transition metal complexes of some derivatives of N-nitrosohydroxylamines and indicated their high explosive abilities. Here we present some comparable crystallographic characteristics and spectroscopic data of complexes of some N-alkyl-N-nitrosohydroxylamines with metals of different types.

Study of combustion mechanism of salt of 5,5'-azotetrazole with guanidine

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Keywords: salt of 5,5'-azotetrazole with guanidine; burning rate; temperature profiles; DSC analysis; manometric experiments; combustion mechanism.

Salt of 5,5'-azotetrazole with guanidine (Gu2AzT) is considered as a perspective component for some gun powders, gas-generating compositions and "green" (free of HCl-containing exhaust gases) double-base and composite propellants. Gu2AzT is of special interest because of its high nitrogen content, high burning-rate, low-temperature and low molecular weight of combustion products. It is also offered as an effective activator of burning rate of double base propellants containing high energetic nitramines, and gas generating agent for automobile airbag system in mixtures with oxidizers (potassium nitrate and copper (II) oxide). This compound is also considered as a low-sensitive explosive. The goal of the present work was to study Gu2AzT combustion behaviors, their combustion wave structure and to determine the location and chemical nature of the leading reaction on combustion. Burn rate measurements were carried out in a constant pressure window bomb with a volume of 1.5 liters. The pressure range studied was 0.1-20 MPa. A video camera was used to determine the character of the combustion process as well as the burning rates. The salt under investigation were placed in transparent acrylic tubes, 4 mm in diameter and 12-15 mm long. Temperature profiles in the combustion wave were measured using P-shaped thin (7 mm) tungsten-rhenium thermocouples. The thermochemical data of the decomposition process of Gu2AzT were obtained with DSC analysis. Manometric experiments were carried out in thin-walled glass manometers of the compensation type (the glass Bourdon gauge). Gu2AzT in the form of samples pressed into acrylic tubes can sustain stable combustion at a pressure above atmospheric. In the pressure range 0.2-20 MPa Gu2AzT burns 1.5 times faster than HMX. It was shown that combustion of salt obeys the condensed-phase mechanism. The high burning rate of Gu2AzT connected with the high decomposition rate. The kinetic parameters of the controlling chemical reaction have been estimated, and the detailed combustion mechanism of Gu2AzT has been proposed.

High bulk density bicyclo-HMX and RDX crystal materials for use in plastic explosives, PBX and propellants

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Keywords: bicyclo-HMX; RDX; plastic explosive; spherical crystals; antisolvent.

To obtain high filling level of solids in plastic explosives, crystal materials were prepared by special crystallization technique. During continual addition of antisolvent to a solution of energetic material surface active agent Tween 20 was continually added. This proce-dure gave wide range of crystals (0,05-0,7 mm) having high bulk density (1,1-1,22 g/cm3). Tween 20 improves shape of crystals too. Obtained bicyclo-HMX is significantly less im-pact sensitive than starting material. Crystallized RDX and bicyclo-HMX were tested as a component of plastic explosives. High filling level of crystalline explosive (90-93%) was achieved.

Kinetic features of NTO/TNT mixtures thermal decomposition

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Keywords: thermal decomposition; 3-nitro-1,2,4-triazol-5-one; NTO; TNT mixtures; autocatalysis.

An experimental investigation of thermal stability of NTO/TNT mixtures was carried out in comparison with earlier studies of solid NTO thermal decomposition. Traditional manometric method to investigate the chemical kinetics of thermal decomposition was chosen for this study, in which pressure of gas decomposition products was measured in glass Bourdon manometer at isothermal conditions. Using this technique revealed some unexpected features of NTO decomposition. At 200-260oC, decomposition has obvious autocatalytic character, and fast pyrolysis of some derivative and/or vapors of NTO precedes to the autocatalytic stage. The crystal shape influences initial pressure growth, and preliminary heating at 180oC strongly enhances decomposition rate at 240oC, this relates especially to the autocatalytic stage. The dependence of global rate constant in Arrhenius coordinates is in fact more complex and includes the low-temperature section corresponding to much smaller activation energy. At 200-250°C first order kinetic constants of thermal decomposition of the crystalline NTO are evaluated to be Ea = 201 kJ/mol, log A = 15.5 (s-1), i.e. are in the range expected for the monomolecular thermal decomposition of nitrocompounds. Decomposition of NTO/TNT mixtures was investigated in the temperature range from 180oC to 260oC. TNT significantly increases the NTO decomposition rate but the reactions of the solved substance and the solvent media are not distinguishable. TNT pyrolysis appeared to be strongly accelerated by NTO addition. At 260oC auto-ignition of the NTO/TNT mixtures as for solid NTO is observed. At lower temperatures and large TNT contents the reaction proceeds in the violent regime with injection of the part of the reaction mass from the reaction vessel into membrane that results in sharp decrease in the reaction rate. NTO/TNT mixtures decompose much faster than both NTO and, moreover, TNT. It is proposed that a sort of NTO-TNT complex is formed that decomposes as a single compound. Reaction is autocatalytic and initial part of the fast pyrolysis is observed for NTO. The total volume of gases corresponds to the sum of gas evolved in NTO and TNT decomposition. The TNT-mixtures decompose faster than solid NTO, but the difference of the reaction rate is unusually small, within the range of one order. Perhaps, thermal decomposition of solid NTO is necessary to be considered as reaction of the liquid/quasiliquid state where the rate of decomposition is much higher than in the solid substance.

Recrystallization studies of triaminoguanidinium azotetrazolate

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Keywords: triaminoguanidinium azotetrazolate; crystallization; needle-like crystal.

Triaminoguanidinium azotetrazolate (TAGAZ) is an important and prospective compounds due to their high-nitrogen content and relatively high positive standard enthalpy of forma-tion. Crude TAGAZ after synthesis and purification in water is in form of long yellow nee-dles which are useless in propellant application. Solubility of TAGAZ in popular solvents like acetone, chloroform, diethyl ether, n- and 2-propanol, carbon tetrachloride is to low for effective crystals shape change. Recrystallization experiments were conducted by mix-ing of non-saturated TAGAZ solutions in NMP/H2O with selected anti-solvents. In typical experiment, solution of TAGAZ in NMP/water system was poured into stirred pure solvent. Solid precipitate was collected by simple filtration, dried and weighed. Triaminoguanidin-ium azotetra-zolate crystals with different morphology were successfully produced. The crystallization products were analyzed by using optical microscopy, DTA/TG and NMR techniques.

Recrystallization of hexanitrohexaazaisowurtzitane (HNIW) using halogen-derivative anti-solvents

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Keywords: CL-20; morphology; precipitation; friction sensitivity.

The effect of halogen derivatives of anti-solvents on CL-20 recrystallization process was studied for a number of organic anti-solvents to show that the crystals obtained differ in size depending on the anti-solvent used. Aliphatic halogen derivatives afford the crystals of rectangular shape, whereas their aromatic counterparts yield round-shape crystals. Different crystallization yield was observed for particular systems. Recrystallization of crude CL-20 allowed to reduce friction sensitivity from 60 N to ca. 110 N. Analysis of the properties of the CL-20 grains permitted to describe the effect of such factors as chemical and crystallographic purity and of the shape of crystals on CL-20 sensitivity.

Preparation and properties of 6,7,8,9-tetranitro-3,4-dihydro-2H-1,5-benzodioxepine (TNDX), a potential new high energy material

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Keywords: 6,7,8,9-tetranitro-3,4-dihydro-2H-1,5-benzodioxepine (TNDX); synthesis; spectra; X-ray crystallography; density; oxygen balance (OB); thermal analysis; HEM.

6,7,8,9-Tetranitro-3,4-dihydro-2H-1,5-benzodioxepine (TNDX) (molecular formula C9H6N4O10) has been shortly described in the 13-th NTREM Seminar and in present paper TNDX was selected for a more detailed research. The two stage method of synthesis was developed (yield =76%). The detailed structure of this compound has been investigated by X-ray crystallography. The experimental density 1,805 g/cm3 was determined by X-ray crystal analysis and it was comparable with obtained by computer calculations (1,799 g/cm3). The spectral properties (RAMAN,FT-IR, NMR) were explored. Calculated oxygen balance OB/CO2 = -53.31%) was almost similar to the OB of known HEMs, N-ethyltetryl (C8H7N5O8) or TATB (C6H6N6O6). This preliminary investigation suggests that TNDX (m.p.=185ºC) might be a potential high energy material with acceptable general proper-ties, however its thermostability is substantialy lower than the value determined previously for the nearest homologous tetranitroderivative TNBD (5,6,7,8-tetranitro-2,3-dihydro-benzodioxine (m.p. 286°C)

The study of heat and kinetics of nitration of 1,2,4-triazol-5-one (TO)

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Keywords: 1,2,4-triazol-5-one; kinetics of nitration; reaction heat; 3-nitro-1,2,4-triazol-5-one.

The heat effects of the nitration and dissolution processes of 1,2,4-triazol-5-one (TO) in an acidic environment were measured. The reaction calorimeter was used in the study. The kinetics of TO nitration in a 200 ml reactor was investigated by a UV-VIS spectrometry. A model of kinetics of synthesis of 3-nitro-1,2,4-triazol-5-one (NTO) was proposed and it was used to simulate the phenomena occurring in the calorimeter and in the reactor. The experimental data were compared with modeling results and parameters of the Arrhenius equation for synthesis of NTO with selected nitration mixtures were determined.

Thermal characteristics of hexamethylenetetraminedinitrate

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Keywords: hexamethylenetetramine dinitrate; HDN; RDX; thermal.

Hexamethylenetetramine dinitrate (HDN) is a rather weak explosive but it has been used as a precursor for the manufacturing of RDX, which is one of the most important secondary nitramine explosive. Nitrolysis reaction of HDN with HNO3, NH4NO3 and (CH3CO)2O is known as the KA Process for the production of RDX. The use of dinitrate salt of hexamine in KA process reduces the amount of HNO3 needed for the nitrolysis reaction. The objective of the paper is to determine the thermal characteristics of HDN, which undergoes violently defragration when heated or ignited, in order to investigate the additional applications in consequence of defragration behavior and described properties as an explosive.

A computational study on Tautomerism of NTO

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Keywords: NTO; tautomerism; explosive; DFT calculation; nitrotriazole.

NTO which is an insensitive high energy material is capable of exhibiting proton tautomerism. In the present study, various tautomeric forms of NTO and the related transition states are subjected to computational treatment at the level of B3LYP/6-311++G(d,p) and MP2/ 6-311++G(d,p). The stabilities follow the order of NTO>I>III>II was found (DFT and MP2). Additionally, some properties , including the ballistic ones, are calculated. It has been found that tautomers I, II and III have better detonation velocity and pressure than NTO, but II has slightly less maximum theoretical density.

Preparing and some properties of spheroid ε-HNIW

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Keywords: HNIW; crystallization; spherical chape; modifying agent; spheroidization.

In this work, based on the experience of obtaining spherical crystals of RDX and HMX by spheroidization (intensive mixing of slurry in a special vessel), spherical crystals of HNIW from two types of crystals were obtained. The crystals of the first type were obtained by evaporation crystallization and had bipyramidal shape. The crystals of the second type were obtained with use of modifying agent and had a round shape. X-ray analysis was carried out. The density of obtained spherical crystals of HNIW was determined. Infrared spectroscopy was used to confirm the polymorph and the absence of inclusions and modifying agent in the crystal structure. As a result of experiments on spherical crystals of HNIW was shown that the original morphology of crystals influences the final morphology of the crystals subjected to the process of spheroidization. The measured sensitivity of different morphology of HNIW to shock and friction showed that the lowest sensitivity to friction have crystals obtained during spheroidization.

Fire and explosion hazard of 5-nitro-2,3-dihydrophthalazine-1,4-dione and its derivatives

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Keywords: 5-nitro-2,3- dihydrophthalazine -1,4-dione; thermal decomposition; mechanism of decomposition; heating rate; nitrogen atmosphere.

The information about fire- and explosive properties of materials, used in technological proc-esses, is a base for development standards to provide fire- and explosion safety on the chemi-cal production. 5-amino-2,3- dihydrophthalazine -1,4-dione is used as a pharmaceutical com-position and a chemiluminescent indicator, used in organic synthesis and biochemistry. 5-nitro-2,3- dihydrophthalazine -1 ,4-dione and its sodium salt are used for its synthesis. The ar-ticle presents general fire and explosion hazard characteristics of these compounds, such as ignition temperature, auto ignition, flash, LFL (Lower flammability limit), received with the help of the OTP (the plant for testing of temperature characteristics of the fire risk) and glass explosive cylinder. It is concluded that the introduction of a nitro group in the structure of the compound instead of the amino group increases its fire and explosion hazard, and the intro-duction of sodium in the structure of single nitro compound leads to momentory flameless flash and increases flammability of dust. Also the article contains derivatograms of substances obtained at different heating rates. Derivatograms obtained in a nitrogen atmosphere can help to explain the mechanism of thermal decomposition. It is shown that the exothermal effect of decomposition is not associated with oxygen, concluded intramolecular decomposition.

Energetic ionic derivatives of 5,5'-dinitromethyl-3,3'-bis(1,2,4-oxadiazole)

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Keywords: oxadiazole; nitrogen-rich salts; explosives; synthesis; characterization.

The reaction of the 3,3´-bis(1,2,4-oxadiazolyl)-5,5´-bis(2,2´-dinitro)-diacetic acid diethyl ester with different nitrogen-rich bases, such as ammonia, hydrazine, hydroxylamine and triaminoguanidine causes decarboxylation followed by the formation of the corresponding salts (cation:anion stoichiometry 2:1). The reactions are easily performed at ambient temperature in H2O/MeOH mixtures and furnish qualitatively pure products showing characteristics of typical secondary explosives. The obtained compounds were characterized by multinuclear NMR spectroscopy, IR and Raman spectroscopy, as well as mass spectrometry. Single crystal X-ray diffraction studies were performed and the structures of all compounds at low temperatures were determined. The thermal stability was measured by differential scanning calorimetry (DSC). The sensitivities were explored by the BAM drophammer and friction test. The heats of formation were calculated by the atomization method based on CBS-4M enthalpies. With these values and the X-ray densities, several detonation parameters such as the detonation pressure, velocity, energy, and temperature were computed using the EXPLO5.05 code.

Theoretical and experimental research of the dynamics the forming process EFP projectiles performed of powder metallurgy

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Keywords: EFP; ANSYS-Autodyn 2D; powder metallurgy.

The paper presents the results of the theoretical - experimental optimization of a small-caliber EFP charges (45mm diameter). The results of computer simulation of the process of the formation of the projectile and then drive the spherical and lens liners cumulative were introduced. The simulations allow to observe phenomena associated with the penetrator formation and multilayered armours perforation. Numerical analysis was performed in the ANSYS - AUTODYN 2D. All the polygon tests confirmed the data obtained from the numerical analysis. Experimental part was registered by using fast camera recorders. A few pictures of selected EFP projectiles charges and multilayered barriers perforation were presented. The most important conclusion is that the tests which were carried out confirmed the authors' assumptions that there is a possibility of constructing EFP charge liners of metal powder (based on copper, tungsten, aluminum) with a comparable (similar) ability to perforation of steel targets just like for EFP charge liners made of solid metal.

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The numerical modeling methods in the research of the linear charges

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Keywords: numerical modeling; shaped charge.

Linear shaped charges are used in the mining industry, police and army. Methods of computer modeling can be used more widely if geometrical and material parameters are selected more accurately. The distance of a shaped charge from the target is one such parameter that can be optimized using computer simulation methods. The geometrical model of a shaped charge impact on the target was developed and verified against real, experimental configurations. The application of these methods can shorten the time spent selecting the parameters and can minimize costs.

Preparation, crystal structure, thermal decomposition and explosive properties of a novelty energetic compound $[Cu(1,1'\text{-azobis}(1,3,4\text{-triazole}))_3(ClO_4)_2\cdot H_2O]_N$

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Keywords: 1,1'-azobis(1,3,4-triazole); Cu(II) energetic compound; crystal structure; thermal decomposition; sensitivities.

The novel energetic coordination compound [Cu(1,1'-ATZ)3(ClO4)2•H2O]n (1, 1,1'-ATZ=1,1'-azobis(1,3,4-triazole)) was synthesized and characterized by elemental analysis and FT–IR spectrum. In addition, vibrational spectroscopy of 1,1'-ATZ group has been investigated at DFT-B3LYP/6-311++g(d,p) level of theory by performing with Gaussian03 program. The crystal structure was determined by X–ray single crystal diffraction. The crystal of 1 belongs to the monoclinic system, space group P21/n, with cell parameters: a=8.2861(17) Å, b=20.232(4) Å, c=8.6664(18) Å, β=92.742(3)°, V=1451.2(5) Å3, Z=2, Dc=1.810 g•cm-3. The central Cu(II) cation is coordinated by six N atoms to form a six-coordinated and distorted octahedral structure. Under nitrogen atmosphere with a heating rate of 10 K•min–1, the thermal decomposition contains two main exothermic stages in the DSC curve corresponding to TG–DTG curves. The non–isothermal kinetics parameters were calculated by the Kissinger's method and Ozawa's method, respectively. The critical temperature of thermal explosion, entropy of activation ($\Delta S\neq$), enthalpy of activation ($\Delta H\neq$), and free energy of activation ($\Delta G\neq$) were calculated. The sensitivities properties were also determined with standard methods and the results showed that 1 had very higher sensitivities and it had an extreme potential application as energetic material.

Polyvinylpyrrolidone complexes for RDX coating process

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Keywords: PVR; RDX; coating; insensitive.

The reduction of sensitivity on impact and friction behaviors of explosive particles by coating with a polymeric material as shock absorber/barrier is one of the key application in the development of insensitive munitions (IM). The necessity and importance of reduced sensitivity for explosive materials has become driving force for researches on polymeric materials, which are compatible and inert for target applications.

Polyvinylpyrrolidone (PVP) is a water soluble polymer synthesized from n-vinyl pyrrolidone monomer. Because of polar aprotic lactam ring in PVP structure, it has strong affinity with polar RDX molecule and applicable for crystallization of RDX. PVP is also suitable for coating of energetic particles. PVP crosslinks with polyacids to form complexes, which are insoluble in water.

The objective of the paper to investigate the PVP based complexes for coating of RDX particles. The embedded RDX particles into PVP based complexes were characterized by XRD spectrometer and thermal analysis techniques.

NTO-graphene nanocomposites

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Keywords: nanocomposite; processing; performances; high explosives.

Hazardous properties of state-of-the-art explosives and polymer bonded explosives have conducted in the past years to the necessity of considering new explosive formulations. RDX or HMX are classic high explosives that tend not to qualify any more in terms of sensitivity and processing. In this regard, taking into account the processing potential of the 3-nitro-1,2,4-triazol-5-one (NTO), there were considered NTO-based composites that include graphene. The tests performed regarding the extrusion and moulding safety and easiness, together with the functioning performances, show that it is possible to include 1% graphene without radically modifying the main explosive performances, meanwhile increasing the processing capability.

The study of TVS for RF protection of SCB initiators

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Keywords: initiators; SCB; TVS; RF.

The TVS chips are chosen for RF protection of SCB initiators, and its protection principles are analyzed in this paper. The affection of TVS parameters on electro-exploding performances of SCB initiators are studied by capacitor discharge experiment. The laws of TVS parameters effecting on RF protection of SCB are investigated by electromagnetic environment experiments. The results show that there is a certain delay in SCB burst time due to TVS shunts current after breakdown when burst voltage of SCB is higher than breakdown voltage of TVS chips. The TVS with a smaller parasitic resistance and a larger capacitance can significantly enhance RF protection capability of SCB initiators.

The mild detonating fuse charged with energetic SY cocrystal

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Keywords: mild detonating cord; mild detonating fuse; high explosives; cocrystal.

SY is an energetic cocrystal which is composed of ethylenediamine perchlorate and triethylene diamine perchlorate. It possesses both performences of primary explosive and those of high explosive. SY is used in this paper as the charge of mild detonating fuse after modifying it with 2% MoS2, 3% powder Al and 1% shellac. Seven sizes of diameter were moulded from 2.00mm to 6.00mm. The VOD and loaded density to each of them were determined individually. The outstanding advantage of such detonating fuse lies in mutually initiating when contact in “T” shape.

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The End