Abstracts of the 17th Seminar on

New Trends in Research of Energetic Materials

NTREM

Pardubice, April 9–11, 2014

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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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Contents

Part 1

Invited Lectures

Presentations

Part 2

Posters

Preface

This seventeenth seminar NTREM takes place in the year of 20^{th} anniversary of the University of Pardubice foundation; today's Faculty of Chemical Technology, existing in Pardubice from 1950, has established this University in 1994 together with that time new Faculties of Transport and of Economics and Administration. Ever since then the University continued to grow into the present state with seven Faculties educating roughly 11 thousand students.

This quick development however resulted in steep fall of the University to the 1409^{th} position in the World ranking of Universities. In 2013 almost three quarters (74%) of the University scientific performance was produced by our Faculty of Chemical Technology. Our Seminars NTREM perceivable positively contribute to evaluation of the mentioned Faculty and subsequently University.

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 enabling attendance of wide range of participants including students and young researchers not yet well financially covered by research grants. For this support we would like to thank all of our sponsors that have decided to support us again this year. Special thanks go to Office of Naval Research Global, Prague; 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, OZM Research; Hrochův Týnec, Institute of Shock Physics at London Imperial College, London; Nicolet, Prague; Centre for Technology and Knowledge Transfer, University of Pardubice; Parr Instrument GmbH, Frankfurt; STV Group, Praha; Poličské strojírny, Polička; IHAS, Ostrava. 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 seventeenth seminar in the second half of April 2014 at the Aula Magna of our University.

Pardubice, March 10^{th}, 2014

Zeman

Svatopluk Zeman

Invited Lectures

Recent efforts in heterocyclic chemistry

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Keywords: oxadiazoles.

Energetic furazan 3,4-bis(trinitroethylamino)furazan (BTNEDAF) was synthesized in 70 % yield. BTNEDAF was characterized as an energetic material in terms of performance, mechanical sensitivity, and thermal stability. BTNEDAF was crystallized from various solvents resulting in multiple polymorphs with varying densities. Some of these polymorphs were characterized with respect to their sensitivity properties. Additionally, the performance of these different polymorphs were calculated using the EXPLO5 code. BTNEDAF was also characterized by vibrational spectroscopy, multinuclear NMR spectroscopy, elemental analysis, scanning electron microscopy (SEM) and calorimetric experiments.

Theoretical investigation on developing smart eutectics by phase diagrams and co-crystals

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Keywords: eutectics; co-crystal; phase diagram; melting points; hygroscopic.

The cast explosives with TNT as the liquid carrier is currently the most widely used military composite explosives. However, in the long-term utilization there still exists many problems affecting the safe use of arms and ammunition, such as permeability, voids, brittleness, etc. Then, study on developing TNT substitutes with excellent comprehensive performance focus many scientists' attention. Characterized by low cost, good safety and high energy, the eutectics based on methyl-nitroguanidine (MeNQ) have been proposed as potential substitute for TNT recently. The first formulation of MeNQ-based eutectic system with mass ratio of MeNQ/NQ /AN/AP=43.5/10.5/10/36 was proposed by Michael in 1990 and had been utilized as a component in AFX-453 cruise missile. However, the melting temperature of this formulation (100 oC) is too high to be applicable to vapour melt-cast technology, and both the mechanical performance and safety need to be enhanced. Most importantly, serious hygroscopic is still needed to be solved. We have developed novel MeNQ-based eutectic system composed of five components with mass ratio of MeNQ/NQ/AN/HN/AP = 37.8/9.1/ 31.3/3.1/8.7, the properties of which is much better than that of Michael. In this paper, we studied the relationship between the various components in the novel MeNQ-based eutectic, to improve hygroscopic and lower the melting point. Firstly, the binary phase diagram with two eutectic points was deduced from the Van't Hoff's Equation. And the experimental and computation results of T-X phase diagram of MeNQ/AN binary system agree with each other very well. Using the phase diagram we explained why Michael chose those distribution ratio, that is, between the eutectic point and the molar ratio of co-crystal. And we investigated the structures of the reported energetic co-crystals. Finally, we obtained accurate phase diagram of the components by fewer experiments, and provided guidance for optimizing the distribution ratio of MeNQ-based eutectic system.

Calculation of detonation velocity and pressure of individual and composite explosives

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Keywords: detonation parameters; calculation; explosive; aluminum; oxidizer.

The regressive analysis of the factors of chemical composition and structure influence on the detonation velocity was conducted at the example of the experimental data for 160 individual and composite explosives with various densities (in total of 460 experiments). As the result of the analysis, the verification of the available data for the detonation velocity and pressure was estimated and the interpolation equations for calculation of the detonation velocity and pressure, as well as the isentrope exponent were received. The applicability of the calculation equations for estimation of detonation parameters for the explosive compositions containing inorganic oxidizers and metals is shown.

Interaction of TNT with certain bioactive molecules

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Keywords: TNT; bioactive molecules; interaction.

Please fill in (or paste) your abstract here. Use about 300 words.

Interaction of TNT with Certain Bioactive Molecules

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Abstract

TNT having three electron withdrawing nitro groups constitutes an electron depleted ring system which is capable of forming π-complexes with certain electron rich systems, if steric requirements are fulfilled. In the present study various biologically active compounds were tested whether they form π-complexes with TNT. Of these, melatonin, N-acetyl serotonin, epinephrine, norepinephrine, estrone and folic acid were found to be undergoing π-complex formation. Computationally some of their properties have been investigated at the DFT level of theory (B3LYP/6-31G(d,p)). TNT is a harmful stuff indeed and maybe the most of the cases the first initiative interaction is of π-type complex formation.

Presentations

Synthesis and properties of 4-azido derivatives of [3,3’:4’,3”]-ter-1,2,5-oxadiazole

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

The results of our studies concerning synthetic routes of 4-azido-4”-R-substituted-3,3’:4’,3”-ter-1,2,5-oxadiazoles preparation, their energetic properties and reactivity are presented. 4,4”-Diazido-3,3’:4’,3”-ter-1,2,5-oxadiazole and 4”-azido-3,3’:4’,3”-ter-1,2,5-oxadiazol-4-amine were prepared by diazotization of 3,4-bis(4’-aminofurazan-3’-yl)furazan by nitrosylsulhuric acid in concentrated sulphuric acid with subsequent treatment of bis-diazonic salt solution obtained by sodium azide. Mechanism of 4”-azido-3,3’:4’,3”-ter-1,2,5-oxadiazol-4-amine formation from bis-diazonic salt is suggested. The alternative pathway for titled compounds synthesis includes nucleophilic substitution reaction of nitrogroup(s) in 4,4”-dinitro-3,3’:4’,3”-ter-1,2,5-oxadiazole (3,4-bis(4’-nitrofurazan-3’-yl)furazan (BNTF)) and 4”-nitro-3,3’:4’,3”-ter-1,2,5-oxadiazol-4-amine, respectively, by the azide one. 4-Azido-4”-nitro-3,3’:4’,3”-ter-1,2,5-oxadiazole was prepared by oxidation of aminogroup of 4”-nitro-3,3’:4’,3”-ter-1,2,5-oxadiazol-4-amine by 35% hydrogen peroxide in concentrated sulphuric acid.

Influence of the shape of explosive charges on the pressure field

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Keywords: shape effect; emulsion explosive.

A majority of scientific articles dealing with the detonation of explosive charges and its surrounding effects supposes that the charge is spherical and centrally initiated. Yet, when discussing the shock wave effect, the charge shape and the location of initiation are as important as the composition or the mass of the considered explosive. Specifically close to the charge (Z < 4 m/kg1/3), the shape may cause significant modifications of the peak overpressure and the first positive impulse compared to the prediction developed for spherical charges. A series of experiments has been carried out, using an ammonium nitrate based emulsion explosive, TNT and C4 charges in order to understand and quantify the shape effect. Spherical charges and cylindrical ones with different length-to-diameter (L/D) ratios ranging from 1 to 14.8 have been fired. The initiation was always central. Pressure in the median plane has been recorded for reduced distances between 0.5 and 5.5 m/kg1/3. All charges were unconfined. Spherical results have showed an excellent agreement with some references as CONWEP or the Kinney-Graham model. The expected change of the peak overpressure and the first positive impulse in the median plane was observed, directly linked with the L/D ratio. Peak overpressure magnifications of up to 2.5 have been measured. The dimensions of the zone within which there is an increase of the shock wave effect have been determined as well. A similar behavior for the pair TNT/C4 has been demonstrated; but a clearly different behavior has been observed for the emulsion explosive. In addition to the potential role of the velocity of detonation, we assumed the non-ideal detonation behavior of such an explosive induced a distinct shape effect. A comparison with numerical simulations has confirmed the conclusions on TNT and C4 charges.

Combustion of metal-containing condensed heterogeneous systems with the use of matal sulphates and carbonates

Alexander Beliakov, Anna Khairullina, Evgeniy Belov, Alexander Korobkov

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Keywords: sasha.

Possibility in principle to use mixtures of sulphates and carbonates containing high-energy ingredients for making commonly used articles based on condensed heterogeneous systems is shown. Patterns of thermic interreacting of metal sulphates and carbonates with combustible constituents are investigated.

Pyrotechnic compositions based on calcium sulfate for processing of oil wells

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Keywords: sasha.

The mechanisms of combustion process of the metal-containing compositions on the basis of semi-water calcium sulfate in the conditions close to borehole ones were researched. Opportunity of using of the effective pyrotechnic structures for oil well treatment in purpose of increase of oil producing was estimated.

Application of group interaction modelling to the shock Hugoniots of double-base propellants

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Keywords: group interaction modelling; double base propellant.

Group interaction modelling (GIM) is a method used for predicting the thermochemical behaviour of polymers from their fundamental structure (Porter D. , 1995). The approach has a quantum mechanical basis and does not rely on empirical fitting of data. The GIM technique been applied to predict the Shock Hugoniots of several double-base propellants. These predictions have then been compared to the Hugoniots obtained through single-shock plate impact loading. The results of these investigations are important when considering performance and life cycles of propellants. In particular, GIM enables predictive modelling and evaluation of key properties of new formulations, without the need to resort to lengthy and expensive experimental testing schemes.

Recent achievements in kinetic modelling of stabilizer consumption and molar mass degradation in NC-based propellants

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Keywords: nitrocellulose; mean molar mass; molar mass distribution function; degradation of nitrocellulose; stabilizer consumption; reaction kinetic description; bimolecular stabilizer reaction.

It seems that nitrocellulose will continue to survive as energetic polymeric binder in gun propellants. Also in modern types of propellants it is not replaceable, which use solid crystalline fillers as RDX to adjust the energetic content, the burning temperature and the force or specific energy of a propellant formulation and last but not least the sensitivity against thermal threat and shock impact by bullet and fragments. With nitrocellulose stabilizers must be used to prevent it against the autocatalytic decomposition. However, the slow intrinsic decomposition cannot be prevented and therefore a slow degradation happens always, which leads to stabilizer consumption and the splitting of the NC chains. The last effect means molar mass degradation of NC. Both phenomena are irresolvable coupled. In splitting off the NO2 radical from the nitrate ester groups R-CO-NO2 the remaining radical function written as R-C-O stabilizes itself by molecular rearrangement of the anhyroglucopyranose ring and by splitting-off stable small molecular species. This means molar mass degradation happens by destruction of chain units and not be mere bond splitting between chain units. This is in accordance with the well observed phenomena of mass loss with NC. Several kinetic descriptions of stabilizer consumption are available, which have proven to be acceptable applicable, but mostly in considering restraints and demanding the use of a simplified model base. In other words the stabilization reaction is still a not easy to handle one in reaction kinetic terms. But a reasonable solution can be achieved by starting with the basic reaction scheme Eq.(1), which shows that the stabilization reaction is a bimolecular one. NC ->(knc) P + NCr S + P ->(kso) S-P Eq.(1) The elaboration of this reaction scheme results in an equation for the bimolecular stabilizer reaction, whereby the preceding production of P (=NO2) from NC is included, because the concentration of P is not constant with time. Molar mass decrease of NC caused by random chain scission is describable with models based on the averaged characterizing parameters of the molar mass distribution (MMD) functions. The correct distribution function in terms of reaction kinetics is the one which counts the numbers (or mols) of polymers in the molar mass fraction M+dM. Based on this models of random chain scission and random chain scission with chain recombination are discussed.

Influence of firing temperature on ballistic, mechanical and sensitivity of gun propellants

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Keywords: firing temperature; gun propellant; ageing; ballistic firing; closed vessel tests; impact test.

Initial firing temperatures play an important role on the combustion rate of propellant. In gun propellants, initial temperature is a key factor for both, accuracy and safety. Ideally, the initial temperature of the propellant should not influence the ballistic properties of the round. Nevertheless, constant initial temperature coefficients can not be achieved easily. This work focuses on the influence of the firing temperature on the ballistic properties, the mechanical integrity and the sensitivity to impact of nitrocellulose based propellants. Combustion rates have been determined with closed vessel tests. Ballistic properties have been investigated by firing 5.56 cartridges. The propellants have been conditioned at temperatures ranging from -54°C to +71°C before firing. The largest temperature coefficient is observed in the range of the high temperatures. The temperature sensitivity of the peak pressure in the combustion chamber can not be fully explained by the changes in burning rate and by the test results from the closed vessel. We speculated that the mechanical behaviour of the propellant grains under low and high temperatures influences also the overall ballistic properties of the round. Impact tests with propellants conditioned at low and high temperatures permit to investigate their mechanical strength under extreme temperatures and to better understand the propellant performance during firing. Tests on aged propellants have been conducted as well.

Explosives at extreme conditions: polymorphism of 2,4-dinitroanisole

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Keywords: 2,4-dinitroanisole; polymorphism; high-pressure; X-ray diffraction; neutron diffraction.

2,4-dinitroanisole (DNAN) is an energetic material, developed as an insensitive replacement for TNT in melt-cast explosive formulations. While DNAN-based formulations demonstrate greatly reduced sensitivity to accidental initiation compared to those using TNT, issues remain with the replacement of TNT with DNAN. For instance, DNAN-based formulations have demonstrated catastrophic levels of irreversible growth during heat-cycling, with volume increases of up to 15% reported.

In order to investigate the role of polymorphism in the irreversible growth of DNAN, high-pressure and variable-temperature neutron and x-ray diffraction studies have been performed. The phase diagrams of both form -I and -II of DNAN have been explored for the first time.

In the case of DNAN-II, two high-pressure phase transitions were found, first to DNAN-III and then at higher pressures, DNAN-IV. In addition, variable temperature studies demonstrated that the DNAN-II to DNAN-III transition also occurs when DNAN-II is cooled. The thermal expansion of the DNAN-II/III lattice was investigated, demonstrating that an abrupt change in the thermal behaviour of lattice parameters occurs at the DNAN-II/III transition. From these combined crystallographic studies, the structure of DNAN-III has been solved, showing it is closely related to DNAN-II.

In the case of DNAN-I, a transition to form III was not found during variable temperature studies, as may be expected given the dissimilarity between the DNAN-I and DNAN-II structures. High-pressure neutron powder diffraction studies, however, demonstrated that DNAN-I does transform at high-pressure to a new form (DNAN-V) that is distinct from DNAN-II,-III or -IV. Warming of DNAN-V causes transformation to another new phase, DNAN-VI, which exhibits a highly planar structure similar to triaminotrinitrobenzene (TATB). Comparison of the behaviour of DNAN-I and –II indicates that the kinetic form, DNAN-II, is the denser phase under all conditions studied. This work highlights the importance of crystallographic techniques in order to understand the polymorphism of energetic materials.

Scale-up and characterisation of 3(5),4-dinitropyrazole (DNP) for its use as a melt-cast matrix

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Keywords: 3(5),4-dinitropyrazole; synthesis; scale-up; characterisation.

3(5),4-Dinitropyrazole (DNP) is under current evaluation as a new matrix in melt-cast charges. The first steps in this work were the scale-up the synthesis and the characterisation of the material. The original synthesis includes three steps with isolation of all intermediates. This procedure was not suitable for scale-up and considerable effort was put into the development of such a method. This resulted in a batch-wise synthesis and successfully production of one kilogram of the desired product. One improvement was that the isolation of one intermediate could be avoided. A new recrystallisation method was developed, which allowed very pure product to be obtained without the use of benzene. Characterisation of the product provided data on its purity, acidity, thermal stability, sensitivity, and compatibility to different fillers.

Synthesis of stabilizers with plastizing properties for nitrocellulose propellants

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Keywords: stabilizer; nitrocellulose; plasticizing properties; synthesis; characterisation.

Propellants containing nitrocellulose (NC) continuously decompose due to an autocatalytic effect caused by the nitrous gases released from the decomposition of NC itself. To prevent autocatalysis, stabilizers are added to NC/NG propellants. The action of the stabilizers is to trap the nitrous gases and form stable compounds, which prevents or delays this process. The most common stabilizers are aniline derivatives. Due to this functionality, they can form potentially toxic and/or carcinogenic nitrosamine derivatives during prolonged storage. This prompted our efforts towards new compounds without any amine moiety.

FOI has developed a new class of stabilizers with plasticizing properties. These compounds are either ethers or esters of triethylene glycol. Examples, with one from each subgroup, are di(2,6-dimethoxyphenyl) triethyleneglycol ether and triethyleneglycol di(2,6-dimethoxybenzoate), respectively. This paper describes the concept of this class of plasticizing stabilizers, the synthesis of these compounds and a basic characterisation. The latter includes an evaluation of their stabilizing effects on NC.

Investigation of commercial precursors for the synthesis of liquid nitroesters

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Keywords: EGDN; liquid explosive; precursor; activation energy; impact test.

Currently, liquid explosives pose a potential threat, either as main explosive charges or as sensitizing agent in readily available explosive materials (ammonium nitrate, for instance). An important phase in the assessment of this threat is to investigate the various synthesis paths leading to their manufacture and to evaluate the potential use of readily purchasable precursors. The aim of this work is to assess the feasibility of the synthesis of ethylene glycol dinitrate (EGDN), a liquid explosive nitroester, using commercially available precursors. The characteristics of the synthesis process (ease and yield of production, ..), the chemical properties of the synthesized product (purity, spectra. . .) and its detonic properties (sensitivities, detonability, . . .) are investigated. Comparisons are drawn between these products and products obtained using laboratory ingredients. Three ingredients have been used: 1) ethylene glycol for laboratory use, 2) water based coolant and 3) ethylene glycol extracted from the coolant fluid. The chemical composition and purity of the synthesized liquid explosive is analyzed by gas chromatography-mass spectroscopy (GCMS), and infrared spectroscopy (IR). Differential scanning calorimetry (DSC) analysis permits to assess the decomposition energy and activation energies. Ozawa and Kissinger models are used. Correlations are made with the sensitivity to impact of the explosive product. Minor discrepancies are observed. Detonic properties of the pure synthesized products and formulation with some other explosives have been tested. Potential use as priming charge or as main charge is assessed.

Phase transitions in binary system: nitrocellulose + stabilizer

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Keywords: nitrocellulose; stabilizer; DSC; enthalpy of melting.

Stabilizers were added to nitrocellulose propellant during production. The binary systems including nitrocellulose (NC) which contains 13.2% nitrogen and stabilizers: centralite 1 (C1), diphenylamine (DPA), 2 – nitrodiphenylamine (2-NDPA), N – nitrosodiphenylamine (N-NODPA) were investigated in the whole range of mass fraction. Differential Scanning Calorimetry (DSC) and Scanning Electron Microscope (SEM) were used for research. In the system NC+C1 the process of melting was observed for mass fractions of NC $x_{wNC} < 0,32$ for short time between measurements made on the same sample and x_{wNC} for long time between measurements made on the same sample. The process of melting was observed for mass fractions of NC $x_{wNC} < 0,92$ for short and long time between measurements made on the same sample in the system NC+DPA, $x_{wNC} < 0,77$ for long time between measurements made on the same sample in the system NC+2-NDPA and $x_{wNC} < 0,82$ in the system NC+N-NODPA for short time between measurements made on the same sample. In the range of mass fraction, where melting of low molecular compound did not appear, molecules were in the liquid phase and strongly bonded with the NC matrix. On the basis of n was determined if low molecular compound penetrated internal or external NC structure.

Comparative analysis of TKX-50, MAD-X1, RDX and HMX blasting performance in one-, two- and three-dimensional geometry

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Keywords: TKX-50 explosive; MAD-X1 explosive; detonation parameters; copper layer; system geometry; blasting performance.

Such new explosives as TKX-50 (bishydroxylammonium 5,5'-bis(tetrazolate-1N-oxide)) and MAD-X1 (dihydroxylammonium 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate) are among the most promising explosives today and each of them can be regarded as a possible replacement for RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and some other industry and military explosives. They both are by their nature nitrogen-rich ionic salts, have very high detonation performance and low thermal and mechanical sensitivity and also can be easily synthesized in industrially viable processes. The safe preparation and characterization of these new explosives using many structural and physicochemical diagnostic methods indicate that they outperform the majority of all other commonly used explosive materials by its technological and performance properties. A wide study of performance characteristics of this material is being conducted using both experimental and calculated methods. In this work a comparative analysis of blasting performance was conducted for TKX-50, MAD-X1, RDX and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclohexane) in the conditions of one-, two- and three-dimensional geometry. Plates, cylindrical shells and spherical shells made of copper were accelerated by detonation of contacted with them charges of considered explosives. The ratio of thicknesses for explosive and copper layers was changed in the range of 2.5-10. Calculated results on determination of detonation parameters and equations of state for detonation products were obtained with the use of computer program EXPLO5 V.6.01 for all considered explosives. Calculations were fulfilled both for explosive materials having the maximum crystalline density and for porous ones right up to 50 % in volume. Influence of the content of plastic binder polyisobutylene right up to 20 % in volume on all specified properties of explosives was examined too. Calculated results on blasting performance of different explosives in various initial states were obtained with the use of computer hydrocode UP-OK. Equation of state for detonation products was used in the form of Zubarev. Possible effect of fracture in copper plates and shells did not take into account. A rather complete comparative picture of blasting performance for all examined explosives was obtained. It was shown that in all cases blasting performances of TKX-50 and MAD-X1 explosives were higher than of RDX and lower than of HMX explosives.

Surface grafting with energetic glycidyl azide polymer (GAP): an efficient way to process ultrafine aluminum powders

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Keywords: aluminum powders; explosive; surface grafting; glycidyl azide polymer.

Aluminum powders are common contributions in explosives to increase detonation energy and work capacity. However, its application was limited by the following reasons: unstable, phobic to organic binders, and being difficult to disperse. To address all these issues at once, the ultrafine aluminum powders were treated by surface grafting with energetic glycidyl azide polymer (GAP) via consecutive TDI-GAP reactions. After surface grafting with GAP, the surface properties of the aluminum powders were significantly changed. The surface exhibits typical hydrophobic character and effectively prevents the aluminum from water oxidation under severe aging conditions (70°C hot water). Therefore, it provides an efficient way to protect ultrafine aluminum powders and a potential route to prepare aluminum explosive formulations using ultrafine powders. The aluminum powders before and after surface grafting was characterized by FTIR, XPS, TG, SEM and surface contact angle measurement.

Synthesis and hydrolysis kinetics of a six-memebered heterocyclic borate ester

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Keywords: heterocyclic borate ester; bonding agent; online infrared spectrum; hydrolysis kinetics.

Borate ester become an important interfaces modifying agent which can reinforce the mechanical and processing property of energetic composites. Thus, we synthesized a borate ester with a six-membered ring by borate acid, 1,3-propylene glycol and 1,2,4-butanetriol through two steps reaction. Chemical structures of the compound were characterized by Fourier transform infrared (FT-IR) spectroscopy. Then the structure of the borate ester was further confirmed by boron nuclear magnetic resonance (^{11}B NMR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The hydrolysis kinetics of the synthesize borate ester in water and in air was investigated by online infrared spectroscopy. The hydrolysis kinetic model was established. The results show that the hydrolysis reaction of the synthesized six-membered ring borate ester followed a pseudo-first-order kinetics on above two conditions. The reaction rate constant of the borate ester in water and in air is $2.06\times10^{-6}\mathrm{s}^{-1}$ and $1.01\times10^{-3}\mathrm{d}^{-1}$, respectively. The half life in water and in air is 93.5 hour and 686 day, respectively. The hydrolysis kinetics results provide the theoretical foundation for revealing the hydrolysis mechanism of borate ester.

Optical diagnostics to study impact initiation mechanisms in modern energetic materials

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Keywords: HMX; petn; llm-105; optical-diagnostics.

Understanding impact sensitivity and subsequent impact initiation is a key element of explosive materials research. A number of standardised tests exist, such as the Rotter or BAM impact tests, which allow the relative sensitivity of different materials to be characterised. However, these provide little insight into the underlying behaviour of the material. The use of a periscopic glass-anvil drop-weight apparatus has proven to provide valuable information about the hotspot initiation of many materials [1,2]. In this paper we describe experiments which apply the technique, in conjunction with high speed video and additional diagnostic instrumentation, to study the mechanism of initiation of modern explosive materials such as TATB, LLM-105, Fox-7, HMX, RDX and PETN.

Novel energetic bistetrazole-N-oxides - synthesis and characterization

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Keywords: energetic materials; tetrazoles; N-oxide; crystal structure; nitrogen-rich.

Investigations on the density and performance increment of tetrazole-N-oxides exemplified by bistetrazole-N-hydroxides and bistetrazole-N-oxides are reported. For this purpose novel bistetrazole derivatives such as 5-tetrazolyl-(1-hydroxytetrazole) and 5-tetrazolyl-(2-hydroxytetrazole) as well as their nitrogen-rich ionic N-oxides (e.g. hydroxylammonium, hydrazinium) were synthesized and characterized using low temperature single crystal X-ray diffraction. All compounds were investigated by NMR and vibrational (IR, Raman) spectroscopy, mass spectrometry elemental analysis and DSC or DTA. The sensitivities towards impact, friction, and electrical discharge, were investigated using BAM standards and a small scale electrostatic discharge tester. The detonation parameters were calculated using the EXPLO5.06 code. Heats of formation were computed by the atomization method based on CBS-4M electronic enthalpies. The density, performance, thermal stability and sensitivity of the newly synthesized compounds were compared to known compounds such as 5,5'-bistetrazole, 5,5'-bis(1-hydroxytetrazole) and 5,5'-bis(2-hydroxytetrazole) as well as the energetic salts thereof.

Methods for preparing spheroidal particles of 3-nitro-1,2,4-triazol-5-one (NTO)

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Keywords: NTO; crystallization; properties.

The paper presents an overview of methods of recrystallization of 3-nitro-1,2,4-triazol-5-one (NTO) with particular emphasis on recrystallization aimed at obtaining spheroidal particles with low porosity. Effect of selected solvents and surfactants on the recrystallization results was checked. The product in the form of spheroidal particles was obtained for the selected solvent-surfactant system. The bulk density, surface area, size distribution, sensitivity to friction and impact were tested for the spherical NTO and thermal analysis was also performed.

Pseudopolymorphic solvates as potential energetic materials

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Keywords: CL-20; HMX; water; molecular crystals; solid composite propellants; ballistic efficiency.

It was found that there are cases when molecular crystals composed of relatively large molecules have rather spacious inner cavities where a small-sized molecule may be placed with no change of the crystal lattice parameters. Among known energetic compounds, the most interesting cases of this kind are γ-HMX and α-CL-20. These substances can hold water molecules in structural cavities of crystals (in α-CL-20 theoretically up to 6, really up to 4-5 mass %, and γ-HMX theoretically up to 2.9, really up to 2.5 mass %). So the same volume of the unit cell contains more molecules, consequently the density increases as compared with water-free products. As a result, the ballistic efficiency of solid composite propellants would increase too (despite the specific impulse decreases a bit), whereas the combustion temperature would decrease as well as impact and friction sensitivity. The size of cavities in the crystal structure of α-CL-20 makes it possible to place there not only water molecules, but also some other, larger ones (e. g. hydrazine). It may result in a higher increase the ballistic efficiency of the propellant based on these co-crystallisates as compared with the crystalline hydrate

Preliminary estimation of the effectiveness of new and predicted energetic compounds as oxidizers for solid composite propellants

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Keywords: solid composite propellants; oxidizer; energetic parameters estimation.

Recently everywhere a lot of scientific teams look for new energetic compounds, able to raise (even a bit) solid composite propellants energy. Mainly it concerns potential oxidizers, because they fill the most mass portion, usually higher than 50%. If other ingredients (components of binder, different additives etc) have remarkable higher energetic parameters it does not affect so strongly the energy of the total formulation because of low content of these ingredients. As the energy level of inorganic oxidizers is almost over, the area of most investigations is high-enthalpy organic compounds, containing additionally some oxidizing fragments. It is known that every oxidizer is more effective for the definite kinds of propellants, some of oxidizers are more effective in formulations with metals as combustible, other ones - in formulations with no metal etc. It depends on the element content of the oxidizer and its enthalpy of formation, briefly there is no simple answer on the question, what oxidizer is the best. unfortunately in many journals, publishing papers on energetic materials, there is a precept for authors of new energetic compounds to furnish the value of the specific impulse (Isp) of these newly obtained substances (when they fill 100% of the formulation), or so called "relative" impulse Irel as compared with HMX. This idea is too harmful, because the researcher may lose the correct solution - there are no solid composite propellants containing one compound only. In the lecture it will be shown (basing on a real papers) how such a method (comparison of the Irel values) may give a wrong conclusion. Simple methods for preliminary adequate estimation of the effectiveness of new and projected energetic compounds as oxidizers will be demonstrated in the lecture

Simulation method for deflagration to detonation transition in energetic materials

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Keywords: deflagration to detonation; energetic materials; numerical simulation.

The phenomenon of the deflagration to detonation transition is of great importance for the safety of energetic devices in application. Experimental explorations have been or will be the major effective ways for the research, but numerical simulation seem to become more and more emergent for addressing this subject. This paper follows the basic framework of Baer and Nunziato multiphase flow theory to establish the governing equations as well as auxiliary equations needed in the simulation. A two-step Eulerian difference scheme is utilized to solve the governing equations system. The auxiliary equations of state for the solid and gaseous phases involved in the simulation are chosen to be Jones-Wilkins-Lee and Mie-Gruneisen forms respectively. The choices are made on the basis of their popularities in the pertinent research fields. Computational example of a packing column of HMX grains with 70% maximum theoretical density is presented to demonstrate the efficiency and accuracy of numerical procedures. Computational results clearly shows the development of the deflagration as well as its transitional tendency to detonation. Keywords: energetic materials; deflagration to detonation; numerical simulation; Eulerian difference scheme; two-phase compressible flow

Energetic co-crystals – structural studies of nitrotriazolone salts and co-crystals

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Keywords: co-crystal; crystal engineering; salts; NTO.

Developments in energetic materials are currently focused on the requirements for safer, yet still powerful materials for uses within mining, munitions and rocket propulsion systems One strategy that can be used to achieve these desirable properties is to synthesise new molecules, but this is both time-consuming and resource-intensive. Instead, another strategy is to crystallise energetic molecules with other molecules to form salts or co-crystals. This approach has been used extensively within the pharmaceutical industry in order to enhance desirable properties, e.g. solubility and bioavailability. To date, however, there has been very little research on the co-crystallisation of energetic materials. Examples include trinitrotoluene (TNT) with pyrene, naphthalene, and CL-20. To start this design process, the relationships between the types and strengths of interactions within a crystal structure and materials properties need to be established. Once these structure-property relationships have been established, the engineering of new and improved energetic materials can be achieved. The main focus of this work is on the energetic material nitrotriazolone (NTO) and the characterisation of a selection of new salts and co-crystals. NTO is an insensitive high explosive that has a similar performance to the more widely used explosive, RDX, yet is more stable, less prone to accidental detonation, and more soluble in water. Its high solubility in water is a major issue, as NTO is biologically active and represents a potential risk to the environment. There are only a few known salts of NTO and no published co-crystals, so the design and preparation of the first NTO co-crystals is a key objective. A selection of crystal structures of salts and co-crystals of NTO with nitrogen-rich aromatic systems has been obtained and the results are presented here. Interesting trends between pKa, functional groups, and intermolecular interactions have been observed.

Universal concept of self-synchronization of the micro/nano-structures of the energetic materials reactionary zones and synthesis of the advanced propulsion materials

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Keywords: micro-scale combustion; reactionary zones; micro/nano- structures; self-synchronization; energetic synergetic geometry.

Fundamental understanding of the micro-scale combustion mechanisms is very essential to the development and synthesis of the advanced propulsion materials. The reactionary zone of the energetic materials can be classified as the synergetic object. Motivated excitation source of the micro/nano-physical structures in the reactionary zones are the micro/nano- structures of the electro-magnetic fields. According our hypothesis the macro-scale phenomena at the energetic materials combustion are result of self-synchronization of the magneto-dipole micro/nano- structures of the reactionary zones. The key to the understanding of this effect is the electro-magnetic phenomena. The hypothesis is supported by the recent experimental data, obtained in the model systems. The phenomenon of self-synchronization of the torch micro-structures in the simple model nonlinear oscillatory experimental system, containing a set of paraffin candles has been examined by Japanese research team. In this study has been experimentally analyzed the characteristics of the oscillation of candle flames. This simple experimental example shows a role of the phenomenon of self-synchronization in the excitation of oscillatory burning. In connection with experiments, provided by Japanese research team, in our paper the model experiment on oxygen/paraffin combustion in e-field opposed flow burner is considered. A paraffin wax fuel was observed to extinguish when an electric field was applied over a wide range of conditions. In the paper the distribution of electric charges in the torch micro-structures and algorithms of possible influence on the synergetic oscillatory systems in the reactionary zone is considered. Self-synchronization of the micro/nano- structures of the reactionary zones also leads to change of electro-physical properties of the reactionary zones. The suggested concept opens new possibilities for development and synthesis of the advanced propulsion materials through programming by electro-magnetic field micro/nano- structures in the reactionary zones. One of the most interesting examples is the re-programming of properties the composite solid rocket propellants containing HMX. Advanced technologies of additive manufacturing, also known as 3D printing, opens new possibilities for synthesis of the synergetic energetic materials and re-programming of their properties. In particular this technique allow to create the synergetic solid propellants with cellular volumetric structures. The main practical result of suggested concept: programming of elf-synchronization of the electro-magnetic field micro/nano- structures in the reactionary zone are capable to provide programming of parameters of the physical micro/nano- structures in the reactionary zones and parameters of the combustion process at macro-level.

The development of novel, low sensitivity, gas-generating formulations for hotwire ignited devices

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Keywords: squib; electro-explosive device; hotwire; gas-generator.

A novel, low sensitivity, gas-generating composition was developed for use in a generic squib device. The novel composition has been based on energetic materials researched from the open literature. These materials were selected according to their hazard properties and perceived potential in the discussed application. The chosen materials (n-guanylurea dinitramide (GuDN), 1-nitramino-2,3-dinitroxypropane (NG-N1), hydrazinium 5-aminotetrazolate (Hy5At) and poly[P-5,6-dinitratohexan-1-oxy/P-2,2,2-trifluoroethoxyphosphazene] (PPZ)) were synthesised or acquired, and then combined in order to produce formulations that would reproducibly ignite when contacted with a hotwire. The compositions were assessed for their hazard properties, chemical compatibility and performance. Each composition was fired within a squib coupled to a sealed pressure bomb. The pressure generation and rise time were measured using a piezoelectric gauge and an oscilloscope. The results showed that a composition that displays low sensitivity to physical stimuli such as impact and electrostatic discharge may be readily ignited by a thermal stimulus and thus may be considered as a replacement to a traditional primary explosive in some applications.

Thin film thermite oxidation behavior at variable time scales

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Keywords: diffusion; thermite; shock.

Inorganic nano-energetic materials, also known as 'metastable intermolecular composites' (MICs) provide the energetics community with new classes of systems that allow for further tailoring of conventional explosives. In the following work we present our investigation into the thin film thermite class of MICs. Previous work by the authors shows the energy release trends exhibited by Al/CuO, Zr/CuO, and Mg/CuO multi-layers at slow heating rates of 5k/min. Within this slow heating realm, it was found that the Al/CuO system required the highest temperature values for the exothermic activity to be seen around 700-900°C, while the Zr/CuO samples displayed exothermic activity at the lowest temperatures of 400-500°C, and the Mg/CuO samples exhibited exothermic activity at intermediate temperatures of 500-600°C. This behavior was then explained by the oxidation occurring by a diffusion mechanism that is mitigates anion transport by terminal oxide diffusion barrier properties. Therefore the terminal oxide with the highest diffusivity values of Al¬2O3 (D 10-22cm2/sec) will yield a less thermally active thin film composite. This behavior based on the self- diffusion mechanism has been shown to be the prime avenue energetics operate at slow heating rates. While it is widely accepted the diffusion mechanism operates at low heating rates, the intricacies of the atomistic transport that occurs still requires further investigation. Nano-Kirkendall diffusion experiments were undertaken to determine the prime diffusing species within these laminate structures. Inert diffusion markers (Pt wires) were e-beam deposited via organo-metallic precursors at the oxide/metal interface. Transmission electron microscopy analysis executed before and after annealing steps reveals the dominant diffusing ion. Most energetic materials however also undergo application environments that expose the energetic components to extremely large pressure and temperature gradients under nano-second time scales. The second portion of our work studies how multilayer thermites behavior is affected by shock compression induced by laser driven flyer plates. To probe these MIC's at shorter time scales Al/CuO, Zr/CuO, and Mg/CuO thin films were exposed to laser induced flyer plate impact testing to explore the shock behavior of nano-thermite. The thin film samples were impacted with flyer plates with variable speeds (.5 to 4 km/s), and threshold detonation energies were calculated.

Study of protective properties of diffraction target against brisanse effect of contact explosive charge

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Keywords: explosive; brisanse; Hess test; diffraction gratting.

A modification of Hess test scheme was developed for the evaluation of protective properties of various obstacles including proposed diffractive gratings. It was shown the contact explosions protective barrier properties of the diffractive grating are better the protective properties of the solid steel of equal thickness. Using the diffractive grating as a model material for protection against contact explosions showed a significant influence of its position (orientation) relative to the explosive charge on its brisance.The proposed method of brisance protection may be apply to create a new type of explosive chamber as well as precise point action of explosion series which produces the diffraction grating in vicinity of tsunami region from the earth or from airplane. The tsunami velocity could be decreased and the wave front could be disturbed.

Innovative technology of creating hypercumulative shaped charges jet

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Keywords: shaped charge; hypercumilation; annular jet; detonation product.

The novel points of view to the formation of hypercumulative shaped charge jets are described. The physics of so-called hypercumulation are described in details and confirmed by numerical simulations. It has been shown that hypercumulation effects allow to increase both the speed and mass of a cumulative jets much more than the theory by Lavrentyev-Birkhoff predict. It was also shown the jet formation is possible based on off-axis interaction of detonation products with collapsing liner. The applications of novel effects are the oil-well perforations. Also such jets can be used to simulate hydrodynamics of astrophysical jets interacting with stellar or interstellar matter.

Percolation of gas and attenuation of shock waves through granular beds and perforated sheets

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Keywords: blast wave; shock tube; perforated sheets; granular beds.

The use of improvised explosive devices (IEDs) has become more widespread in recent decades causing significant injury from blast effects, not only to military personnel, but also civilians, including former zones of conflict. In order to study such injuries of high complexity, it is essential to isolate the different time-dependent effects such as initial accelerations by shock waves and impacts due to loading geometry. The shock tube is a versatile experimental platform that is capable of reproducing those elements of blast waves on a laboratory scale. In this paper, investigations of the percolation of gas and attenuation of shock waves through inserted granular beds and perforated steel sheets using an air-driven shock tube are presented. Experiments were performed with blast waves of Mach number 1.31 ± 0.01, 1.26 ± 0.01 and 1.20 ± 0.01 produced with 50μm Mylar®, 23μm Mylar® and 40μm aluminium diaphragms respectively. These output blasts were equivalent to those from denotations of 20 kg TNT at 9.0 m, 10.8 m, and 12.6 m away from the source [1]. The evolutions of shock pressures were measured before and after the insertions. Overall, results are highly reproducible and show that the peak shock pressure can be reduced linearly with the open area of the perforated sheet, the Carman-Kozeny permeability of the granular bed and the bed depth. After attenuating the shock front, the granular bed also caused a gradual rise in pressure due to the filtration of gas through the granular medium. The impulse of the positive shock region was calculated for both transmitted and reflected shock waves from the perforated sheet, showing linear relationships with the percentage of open area. About 5% of impulse was found to be absorbed by the perforated sheets.

Initiation of PETN explosion when exposed to a pulse of the second harmonic of a neodymium laser

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Keywords: laser; petn; explosive.

The mechanism of decomposition of high explosive materials when exposed to laser pulses does not currently have a unique interpretation . The key issue at the initial stage of the interaction of radiation with high explosive (HE) is the mechanism of energy absorption in the sample. A common view is that with the increase in the energy density of the laser pulses at certain values of H^* H is less than the critical value in the affected area there are free electric charge carriers as a result of ionization of the crystal defect locations. This leads to a non-linear increase of absorption , reproduction free carriers avalanche mechanism and optical breakdown threshold H^* is associated with a threshold of cratering. It should be noted that the systematic study of the dependence threshold of explosive decomposition of explosives on the wavelength of radiation were not conducted. As objects of study used PETN compressed tablets. Used YAG:Nd^{3+} - laser operating in Q-switched mode at the second harmonic (λ=532 nm) with a pulse duration of 12 ns, the maximum pulse energy at the fundamental frequency of 0.8 J and intensity distribution over the beam cross section, almost rectangular. When using the second harmonic laser revealed the possibility of ignition of PETN . We measured the dependence of the probability density of samples from the explosion energy of the initiating pulse. Critical energy density corresponding to 50% probability of explosion determined from experimental data, amounts to 12.3 J/cm^2. Thus, the initiation threshold PETN with a density $\rho \approx 1.73$ g/cm^3, with the second harmonic of a laser , at least more than an order of magnitude lower than when using the first harmonic ! This result allows us to express doubt that , at least when using the second harmonic of the laser , the initial stage of ignition occurs as a result of defective seats ionization of the sample heating of free charge carriers, avalanche ionization and optical breakdown. We hypothesized that at the initiation of the second harmonic laser samples ionization of molecules of PETN can occur for two-photon absorption mechanism of two-photon absorption coefficient c β = 300 cm/GW. The reported study was partially supported by RFBR, research project No. 13-03-98032.

Laser initiation of mixed-based composition PETN and the inclusion ultrafine metal and carbon materials

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Keywords: laser; petn; carbon; explosive.

Investigation of the mechanism of laser initiation of explosives (HE) is a complex, multidisciplinary task had not yet found a final decision. In accordance with the literature data explosion initiating explosive when exposed to laser pulses can occur as a result of optical breakdown, due to the thermal explosion in microcenters. Recently, the mechanism of initiation photoresonant to improve the efficiency of which is necessary to introduce the light-scattering inclusions in the HE to increase path of the photons in the material. The dependence of the probability of explosions for samples with a certain content of impurities (Al, Ni, Co, Al-C, C) and determined the critical energy of initiation, corresponding to a 50% probability of explosion for samples with different content of inclusions. The result shows that, as the most promising of the additive materials is investigated aluminum and nickel. An experimental study of thresholds of explosive decomposition of mixed compositions based on PETN and Al nanoparticles by laser initiation of the first harmonic as a function of the mass ratio of the core-shell (Al/Al_2O_3). It is known that nanoparticles coated aluminum from aluminum oxide (Al_2O_3), which increases as the storage . The dependence of the probability of the explosion of samples with inclusions of 0.1 % by weight with a different aluminum content in the nanoparticle of the initiating pulse energy density and the critical energy density determined by a pulse. Shown that the decrease of the metal content in the nanoparticle from 74% to 13% increases the threshold of explosive decomposition of 12.5 times. Test conducted on the basis of the mix of PETN with inclusions of aluminum sensitivity to shock. It is shown that the sensitivity to the impact of the mix on the basis of PETN and 0.1% by weight of Al nanoparticles inclusions decreases relatively pure PETN , while the threshold for laser initiation of the mix of this is minimal. The reported study was partially supported by RFBR, research project No. 13-03-98032.

Interactions among isomers of mononitrophenols during biodegradation of their mixtures

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Keywords: mixture of mononitrophenols; biodegradation; packed bed reactor; interactions of pollutants.

Aerobic biodegradation of mixtures of 4-NP, 3-NP and 2-NP in simulated wastewater was investigated. Continuous degradations were performed in a packed bed reactor with a mixed microbial culture immobilized on expanded slate. Changes of a loading rate were carried out by increasing concentration of one isomer while keeping the other two at the constant values. The results revealed different impacts of the individual isomers on a suppression of the degradation rates of other ones. In addition to the steady states, also significant transient states resulting from step changes of loading were detected. Changes of a biofilm composition during a long-term operation were identified. The results allowed us to find-out conditions here stable and effective removal of these pollutant mixtures can be achieved.

The influence of structural-chemical parameters of cellulose nitrates on energy and acid-base properties of their surfaces

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Keywords: nitrocellulose; interphase interaction; chemical&structure constitution of surface; indicators method of DCA; RS-spectroscopy.

By ensuring the adhesion interactions and explaining the process, which are proceed incidentally, the main task is to be the research surface of contact solids and determination possibility of origin different kind of combination bonding on the surface of boundary phases. Earlier studies by the method of contact angle were founded that surfaces of the cellulose nitrates are weakly acidic (parameter acidity for NC (13,1% N) is 1,35 mN/m1/2, for NC (12,9% N) 1,32 mN/m1/2, NC (12% N) 1,03 mN/m1/2), and the value of the surface free energy (SFE) be in the range of 53,18 to 59,06 mN/m. To identify the active sites of interaction for the cellulose nitrates surfaces in term of acid-base basic concept of the molecular theory of adhesive was used by a number of theoretical and experimental research methods: IR and RS-spectroscopy, indicator method of distribution centers of adsorption on solid surfaces (DSA). Joint analyze of the calculated and experimental data, taking into account the previously determined values of SFE and acidity parameters studied cellulose nitrates revealed a relationship between the chemical structured of the surface, its energy and acid-base properties [1]. Were determined, that considerable amount of functional nitro-groups are fixed by intermolecular and intramolecular hydrogen bonds, what is lead to an impossibility of the existence of given groups as an active centers of adhesion interactions, but promote of rise total polarity of macromolecule's surface nitrocellulose with various substitution degree. Were discovered that on the surface of analyzing cellulose nitrates with various substitution degree have presented Brønsted acid sites (CH) and base sites of several types: Lewis site – oxygen atom and Brønsted site nitro groups (NO2). Strength of acid sites is rather stable for all makes of nitrocellulose. On an increase in the substitution degree is taking place a small increase in the strength of acid sites, than probably due to rather difference between parameter acidity values for nitrocellulose makes NC (12% N), NC (12,9% N), NC (13,1% N) published previously [1]. The results may be useful for the prediction and control of interfacial adhesion interaction and physical and mechanical properties in composites which based on cellulose nitrates.

A unique energetic heterocycle containing both N-amino and N-oxide functionalities on the same ring (DPX2)

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Keywords: N-oxide; N-amino.

The oxidation of 1-amino-1,2,3-triazole with hypofluorous acid gives a mixture of products, including 1-amino-1,2,3-triazole-3-oxide, the first energetic heterocycle containing both an N-amine and N-oxide. The structure of this material was characterized by x-ray crystallography and the physical and explosive properties investigated.

Simulation study on the GAP-based comb-like polyurethane modifier used for TNT-based composite explosive

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Keywords: composite explosive; modifier; molecular dynamics; miscibility; mechanical property.

The GAP-based comb-like polyurethane modifier used for TNT-based composite explosive was investigated by molecular simulation and calculation. Amorphous cell models of the modifier, TNT and TNT/modifier blend at the melting point of TNT were constructed and optimized, the cohesive energy densities and the solubility parameters were obtained through molecular dynamics simulations combined with thermodynamic calculations, and the miscibility of the modifier in melting TNT was predicted. Then the solid-phase models of the modifier with TNT along three crystal faces at normal temperature were constructed and optimized one by one, the interaction energies and the mechanical properties were obtained by molecular simulations and mechanical calculations, and the improvement of the mechanical properties was predicted. The results are of significance in the design of the modifier and the research of its modification mechanism.

Research of intensity of Pyrotechnic Glitter Phenomenon at burning of the pyrotechnic composites made by through passage pressing

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Keywords: pyrotechnic Glitter Phenomenon; through passage pressing; structurally-mechanical characteristics.

Influence of composition-technological features of the pyrotechnic firework structures on a polymeric basis on intensity of display of pyrotechnic Glitter Phenomenon at its burning is considered. At burning of such spark-forcing compositions instead of the shone heated sparks, are formed boiling shone drops which within several seconds after formation chaotically flash white flashes, giving thus a characteristic sound. Such process leads to formation of shone "tail" in length to 3 metres. All known composites are made by a method of deaf pressing. Distinctive feature of the samples investigated in the present work, that they are processed in finished articles by a high-efficiency method of through passage pressing. It has demanded, along with an establishment of features of burning of samples, to investigate and optimise its structurally-mechanical char-acteristics. Influence of a kind polymeric binding, quantities of the fillers and its dispersion degrees, intensity and duration of mechanical influence at manufacturing of samples on quantity of flashes on length of "tail" at burning of composites is established .

Investigation of long term aged propellants

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Keywords: hydrolyze; single and double based propellants; FTIR spectra.

It was investigated the hydrolyze of single- and double based propellants (SBP,DBP), produced in 1983 years and were determined the rate (W, N2 %/min) and activation energy (Eact, kJ/mol) of the process. The rates were 0.087, 0.13333 %/min for DBP at 292 and 313 K and 0.0926, 0,1189 for SBP at the same temperatures. The values of Eact, were 3.6935 and 2.1636. By FTIR spectroscopy were determined the influence of the time of ageing (69, 58,54,30 years) and the thickness (from 4.5.10-2 to 10.10-2mk) of investigated samples of SBP on their IR spectra. Key words: hydrolyze, single and double based propellants, FTIR spectra

An unexpected reaction of 1,5-diaminotetrazole: novel preparation of 5-picrylamino-1,2,3,4-tetrazole (PAT)-highly insensitive energetic compound

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Keywords: tetrazoles; energetic materials; X-ray diffraction; picryl group.

This work reports on the preparation of 5-picrylamino-1,2,3,4-tetrazole (PAT) by an unexpected reaction of 1,5-diaminotetrazole (DAT) with picryl chloride (PiCl). The structure of PAT was confirmed by single-crystal X-ray diffraction. A suggested mechanism for its formation was presented. Some of the energetic properties of the synthesized compound were also studied. The results show that PAT is highly insensitive.

Phenomenological models of explosive systems initiation at mechanical influences

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Keywords: mechanical sensitivity; liquid explosive; initiation; detonation.

In work existing experimentally-theoretical techniques of explosive materials sensitivity definition to mechanical influences are considered. It is shown that the probability of explosion initiation depends not only on the chemical nature of substance, but also a wide set of various characteristics of external influence. In that case, the important role is got by methods of separate stages modelling processes of reception, processing, storage and application of chemically reacting systems. Process of liquid explosive systems initiation of with gas bubbles is considered at mechanical influences. The analysis of hydrodynamic and thermal processes mathematical models in liquids is made. Process initiation of firm explosive materials with gas inclusions at mechanical influences is theoretically investigated.

Obtaining, structure and basic properties of CL-20 and DNP energetic bimolecular crystal

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Keywords: CL-20; DNP; crystallization; BMC.

A novel 2:1 cocrystal of 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20) and dinitrodiazapentan (DNP) has been prepared. The structure of this cocrystal was characterized by X-ray diffraction. Properties of the cocrystal including thermal decomposition and detonation performance were studied. It was shown that the detonation power of novel cocrystal comparable to cocrystal 2:1 CL-20:HMX.

Effect of moisture content and ambient humidity on the thermal stability of pyrotechnic compositions

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Keywords: moisture content; humidity; pyrotechnic; thermal stability.

Pyrotechnic composition is sensitivity with the effect of temperature or humidity. The burning explosion accidents of pyrotechnic composition usually are caused by severe environment during its storage, processing, transportation. The effects of moisture content and ambient humidity on the thermal behavior of a typical red pyrotechnic composition were investigated using SETARAM Evolution thermal analyzer. The thermal stability of the mixture was evaluated using the parameter of critical temperature of thermal explosion (Tb). The results show that the decomposition temperature of the mixture increases with the increasing of moisture content, it means that the mixture is insensitiveness by the effect of moisture content. The thermal stability of the mixture enhance with the moisture content increasing. However, the decomposition temperature and critical temperature of thermal explosion all decrease with ambient humidity increasing, then the thermal stability decrease. It illustrates that the effect of moisture content and ambient humidity have the different influence on thermal stability of this red pyrotechnic mixture.

A simple method for predicting detonation performances of boron derivatives and aluminized explosives

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Keywords: k-j equation; desk calculation ; metallic explosives.

To accurately predict detonation performances of different kinds of energetic materials is a continuous pursuit of scholars in the field. Kamlet-Jacobs equation is till an efficient and reliable way to estimate CHNO explosives. However, with the development of energetic materials, explosives are no longer restricted to CHNO elements. In this study, we extended K-J equation to calculate boron compounds and some aluminum containing composite explosives. A method of treating metal elements to form metallic oxides was proposed by considering the largest exothermic principle. The oxides are deemed as inert solids which give off heat other than gases. As a consequence, boron and aluminium containing explosives can be calculated as well as CHNO explosives. For validating the accuracy of the method, EXPLO5 were used to estimate compounds in the study either. Their different ways of treating products are discussed. And detonation parameters calculated by two methods are compared directly. Results indicated that explosives considered in the study have high Q values due to large negative HOF of B_2O_3 and Al_2O_3. Relative deviations' MAVs (mean absolute values) of D and P between two methods are 5 % and 10 % approximately. Good accuracy made the new method an efficient way to primarily estimate these explosives' performance without relying on a computer program. And the method could be helpful in designing and synthesizing new boron or aluminum based energetic materials.

The high-nitrogen energetic ionic salts

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Keywords: energetic ionic salts; synthesis; characterisation; review.

Energetic ionic salts as a unique class of energetic materials have been investigated widely in recent years, since they possess advantages over their similar non-ionic analogues —- tend to exhibit lower vapor pressures, higher densities and higher thermal stabilities. Furthermore, these salts are readily improved through the appropriate combination of different cations and anions. Our group's work over the last twenty years on ionic materials is reviewed in the present review. This review elaborating an overview on the various studies dealing with the synthesis aspects and some of the physic-chemical properties of ionic materials that based on ammonium, guanidine, semicarbazide, carbohydrazide, tetrazine, tetrazole, triazole and imidazole. In addition, the potential application of these ionic compounds on explosives and propellants is discussed. Herein we hope these investigations are helpful for providing wider insight into the future research in the area of energetic ionic salts.

Discussions on the all nitrogen high energetic materials

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Keywords: all-nitrogen compound; energy; structure; poly-nitrogen compound.

The performance related to structure of all–nitrogen energetic materials was reviewed. A method for calculating the energy of all-nitrogen materials with linear structure was proposed. It was suggested that the tridimensional cage structure or at least the cyclic annular structure could be in favor of ultra-high energy. At the same time, several kinds of poly-nitrogen materials, that might have good prospects, were introduced.

Kinetic predictions for CL-20 and its PBXs using models obtained by master plots and combined kinetic methods

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Keywords: PBX; decomposition models; time to explosion; CL-20.

In this paper, the decomposition reaction models and thermal hazard properties of different 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) crystals and their PBXs bonded by Semtex 10, C4, Viton A and Fluorel polymer matrices have been investigated based on master plots and combined kinetic methods. The established kinetic triplets are used to simulate isothermal behaviour at temperature of 82 °C. It has been found that the use of "isoconversional and combined kinetic analysis" method yield reliable kinetic triplets, which could be employed to predict the thermal behaviour of energetic materials. The effect of the Fluoropolymers on the decomposition mechanism of CL-20 is and significant and similar. They can change its decomposition mechanism from "AC1, first order autoaccelerated model" to "A3, three dimensional nucleation and growth model". It has also been shown that the polymer matrices containing mineral oil materials and plasticizers (Semtex and C4) have little effect on decomposition mechanism of CL-20, resulting in comparable activation energies and model. According to isothermal simulations, he threshold cook-off time until loss of functionality at 82 °C for all involved materials are much more than 500 days, and under the effect of polymer matrices, the storage time of CL-20 has been greatly extended.

Application of DSC method for porous structure of single-based propellant

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Keywords: nitrocellulose; volatile components; DSC; single-based propellant; decomposition kinetic.

The method of DSC was used to determine the effects of powders grains structure on the thermal decomposition process. Studies of the change of the decomposition rate were performed. The dependence of decomposition rate was divided into three ranges. These ranges arise from the porous structure of powders. It was shown, that in low-temperature area decomposition occurred in closed pores and in high-temperature area - in opened pores. Powders conditioned at high temperature, compressed powders and powders with high value of volatiles components are decomposed in accordance with zero-order kinetic model. The introduction of the modifier into the burning layer of powder causes homogenization of grains. Nitrocellulose has only opened pores and its decomposition takes place by homogenous mechanism.

Phenyl-N-methylnitroamines: their preparation, electron- accepting potency and enzymatic reactivity

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Keywords: high energy materials; nitrocompounds; phenyl-N-methylnitroamines; tetryl; nitroamines; preparation; quantum mechanical calculation; potential; enzymatic reactions; nitroreductase; LC-MS analysis.

Nitroamine derivatives, possessing N-NO2 fragment, are one of the most important groups of energetic materials. In the present work three aromatic nitroamine derivatives: 4-nitrophenyl- , 2,4-dinitrophenyl- and 2,4,6-trinitrophenyl- N-methylnitroamines were synthesized by modified method and their structures were characterized by spectroscopic (UV, FT-IR and NMR) methods. Their electron-accepting parameter values and other physico-chemical characteristics were assessed. The enzymatic reactivity of the compounds towards single-electron electron-transferring flavoenzyme NADPH:cytochome P-450 reductase (P-450R, EC 1.6.2.4) and two-electron transferring flavoenzymes Escherichia coli nitroreductase (NR, EC) and NAD(P)H:quinone oxidoreductase (DT-diaphorase, NQO1, EC 1.6.99.2) were investigated. The reactivity of the compounds, expressed as their apparent second-order rate constants (kcat/Km) increased with an increase in their electron accepting potency. The enzymatic reduction of the compounds was accompanied by formation of their reductive products as identified by applying LC-MS analysis methods.

X-ray structure of S,S'-dimethyl-N-nitroimidodithiocarbonate

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Keywords: S,S'-dimethyl-N-nitroimidodithiocarbonate; nitrimines; X-ray analysis; molecular structure.

The molecule of S,S'-dimethyl-N-nitroimidodithiocarbonate (I) is highly planar(except H-atoms of methyl groups). In contrast to derivatives of nitroguanidine bond lengths of nitrimine fragment C=N-NO2 of (I) have normal distances in compliance with traditional valence formula. The molecule of (I) is characterized by the presense of the shortened intramolecular S...O contact. This conformation is stabilized via electrostatic attraction forces involving oppositely charged oxygen and sulphur atoms. The feature of the crystal structure of (I) is a low energy of crystal lattice.

Computational studies on some well-known nitramine type energetic compounds

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Keywords: nitramines; detonation parameters; stability; DFT.

Some of the well-known cyclic nitramine type energetic molecules (1,3,5-trinitro-1,3,5-triazinane (RDX) etc.) were investigated by using semi-empirical and Density Functional Theory (DFT) computational tools. Hypothetical chemical structures, based on the well-known cyclic nitramine molecules were also analysed to discover "stability" of those energetic molecules. Also certain thermochemical and detonation parameters of concerned thirteen cyclic nitramine compounds were predicted.

Michael addition of nitroform as a source of energetic materials, synthesis and characterization

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Keywords: michael addition; nitroform; bomb calorimeter; energetic properties; crystal structure.

The nucleophilic Michael addition of nitroform to unsaturated carbonyl compounds creates a wide variety of energetic products. All presented compounds were characterized, including multinuclear NMR spectroscopy, vibrational analysis (IR, Raman), mass spectrometry, elemental analysis as well as single crystal X-ray diffraction. The thermal stability is studied using differential scanning calorimeter. The energies of formation are calculated on with different levels of theory using Gaussian 09 Revision A.02 and compared with the heat of combustion by measurement with static bomb combustion calorimeter.

Detonation pressure of plastisol compositions containing the inorganic fuel and oxidizer

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Joint stock company «State scientific research institute
of mechanical engineering after V.V. Bakhirev»

Keywords: detonation pressure; plastizol compositions; inorganic combustible; inorganic oxidizers.

Measurement of detonation profiles is executed and detonation pressure for three compositions on the basis of plastizolny binding are determined. It is revealed that in powerful compositions on the basis of the octogene, containing 30% of aluminum, the current behind the detonation front has isoentropy character. Thus there is no the energy release connected with oxidation of aluminum. With replacement of a half of aluminum by ultradisperse silicon intensive energy release is recorded and the size of a pause of energy release is determined.

Prediction of high explosives' detonation characteristics using a simplified thermochemical approach

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Keywords: detonation; high explosives; thermochemical model.

Prediction of detonation characteristics of high explosives can be done using different calculation methods with satisfactory accuracy. Detonation characteristics are mostly determined with detonation pressure and velocity. The calculation of detonation parameters was done using a simplified thermochemical model of detonation. The accuracy of obtained results was analyzed using a comparison with experimental data and calculation results using other models. The calculation results for detonation velocity and pressure show acceptable correlation with experimental data.

Atomistic simulation of the temperature dependence of density and van-der-Waals interactions of binders, plasticizers and mixtures of them

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Keywords: intermolecular energetic interactions; binder HTPB; plasticizers; atomistic simulation; cohesive energy density; rubber-to-glass transition.

The intermolecular interactions between binders, plasticizers and fillers in elastomer bonded composite rocket propellants (CRP) and elastomer bonded high explosives charges (HEC) control the glass to rubber transition in these elastomer systems, besides the basic chemical structures and conformations of the binder constituents. Using the program package Materials StudioTM (MS) version 6 from company Accelrys, Inc., San Diego, CA, USA, an atomistic simulation of such interactions is possible. Here the van-der-Waals and the electrostatic interactions between binders and plasticizers will be considered. The substances investigated are hydroxyl terminated polybutadiene (HTPB), dioctyl adipate (DOA) and polypropylene oxide (PPO), which serves as a first step towards GAP. For energetic equilibration of the molecules and of the configuration to each other and for the calculation of the global energy terms of the systems under consideration, molecular dynamics simulations were performed by the programme part Forcite of MS in NPT ensembles with a Berendsen barostat to control the pressure and the thermostat algorithms of type Andersen or Nose to control the temperature in the simulation cell. From the obtained NPT structures the cohesive energy densities are calculated, which reflect the intermolecular energetic part in the systems. The temperature dependent calculations are shown to point the rubber-to-glass transitions.

Influence of soot on combustion regularities of high-energetic propellant

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Keywords: propellant; soot; combustion rate; temperature distribution.

It is known that significant effect of the catalysts on the combustion of high-energetic propellants without additional plasticizers only with black loading is appeared. It was assumed that the primary role of the soot in combustion catalysis is that the soot together with the condensed products of the nitrocellulose decomposition are forming the carbonaceous skeleton on the combustion surface where accumulation of catalyst particles without their agglomeration is happen. The main purpose of this work was to study the influence of different (0,1 - 15 %) amount of ultra-fine soot on the combustion rate and parameters of the combustion wave of model high-energetic propellant. It is shown that depending on the amount of ultra-fine soot in the propellant and pressure at which combustion occurs soot may either increase (by 10-20 % with 0,1 - 1,5 % of the soot) the burning rate and decrease it (by 50 % at 15 % of the soot). By increasing the amount of soot has a significant and complex influence on temperature distribution in gaseous zone, probably, for the account of catalytic effect on the exotermic redox reactions involving NO and endothermic interactions with CO_2 and H_2O, but not in the area affecting the burning rate.

Regulating of combustion behavior of aerosol-forming fire-suppressing compounds by means of catalysts

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Keywords: aerosol fire-fighting; aerosol-forming fire-suppressing compounds; burning rate; fire-suppressing ability; phenolformaldehyde resin; potassium nitrate; combustion catalysts.

In our first article at this conference results of research of properties of aerosol-forming fire-suppressing compounds (AFC), processed into finished articles with use of rolling and through passage pressing method, based on plasticized phenolformaldehyde resin are pre-sented. For creation of generators of the aerosol intended for the various purposes and facili-ties, compounds with varied burning rate and having simultaneously good fire-suppressing ability (FSA) are necessary. Therefore in the present work influence of various catalytic addi-tives on specified characteristics of AFC of various composition at oxidizer-to-fuel ratio, changing from 0.8 to 1.1 is investigated. As catalytic additives used various compounds of iron and copper. It is shown, that the most effective combustion catalysts of AFC are copper compounds: oxide, hydroxide, salts of organic acids (salicylate, butyrate, citrate, oxalate) which at their in-troduction at various amounts allow to control burning rate from 1.6 to 8 mm/s and to improve FSA. Most effective of the studied additives is copper salicylate. The compounds containing 3% of copper salicylate, stably burn at atmospheric pressure with a burning rate from 4.5 to 7.5 mm/s (depending on value of oxidizer-to-fuel ratio) and have high FSA which is in the range from 8.5 to 10 g/m3. In that way they are ecologically safe and practically do not contain toxic (CO, NOX) and fire-explosive (CO, H2) gases.

Regularities of combustion of aerosol-forming fire-suppressing compounds of through passage pressing

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Keywords: aerosol fire-fighting; aerosol-forming fire-suppressing compounds; burning rate; fire-suppressing ability; phenolformaldehyde resin; potassium nitrate.

Within nearby 30 years in Russia the systems of aerosol fire-fighting are designed. In this systems as a source of fire-suppressing substance aerosol-forming fire-suppressing compounds (AFC) are used. Particles formed at combustion of AFC break off the chain reactions proceeding in a flame of various organic materials at their combustion on air. Well-known AFC are differed on composition, fire-suppressing ability (FSA), combustion temperature, burning rate and other characteristics. In the majority of cases charges of AFC make by a blind die moulding. In Mendeleev University besides blind die moulding compounds the compounds which are processed into finished articles with use of rolling and through passage pressing develop. Among such compounds the most perspective are compositions based on plasticized phenolformaldehyde resin (PFR). Influence of changing the contents of components of AFC on their key properties - burning rate at atmospheric pressure and FSA are investigated. The type and content as fuel (PFR, triethyleneglycol, dicyandiamide, etc.) and an oxidizer (potassium nitrate and its mix with potassium perchlorate) are varied. Because of this fact compounds with various values of oxidizer-to-fuel ratio have been designed. Compounds are stably burning at atmospheric pressure that is important for maintenance of safe operation of fire-suppressing generators. Burning rate varies from 2 to 6 mm/s, and FSA - from 9 to 13 g/m3. All investigated compounds practically do not contain toxic and fire-explosive substances in combustion products. Structurally-mechanical and the processing be-haviour of these compositions optimised by addition into their composition of the modificator (PTFE), which allows to process them into finished articles by a through passage pressing method.

Preparation and stablilty investigation of the Ti-N cluster

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Keywords: Ti-N cluster; TiN12; laser ablation; geometry optimization.

The titanium-doped nitrogen clusters were prepared by laser ablation of Ti/BN discs. The mass spectra of generated clusters show that there was no other TiNn+ except TiN12+, which suggests that the TiN12+ is the most stable Ti-N cluster. The stable state of TiN12+ was investigated by selecting eight initial structural isomers and fully optimizing the geometry of them by DFT. The isomer that consists of one Ti and six N2 molecules and has Oh symmetry was considered to be the stable structure of TiN12+, in which the Ti+-N2 distance and N-N bond length were estimated to be 2.17 and 1.11 Å, respectively. The electronic and magnetic properties of the most stable structure of TiN12+ were calculated further, and the results show that the energy gap between HOMO and LUMO is 2.8 eV and the magnetic moment is 3.0 μB. The structures and properties of the corresponding neutral cluster TiN12 were also discussed.

Sensitivity to impact of fluoropolymer F-2M with aluminium

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Keywords: polymer; explosion-like and explosion reactions; explosive mixtures; sensitivity to impact.

It has been done the analysis of the impact fluxion of explosive reaction in the polymer F-2M (PVDF) and potassium perchlorate and identified the critical parameters of initiation. Figures of explosion initiation of mixtures F-2M with KClO4 and aluminum has been obtained and thermodynamic characteristics of the explosion products have been calculated. Depending on the nature of the second polymer component P-2M exhibits oxidation (in mixtures with Al) or restorative properties.

Calculation of the detonation concentration limits of liquid homogeneous explosive systems

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Keywords: explosive; mixed system; critical heat of detonation.

Perspective direction to improve the safety of explosive liquids use is to study the concentration limits (CL) of detonation for homogeneous liquid explosive systems. The concentration limits can be approached by adding to the liquid explosive knock-free component. In this paper, were summarized the results of the experimental determination of the CL for binary systems based on tetranitromethane and fluoronitromethane. We found universal line (for the standard explosives with the atomic composition C,H,N,O,F) separating plane of dimensionless pairs of parameters “coefficient of excess oxidant / heat of explosion” to the region of detonating solutions and region of solutions, which are not capable of detonation. The calculation of the explosion heat is based on the previously proposed mathematical model describing a quasi-equilibrium composition of the detonation products for multicomponent mixture of explosives.

Effects of catalyzer and total binder content on the combustion/explosion energy and burning rate of HTPB propellants

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Keywords: factorial design; HTPB propellant; copper chromite; binders.

The main objective of this study is to use linear 22 factorial design experiments planned to evaluate quantitatively the effects of the addition of copper chromite (CC) and of the increase of binder content in the explosion heat, combustion heat and in air atmospheric burning rate of a HTPB-based composite propellant. Two levels of such both factors were used in this study, namely 0% and 1% wt. of copper chromite addition and an increase of 20% to 22% wt. of binder content in a HTPB/TDI based propellant. Analysis-of-variance (ANOVA) tables and a F-test were used at significance level of 95% and 99% to statistically evaluate the effect of each factor in the final response of explosion and combustion heat (J/g) and in burning rate (mm/s). Heat of explosion increases with decreasing binder and CC content, while combustion heat increases with binder content. Burning rate increases with CC and with less binder.

Synthesis of nitroheterocycles by ionic-liquids promoted [3+2]-cycloaddition reactions to nitroformonitrile oxide generated by cycloreversion of dinitrofuroxan

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Keywords: dinitrofuroxan; nitroformonitrile oxide; nitroheterocycles.

One of the usual methods for the generation of nitrile oxides is a thermolysis of symmetrically substituted furoxans, however, this process proceeds at high temperature. Dinitrofuroxan (DNFO) is a unique example of furoxan ring cycloreversion occurring already at room temperature. New, general and safe methods for the synthesis of 3-nitroisoxazoles 1 and 3-nitroisoxazolines 2 were developed on the basis of [3+2]-cycloaddition reactions of nitroformonitrile oxide (NFNO), generated in situ by cycloreversion of dinitrofuroxan, to dipolarophiles of acetylene and ethylene series, accordingly. In addition, two representatives of nitroheterocycles with three heteroatoms (3-nitro-1,2,4-oxadiazole and 3-nitro-1,2,4-dioxazole) were obtained. All reactions are promoted by catalytic amounts of ionic liquids.

Synthesis of potassium salts of 2,4-diamino(alkylamino)-6-dinitromethyl-1,3,5-triazine salts and of 2-hydrazinyl-4-amino(alkylamino)-6-dinitromethyl-1,3,5-triazine

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Keywords: potassium salt of 2,4-dimethoxy-6-dinitromethyl-1,3,5-triazine; nucleophilic substitution; ammonia; substituted amines; hydrazine; potassium salts of 2,4-diamino(alkylamino)-6-dinitromethyl-.

The interactions of 2,4-dialkoxy(diaryloxy)-6-dinitromethyl-1,3,5-triazines potassium salts and ammonia, substituted amines and hydrazine in various solvents were studied. The general synthesis of potassium salts of 2,4-diamino(alkylamino)-6-dinitromethyl-1,3,5-triazines and 2-hydrazinyl-4-amino(alkylamino)-6-dinitromethyl-1,3,5-triazines using 2,4-dimethoxy-6-dinitromethyl-1,3,5-triazine potassium salt as starting material was developed. A one-step mode allows to prepare corresponding symmetrically 2,4-disubstituted 6-dinitromethyl-1,3,5-triazines, and a two-step mode allows to prepare corresponding unsymmetrically 2,4-disubstituted 6-dinitromethyl-1,3,5-triazines.

The correlations between the high explosives' critical temperature of thermal explosion with the flash point and decomposition temperatures

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Keywords: critical thermal explosion temperature; DTA; decomposition temperature; flash point temperature; correlation relations.

Based on the experimental values of Tcr – critical temperature of thermal explosion, Tidb(8°), Tidb(16°) – intensive decomposition beginning temperatures, Tw(8°), Tw(16°) – maximum decomposition rate temperatures, Tmax(8°), Tmax(16°) – maximum decomposition temperatures at heating rates 8 and 16 degrees per minute correspondingly (DTA method), Tfp(1)- flash point temperatures found using express-method with valuable temperature, Tfp(5s) – 5-second-delay flash point temperatures, the linear correlations between Tcr and Tdb(8°); Tcr and Tdb(16°); Tcr and Tw(8°); Tcr and Tw(16°); Tcr and Tmax(8°); Tcr and Tmax(16°); Tcr and Tfp(1); Tcr i Tfp(5s) for TNT, hexanitrostilbene, TATB, RDX, HMX, nitroguanidine, benzotrifuroxane and PETN were found.

Synthesis of 1,4-di(azidomethyl)-1',4'-dimethyl-2-tetrazene ($C_4H_{10}N_{10}$) – Promising fuel for bipropellant systems

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Keywords: azidonation; alkyltetrazene; nuclear overhauser effect; quantum chemical calculations.

Cryogenic propellants as LOX/LH2 system have the highest specific impulse. However, the speed of gas ejection is not the only parameter of performance in space propulsion; one must take into consideration the density of these materials. Low-density propellants need great storage volume which requires the increase of the mass of the launcher. Additionally, cryogenic fuels need thermal insulation which make difficult to store them over a long period of time. On the over hand, storable fuels as hydrazine, monomethylhydrazine and unsymmetrical dimethylhydrazine are easier to store but they present lower performance and higher toxicity. The REACH regulation classifies most of hydrazines into CMR compounds (carcinogenic, mutagenic and reprotoxic), which implies that these compounds should be handled, transported and stored with extreme caution. Hence, the use of hydrazine-based propellants for future space missions will become problematic according to REACH. In this context, chemists are faced to develop a new generation of storable propellants fulfilling a list of benchmarks: high specific impulse, great stability and low toxicity. The synthesis of alkyltetrazenes is well known and these compounds are good candidates for the replacement of hydrazines in bipropellant systems. Among them, tetramethyltetrazene possesses great specific impulse similarly to hydrazines. Regarding its toxicity, studies are ongoing. In this framework, our group is developing some derivatives of tetramethyltetrazene with higher nitrogen content.

This work is conducted within the framework of a French national R&T program. Financial support by the Centre National d'Etudes Spatiales (CNES) and Herakles (Safran) is gratefully acknowledged.

Comparative analysis of shock wave action of TKX-50 and some other explosives on various barriers

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Keywords: TKX-50 explosive; other explosives; shock wave action; various barriers; detonation parameters; loading parameters.

TKX-50 (bishydroxylammonium 5,5'-bis(tetrazolate-1N-oxide)) is one of the most promising explosives today and can be regarded as a possible replacement for RDX and some other industry and military explosives. The compound is by its nature a ionic salt and can be prepared 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 and other products. The safe preparation and characterization of this new explosive using many structural and physicochemical diagnostic methods indicate that TKX-50 outperforms the majority of all other commonly used explosive materials by its technological and performance properties. A wide study of detonation characteristics of this material is being conducted using both experimental and calculated methods. In this work a comparative analysis of shock wave action of TKX-50 and several other explosives such as TNT, RDX, HMX and CL-20 on various barriers in a wide range of their shock impedance has been performed. Calculated results on determination of detonation parameters and equations of state for detonation products were obtained with the use of computer program EXPLO5 V.6.01 for all considered explosives. Calculations were fulfilled both for explosive materials having the maximum crystalline density and for porous ones right up to 50 % in volume. Influence of the content of plastic binder polyisobutylene right up to 20 % in volume on all specified properties of explosives was examined too. Calculated results on shock wave loading of various barriers under explosion on their surfaces of explosive charges of a concrete size were obtained with the use of computer hydrocode UP-OK. Barriers of such materials as polystyrene, textolite, magnesium, aluminum, zinc, copper, tantalum and tungsten were used for examination. Interface loading parameters and the character of propagation and attenuation of shock waves in barrier materials were obtained for all possible situations. A rather complete comparative picture of shock wave action of TKX-50 and other explosives on various barriers was obtained. It was shown that in all cases the shock wave action of TKX-50 was more intensive than the shock action of RDX.

Comparative analysis of shock wave action of MAD-X1 and some other 3,3’-Dinitro-5,5’-bis-1H-1,2,4-triazole-1,1’-diol derivatives on various barriers

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Keywords: MAD-X1 explosive; 3,3’-Dinitro-5,5’-bis-1H-1,2,4-triazole-1,1’-diol derivatives; shock wave action; various barriers; detonation parameters; loading parameters.

MAD-X1 (dihydroxylammonium 3,3’-dinitro-5,5’-bis-1,2,4-triazole-1,1-diolate) is one of the promising explosives today and can be regarded as a possible replacement for RDX and some other industry and military explosives. The compound is one of the studied ionic salts of 3,3’-dinitro-5,5’-bis-1H-1,2,4-triazole-1,1’-diol and shows a straightforward synthesis including only four cheap and facile steps. The safe preparation and characterization of this new explosive using many structural and physicochemical diagnostic methods indicate that MAD-X1 outperforms the majority of all other commonly used explosive materials by its technological and performance properties. A wide study of detonation characteristics of this material is being conducted using both experimental and calculated methods. In this work a comparative analysis of shock wave action of MAD-X1 and several other derivatives of 3,3’-dinitro-5,5’-bis-1H-1,2,4-triazole-1,1’-diol such as diammonium 3,3’-dinitro-5,5’-bis-1,2,4-triazole-1,1-diolate, dihydrazinium 3,3’-dinitro-5,5’-bis-1,2,4-triazole-1,1-diolate, diguanidinium 3,3’-dinitro-5,5’-bis-1,2,4-triazole-1,1-diolate, di(aminoguanidinium) 3,3’-dinitro-5,5’-bis-1,2,4-triazole-1,1-diolate and di(triaminoguanidinium) 3,3’-dinitro-5,5’-bis-1,2,4-triazole-1,1-diolate on various barriers in a wide range of their shock impedance has been performed. Analogous results for RDX were also used for comparison. Calculated results on determination of detonation parameters, equations of state and composition of detonation products were obtained with the use of computer program EXPLO5 V.6.01 for all considered explosives. Calculations were fulfilled both for explosive materials having the maximum crystalline density and for porous ones right up to 50 % in volume. Influence of the content of plastic binder polyisobutylene right up to 20 % in volume on all specified properties of explosives was examined too. Calculated results on shock wave loading of various barriers under explosion on their surfaces of explosive charges of a concrete size were obtained with the use of computer hydrocode UP-OK. Barriers of such materials as polystyrene, textolite, magnesium, aluminum, zinc, copper, tantalum and tungsten were used for examination. Interface loading parameters and the character of propagation and attenuation of shock waves in barrier materials were obtained for all possible situations. A rather complete comparative picture of shock wave action of MAD-X1 and other derivatives on various barriers was obtained. It was shown that in all cases the shock wave action of MAD-X1 was more intensive than the shock action of RDX.

Mechanisms and energetics of decomposition of TATB molecules

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Keywords: TATB molecule; ground state; density functional theory; decomposition mechanism; decomposition energetics.

TATB (2,4,6-triamino-1,3,5-trinitrobenzene) is the most outstanding representative of the class of insensitive high explosive substances. It possesses the extremely low sensitivity to thermal effect, mechanical impact and shock wave action and is widely utilized in the most responsible military and industrial applications. Together with this, TATB continues to be studied extensively both in experimental and calculational directions. One of the important things here is the study of decomposition phenomenon, its mechanisms, kinetics and energetics. In works concerned with these problems several possible primary mechanisms were revealed and analysed but the complete understanding of the process was not achieved yet. Along with the more studied simple decomposition mechanisms such as nitro group bond fission, nitro-nitrite isomerization and intramolecular hydrogen transfer the more complicated mechanism of decomposition was proposed earlier but the energetic barriers of progressing reactions were not calculated. These reactions were the formation of the intermediate state from the biradical state obtained as a result of intramolecular hydrogen transfer and the destruction of this intermediate state with formation of benzofurazan and water molecules. The calculations of this decomposition mechanism were conducted in this work not only for the ground states of molecules but also for their exited and charges states. Gaussian 09 computer code was used for electronic structure calculations using density functional theory with the B3LYP hybrid functional and 6-31+G(d) basis set. Zero point corrections were taken into account for all stationary and transition states of the considered molecules. Additional clarification calculations were also conducted for the energetic barriers of other decomposition reactions. So the complete picture of mechanisms and energetics of decomposition of TATB molecules was obtained.

Action of a sliding detonation wave in a thin explosive layer on plates of different materials and spallation of the plates under such loading

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Keywords: sliding detonation wave; thin explosive layer; barrier plate; intensive impulse action; spallation.

Loading of different barriers by a sliding detonation wave in a thin explosive layer is widely applied in various technical applications. One of such applications is testing of dummy and full-scale special structures for a short-term intensive impulse action. Study of such sort of action on barriers was conducted in a number of works using both experimental and calculational methods. As a result common character of that action is understandable enough now if not to take into account some fine features associated with a real shape and thickness of a detonation wave propagating in a thin explosive layer on the surface of a rather hard barrier. In the case of barriers in the form of not very thick plates or shells, under certain loading conditions characterized by the geometry of a system and the properties of an explosive and barrier materials, the last can undergo spallation. In this work the effects of barrier material properties on the shape of a sliding detonation wave and on the character of impulse action on barriers were considered using ANSYS Autodyne computer program in two-dimensional statement. Using these results many obtained earlier experimental results on spallation of different materials were processed computationally for obtaining their strength properties under such loading conditions. A plastic bonded explosive formulation on the base of PETN with 17 mass.% of a polyisobutylene was used in calculations and experiments. Calculations results on determination of detonation parameters and equations of state for detonation products for this formulation in the form of Jones-Wilkins-Lee were obtained using EXPLO5 V.6.01 computer program. The obtained detonation parameters were in a good agreement with their experimental values. A lot of barrier materials in a wide range of their shock impedances were examined, from polyethylene to tungsten. Polynomial equation of state was used for them. Parameters of this equation of state were fitted carefully on the base of experimental shock wave data. All materials were considered in calculations as elastic-perfectly plastic media. Different frameworks were used for calculations of detonation and shock processes in an explosive layers and in a barrier plates, Eulerian in the first case and Lagrangian in the second. A lot of calculations were conducted for describing of experimental results on spallation of plates made of some polymeric materials such as polyethylene, polymethylmethacrylate and polytetrafluoroethylene and some metals such as aluminum, titanium, iron, copper, nickel and lead.

Effect of charged and excited states on the primary decomposition mechanisms of tetrazole and triazole molecules

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Keywords: triazole molecule; tetrazole molecule; density functional theory; decomposition mechanism; charged state; excited state.

Triazole and tetrazole rings are highly explosophoric moieties and widely used in the design and production of different energetic materials. Incorporating of them into molecular structure of explosives leads to increasing thermal stability and performance, decreasing sensitivity to shock and impact. It is naturally that physicochemical properties of isolated molecules of triazole and tetrazole are interconnected with the properties of corresponding moieties in the structure of explosive molecules and consequently with the properties of explosives themselves. Decomposition mechanisms and their energetic have been studied in the work for specified molecules not only for the ground stste but also for the exited and charges states. A molecule of tetrazole, and both the tautomeric forms for each of 1,2,3-triazole and 1,2,4-triazole molecules were examined. Gaussian 09 computer program was used for electronic structure calculations. This calculations were conducted at the B3LYP/6-31+G(d) level of theory for all molecules in different initial states. The ground states, positively and negatively charged states, and the lowest triplet states were taken as the initial states of molecules. For every concrete case the weakest ring bond was detected in the molecule. The strength of this bond was obtained, thereto a potential energy curve was calculated during rupture and a transition state was determined. Zero point corrections were taken into account in calculations of all stationary and transition states. In some cases the addition destruction phenomena were initiated during the process of bond elongation as, for example, the separation a nitrogen molecule. As a result of performed calculations a rather complete picture of decomposition phenomenon for considered molecules in different initial states was obtained. Practically for all molecules the positive charging does not lead to significant change of the energy barrier of decomposition, the negative charging leads to its decreasing and at the lowest triplet state the energy barrier of decomposition has its minimal value.

Modification of coating to enhance fire-proof efficiency of wooden crating for the storage of high-energy materials at low storage temperature

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Keywords: fire resistance ; power-intensive materials.

Tne possible ways of increase of fireproof properties of the special container applied to storage and packing of power-intensive materials with a low temperature of ignition are shown. It is reached by reduction of temperature of the beginning of formation of fireproof coke, stabilization of binding components and strengthening of resistance to the atmospheric phenomena.

The Modern perforating and fracturing tools – the concept and firing ground testing

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Keywords: gas-fracturing ; cumulative perforation ; new shooting equipment.

The article presents the results of the research of highenergy materials ignition applied to the perfo-generator (comprehensive tool dedicated both for perforating and stimulation job in a borehole). The experiments were carried out with use of special pressure chambers located in Oil and Gas Institute Krakow, as well as Institute of Organic Industry Warsaw, Krupski Młyn Branch. Those chambers are equipped with ultra fast pressure changing recorders which enable us to build the profile of propellant combustion pressure. The authors has successfully performed three different types of propellants ignition: with use of cumulative stream, detonating fuse, and explosive charge, respectively. Final results of experiments show a positive ignition and fully propellants combustion at each test configuration.

Energetic salts of 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazole

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Keywords: primary explosive; triazoles; tetrazoles; azides.

Several metal and nitrogen-rich salts of 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazole (AzTT), including silver (1), potassium (2), cesium (3), ammonium (4), and guanidinium (5), as well as the respective double-salts of 2, 3, 4 and 5, were prepared and well characterized by IR and multinuclear (^{1}H, ^{13}C, ^{14}N) NMR spectroscopy, DSC, mass spectrometry, elemental analysis and one (3) additionally 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 insensitive.

Synthesis and properties of poly-2,4,6-trinitrosterene

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Keywords: 2,4,6-trinitrosterene; polymerization.

Poly-2,4,6- trinitrosterene (poly-TNS) is a perspective energetic polymeric material being in use in different branches science and engineering applications. Poly-TNS is generated in the reaction of TNS polymerization. The mechanism of this reaction is not fully investigated. The present work is devoted to the investigation of the detailed mechanism of the anionic polymerization TNS in the presence of sodium alcogolate. Spectral methods and Gel-penetrating chromatography are used in the experiments.

A DFT study of 1-amino-2,4-dinitroimidazole and its three derivatives

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Keywords: DFT; 1-amino-2,4-dinitroimidazole; density; detonation performance.

In this study, density functional theory (DFT) investigation at B3LYP/aug-cc-pVDZ level were performed to explore the geometric and electronic structures, band gaps and heats of formations of the energetic compounds, 1-amino-2,4-dinitroimidazole(R1) and its three derivatives:1-nitroimidazole-2,4-dinitroimidazole(R2), 1,2,4-trinitroimidazole(R3) and 1,2-bis (2,4-dinitro-1H-imidazol-1-yl)diazene(R4). The detonation properties and densities of these compounds were evaluated by VLW equation and experiential methods, respectively. Results show that these compounds have high densities (1.791 to 1.938 g•cm-3)and excellent detonation performance (D 8.74 to 9.21 km•s-1, P 35.90 to 55.63 GPa). All of them appear to be potential explosives compared with the well known ones, 1,3,5-trinitro-1,3,5-triazine (RDX, 8.75 km•s-1, 34.70 GPa) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocane (HMX, 8.96 km•s-1, 35.96 GPa) 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20, 9.40 km•s-1, 42.00 GPa), especially R3 (9.21 km•s-1, 55.63 GPa). In addition, different substituted groups determine the heat of formation, stability, sensitivity, density, and detonation performance of these compounds.

Synthesis and characterization of alkylated trinitromethyl- and fluorodinitromethyl-tetrazoles

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Keywords: tetrazoles; polynitro compounds; sensitivities; thermal analysis; structure elucidation.

Here we report about the synthesis of 2-(2-nitro-2-azapropyl)-5-(trinitro-methyl)-tetrazole and analogue 2-(2-nitro-2-azapropyl)-5-(fluorodinitromethyl)-tetrazole. The prepared materials were characterized thoroughly including single crystal X-ray diffraction and differential scanning calorimetry measurements. The sensitivities towards impact, friction and electrostatic discharge were determined. In addition, the performance of the materials was calculated using the EXPLO5 computer code, with heats of formation calculated at the CBS-4M level of theory and densities obtained from pycnometer measurements.

Quantum-chemistry analysis of electrophilic nitrating agents and nitration processes

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Keywords: DFT; nitration agents; electrophilic nitration; dinitrogen pentoxide.

The model benzene nitration was simulated by quantum-chemistry methods. Nitric acid (HNO_3), nitric anhydrid (N_2O_5), nitryl chloride (NO_2Cl) and nitryl flouride (NO_2F) were taken as nitrating agents. Impacts of protic (H_2SO_4) and aprotic (BF_3, $AlCl_3$) acid catalysis to the nitration reactions (energy aspects) were investigated. The synthesis of a promising nitrating agent dinitrogen pentoxide by the ozonolysis of dinitrogen tetroxide was simulated.

Zwitterionic explosives based on 4,6-dinitrobenzotriazol-3-ium-1-oxide

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Keywords: N-oxide; amination; secondary explosives; energetic performance; crystal structure.

The energetic properties of the zwitterionic 4,6-dinitrobenzotriazol-3-ium-1-oxide and its nitramine 1-(4,6-dinitrobenzotriazol-3-ium-1-oxide-3-yl)-2-nitrazapropane were investigated. 7-Amino-4,6-dinitrobenzotriazol-3-ium-1-oxide and 5,7-diamino-4,6-dinitro-benzotriazol-3-ium-1-oxide were obtained by direct amination using vicarious nucleophilic substitution (VNS) methodology. The observed amination pattern was analyzed by quantum-chemical calculations of the distributions of the electron spin densities in the corresponding radical anions. The zwitterionic structures of 4,6-dinitrobenzotriazol-3-ium-1-oxide, its nitramine and 7-amino-4,6-dinitrobenzotriazol-3-ium-1-oxide were confirmed by single crystal X-ray diffraction. All presented compounds were characterized by multinuclear magnetic resonance spectroscopy (1H, 13C1H, 14N1H), vibrational analysis (IR and Raman), mass spectrometry and elemental analysis. Their thermal stabilities were studied by using differential scanning calorimetry and detonation parameters were calculated using the EXPLO5 computer code based on CBS-4M computed enthalpies of formation. The influence of the N-oxide moiety on the energetic properties, especially the sensitivities, is evaluated by comparison with the corresponding derivatives of 5,7-dinitrobenzotriazole.

Aquatic toxicity determination of energetic materials using the luminescent bacteria inhibition test

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Keywords: luminescent bacteria inhibition test; aquatic toxicity; energetic materials.

The aquatic toxicity (EC50 after 15 min and 30 min) of several neutral as well as ionic energetic materials was determined by the luminescent bacteria inhibition test. The measurements were performed at 15 °C on a LUMIstox 300 obtained by the HachLange GmbH. Liquid-dried luminescent bacteria of the strain vibrio fischeri NRRL-B-11177 were used. In addition to well known energetic materials such as hexogen, sodium azide, ammonium nitrate, ammonium perchlorate etc. numerous new materials based on tetrazole and furazane backbones were tested e.g. sodium 5-nitrotetrazolate. In case of ionic materials the toxicity of different anions is assessed by using combinations with relatively low toxic ammonium counter-cations.

Synthesis of copper salts of 1-substituted-5-nitriminotetrazoles

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Keywords: tetrazoles; energetic materials; X-ray.

Different 1-substituted-5-aminotetrazoles (1-R-5AT) have been synthesized by the reaction of cyanogen azide and selected amines. The corresponding 5-nitriminotetrazoles (1-R-5-HATNO$_2$) were prepared using various nitration agents: HNO$_3$ (100%), HNO$_3$/H$_2$SO$_4$, HNO$_3$/(CH$_3$CO)$_2$O, and NO$_2$BF$_4$. The products were reacted with copper(II) nitrate yielding the copper salts [Cu(1-R-5-ATNO$_2$)$_2$(H$_2$O)$_n$] with high yields and purities. Obtained compounds were characterized using vibrational (IR, Raman) and multinuclear NMR spectroscopy (^{1}H, ^{13}C), mass spectrometry, elemental analysis. The structures of the crystalline state were determined using low temperature single crystal X-ray diffraction.

Synthesis and properties of new polyfunctional organic compounds derived from 2,4,6-trinitrotoluene

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Keywords: 2,4,6-trinitrotoluene; derivatives; electrophylic substitution.

As it is evident from the investigations performed during the last decade, the 2,4,6-trihydroxytoluene (MPG) which is effectively and cheaply derived from 2,4,6-trinitrotoluene possesses high and specific reactivity in the reactions of electrophilic substitution. The results of studies of carboxylation of MPG and its transformation into O-heterocyclic compounds, benzannelated pyrane derivatives in particular, are discussed.

Serial chamber gun

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Keywords: interior ballistics; serial chamber gun; ballistic pressure; muzzle velocity.

Serial chamber gun is the barrel weapon designed for the purpose of gaining higher muzzle velocity of the projectile. This objective is achieved by increasing the mean ballistic pressure with the use of additional combustion chambers placed alongside the barrel bore. The problem was described by the interior ballistics model and solved by the numerical computation. The results were compared to the experimental shooting of caliber 12.7 serial chamber gun system. The significant increase in the projectile's muzzle energy was observed.

Model of the photostimulated fragmentation of PETN molecules by 1060 nm laser radiation

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Keywords: laser initiation; hot spots; thermal explosion; photoinitiation.

A model of the photostimulated fragmentation of the PETN molecule irradiated by the first harmonic of a neodymium laser (1060 nm) is proposed. Photoexcitation at 1060 nm leads to the n → π^* transition of the 2p nonbinding electron of the oxygen to the π^* antibonding orbital, a transition that causes the rupture of the O–N bond and the formation of $NO_2{}^*$ radicals, thereby ensuring a further development of explosive decomposition. In the case of a free molecule or a molecule located on the surface of a microcrystal, the process does not require any thermal activation. In the case of a molecule at a regular lattice site, an additional activation energy (0.4 eV) is needed to overcome the potential barrier associated with the passage of $NO_2{}^*$ through a bottleneck between the nearest-neighbor molecules.

Thermal decomposition of N-bis-polyfunctionally substituted N-nitramines

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Keywords: polyfunctional nitramines; kinetics; thermal decomposition; activation parameters; induction effect; correlation.

Kinetics of thermal decomposition of secondary nitramines on the base of nitramide with β- and γ-polyfunctional substituents in diluted solutions (2-2.5 % mass) of dibutyl phthalate are investigated and structural-kinetic laws are established. For the limiting stage the kinetic parameters are determined. It is shown that logarithms of the rate constants correlate with Taft's σ* constants. The correlation dependences are found, which allow forecasting the reactivity of polyfunctionally substituted nitramines in the reaction of homolytic decomposition.

Spall velocity of blast loaded concrete specimen

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Keywords: concrete; free surface velocity; photonic doppler velocimetry; plastic explosive; framing camera.

The paper is focused on free surface velocities measurement of blast loaded concrete samples. The tests were performed using small scale plain concrete tiles (300 × 300 × 33 mm). Small charges of Semtex 1A industrial plastic explosive (10 to 92 g) were used as shock wave generators, being placed in contact with the samples. The free surface velocity was measured on the soffit using simple photonic Doppler velocimetry setup while the whole process of blast induced spall formation was recorded by high speed framing camera. The results and instrumental methods tested during these experiments will be useful for future measurements on real concrete slabs.

Optimal ratio between NO2 and NF2 fragments in model formulations tetranitromethane + tetra(difluoramino)methane as oxidizer and either polyethylene or carbon, or boron as combustible

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Keywords: difluoramines; solid composite propellants; specific impulse; optimal formulation.

Model formulations of solid composite propellants containing NF2-groups together with NO2-groups have been considered. Polyethylene (PE), carbon and boron have been considered as combustible and tetranitromethane (TNM) in the mixture with tetra(difluoramino)methane (TDFAM) as a mixed oxidizer. The most interesting data have been obtained with the system PE + TNM + TDFAM - the maximal value of specific impulse (Isp= 290.3 sec at Pc:Pa=40:1) is realized at the formulation where atom ratio H/F=1 and C/O=1. Sure, there is only one formulation satisfying these ratios (PE = 13.5% , TNM=52.5%). As soon the PE amount increases the maximal ratio TNM/TDFAM is achieved when C/O=1 while if the PE amount decreases the maximal ratio TNM/TDFAM is achieved when H/F=1. In the hydrogen-free formulations (if carbon is combustible instead of PE) there are no such bright regularities as in the case with PE. If the carbon amount is higher than 9-10% there is no necessity to add TDFAM to TNM, the maximal value of Isp is about 245 sec at 20-21% carbon). Thermodynamic analysis of combustion products allowed to explain the observed regularities

Triazines as a basis for new energetic compounds creation

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Keywords: solid composite propellants; specific impulse; active binder; furazanetetrazinedioxide; triazine derivatives.

A few high-enthalpy triazine derivations having the same element content (C2N6O3)n, including recently synthesized 2,4-dizido-6-trinitromethyl-1,3,5-triazine (I), not synthesized yet hypothetical 5-trinitromethyl-bistetrazolo[1,5-a:1',5'-c][1,3,5]triazine (II), and 2,4-di(1H-triazirin-1-yl)-6-(trinitromethyl)-1,3,5-triazine (III) have been considered as compounds of solid composite propellant (SCP). Enthalpies of formation of these compounds have been estimated - 800; 972 and 1223 kJ/mol for I; II and III respectively. It was shown that active binder with high oxygen access is the best one for these compounds. The fraction of the active binder has been varied from 15 up to 20 volume %. At such high enthalpies of formation (for I; II and III 2564; 3115 and 3921 kJ/kg respectively) there is no need to introduce aluminum as energetic compound any more. Energetic properties of SCPs based on compounds under consideration were compared with similar compositions basing on furazanetetrazinedioxide (FTDO) - the most energy-intensive compound among all actually existing ones that has the same element content than I-III. The formulation basing on I has the specific impulse value Isp =255 s (at Pc:Pa=40:1) that is rather high for formulations with no metal (e.g. the similar formulation with HMX provides Isp 251.5 s only), combustion temperature Tc is settled in rather admissible area (3650 K). The formulations with II (with 18% active binder too) has Isp= 262.5 s - so high Isp value may be achieved today with recently used oxidizers only if there is metals or hydrides in the formulation. Formulations with II have Tc about 3800 K, that is rather high but still admissible). The most powerful among compounds under consideration is III, it allows to achieve Isp=272 s. This value is rather close to the Isp (275 s) of the formulation "FTDO with 18 vol.% of active binder", but so high Isp values may be achieved at very high Tc values (3950 and 4050 K for formulations with III and FTDO respectively), so in inadmissible range.

Synthesis and properties of some new salts of 4,4’,5,5’-tetranitro-2,2’-biimidazole

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Keywords: TNBI; energetic salts; synthesis.

Nitro derivatives of imidazole form an interesting group of high-energy materials. One of them is 4,4’,5,5’-tetranitro-2,2’-biimidazole (TNBI) which has high detonation parameters and could be used in modern propellants or explosive compositions. Unfortunately it is very hygroscopic and can be used only in form of salt. An important feature of this material is its low sensitivity to mechanical stimuli. In a past few years a number of publications about TNBI and its salts has been released but still there are no results of complex study on detonation parameters. In this work new salts of TNBI were synthesized. The structure of obtained compounds was confirmed with NMR spectroscopy. Thermal properties were investigated with DTA/TG analysis.

High thermally stable and insensitive energetic salts based on s-triazine cation

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Keywords: triazine; energetic salts; thermally stable; insensitive.

In the pursuit of new high-energy-density materials (HEDMs), high energy compounds with high thermal stabilities and low sensitivities received more and more attention. In the past decade, a new class of high energetic compounds composed of nitrogen-containing heterocyclic anions and/or cations has been developed to meet the continuing need for improved energetic materials, which displayed attractive energetic properties due to the special properties of ionic compounds, such as lower vapor pressure, and higher densities than their atomically similar nonionic analogues. But oxygen-containing cations remain elusive because once nitrated or oxidized, the ability of neutral Lewis bases to form cationic species is greatly reduced. Triazine rings have been studied for use in a number of applications, which is an ideal backbone for constructing energetic compounds due to its three readily tunable ring carbon positions. However, triazine-based energetic salts have been investigated to a lesser extent than the azoles. Current research in this field is only limited to substituent triazine anions. Recently, we designed and synthesized a series of energetic salts based on 2,4-diamino-1,3,5-triazine-6-one cation, which showed excellent thermal stabilities and low sensitivities towards impact, friction and electrostatic charge. Most of the salts decompose over 180 °C, especially the salts nitrate and perchlorate, which decompose at 303.3 °C and 336.4 °C. Furthermore, most of the salts exhibit excellent impact sensitivities (>40 J), friction sensitivities (>360 N), and are insensitive to electrostatics. The measured densities of these energetic salts range from 1.64 to 2.01 g cm-3. The detonation pressures (P) values calculated for these salts range from 14.6 to 29.2 GPa, and the detonation velocities (D) range from 6536 to 8275 m s-1, making the salts potential candidates for thermally stable and insensitive energetic materials.

Thermal properties and combust activation of boron aluminum combustible agent

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Keywords: boron powder; nano-aluminum powder; wet ball mill ing; TG-DSC; activation energy.

The thermal performance and combust activation of different proportions of boron/aluminum combustible agent were investigated. Aluminum content is varied from 10% to 50% in 10% steps. The Thermogravimetricanalysis-Differentical scanning calorimetry analysis(TG-DSC) results showed the weight gain augments with the increase of aluminum content by dry mixing, but the change tread was opposite after milling and in contrast to the theoretical weight gain trend. The best effect happened at the aluminum content of 10% after wet ball milling, the mass gain increased by 89%, the heat release increased 138% ,the onset temperature was ahead of 17°Cand the highest burning rate of 14mm/s. The activation energy reduced 91kJ/mol.

Structure and characteristics of new types cellulose nitrate solutions

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Keywords: cellulose nitrates; power condensed systems (PCS).

The CN solutions' viscosity is often one of the main requirements for technological process of their preparation. It significantly predetermines the physical and mechanical properties of cellulose-nitrate substances, coatings, films, nitrate varnishes. The systematic studies of the plasticised CN course regularity with various substituting range in the wide concentrations interval in different by nature solutions and regimes allowed to receive the complex enough representation regarding the course mechanism of the NC concentrated solutions, including the compositions area, similar to the real PCS. However, there is virtually no evidence data regarding the low-concentrated CN solutions. The timeliness of the complex studies of the rheological and structural characteristics of low- and medium-concentrated CN solutions and identification of factors influencing the quality of the finished products is associated by the new areas of CN application derivation. Carried out the research and development to study the rheological and structural charachteristics of low- and medium-concentrated cellulose nitrates' solutions applying the modern methods: rotary viscosimetry, IR-NMR13S-spectroscopy, gel-penetration chromatography, X-ray diffraction analysis, photocolorimetric method. The studies showed the interference of the polymer structure and its solutions with physical-chemical and physical-mechanical characteristics. Demonstrated that the studied CN samples (N= 10,9-13,3%) display the course disturbance. Defined the solutions' structuredness value (lgK), which allows to identify the interference of rheological and structural parameters of CN solutions with concentration of 0,8- 6,4% mass. Identified that the structure and particulary the structural non-homogenity of CN solutions is defined by the fraction composition, quality and size of the over-molecular particles, which associated with the evidence of the CN's molecular, chemical and morphological non-homogenity. Defined the interaction of the CN structural regularity with the cellulose-nitrates substances' characteristics. Developed the mathematic model of the rheological performance of the CN solutions in order to create the new types of the cellulose-nitrates substances with the regulated characteristics. Developed a number of the new technological approaches to produce the CN.

Methods of obtaining of high purity TNT

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Keywords: TNT; crystallization.

Proposed method of obtaining of TNT gives lower amount of wastes in respect to another methods. The basis of this method is nitration of ortho-nitrotoluene. Crude product contains significantly less undesirable impurities. Moreover, the impurities can be removed in environmental-friendly processes. Tests carried out that crystallization processes can be simultaneously very simple, inexpensive and very efficient.

Method for estimation of thermochemical properties for salt compounds

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Keywords: salt compound; enthalpy of formation; enthalpy of dissolution; ion; ligand.

The enthalpies of formation for the wide set of transitive metals complex salts with various ligands and anions have been investigated. To determine the enthalpies of complex salts, the cycles of thermochemical reactions including measurement of combustion energies, enthalpies of solution and dissolution, heats of reactions have been elaborated. Measurement of such variety of thermodynamic values has demanded the use of a set of methods – calorimeties of burning, reactions and dissolution, as well as microcalorimetry. The data obtained allowed to analyze the formation enthalpies of the complex salts from different chemical classes. As a result, the regularity in the energy contribution of the ligands and the outer-sphere anion into formation enthalpy of the salt compounds has been established. This makes it possible to calculate the enthalpy of formation for the complex salt compounds.

Photo-initiation of the explosive chain reaction in molecular materials: the role of photo-excitation density fluctuations

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Keywords: energetic materials; high explosive decomposition; laser excitation.

We propose a fluctuation model of the photochemical initiation of an explosive chain reaction in energetic materials. In accordance with the developed model, density fluctuations of photo-excited molecules serve as reaction nucleation sites due to the stochastic character of interactions between photons and energetic molecules. A further development of the reaction is determined by a competition of two processes. The first process is growth in size of the isolated reaction cell, leading to a micro-explosion and release of the material from the cell towards the sample surface. The second process is the overlap of reaction cells due to an increase in their size, leading to the formation of a continuous reaction zone and culminating in a macro-explosion, i.e., explosion of the entire area, covering a large part of the volume of the sample. Within the proposed analytical model, we derived expressions of the explosion probability and the duration of the induction period as a function of the initiation energy (exposure). An experimental verification of the model was performed by exploring the initiation of pentaerythritol tetranitrate (PETN) with the first harmonic of YAG: Nd laser excitation (1064 nm, 10 ns), which has confirmed the adequacy of the model. This validation allowed us to make a few quantitative assessments and predictions. For example, there must be a few dozen optically excited molecules produced by the initial fluctuations for the explosive decomposition reaction to occur and the life-time of an isolated cell before the micro-explosion must be of the order of microseconds.

Kinetic Laws and Calorimetric Properties of Epoxy Composite Rocket Propellants Modified by Nanoparticles

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Keywords: composite propellant; epoxy binder; nanoparticles; Crawford's technique; calorimetric potential.

The composite rocket propellants are highly filled composite materials. The typical composition of composite solid rocket propellant is based on crystalline solid oxidizer bound together with polymeric matrix. Many other additives like metal particles, nitramine crystals, ballistic modifiers, may be included in the final mixture depending on the desired use of the propellant. The aim of the work is to study the effect of adding nanoclays such as montmorillonite type one, on the kinetic and calorimetric properties of a rocket composite propellant based ammonium perchlorate as oxidiser and epoxy/amine binder system. The first part of the study deals with the preparation of rocket propellant specimens adapted for Crawford's and adiabatic calorimeter tests, loaded with different types of nanoclays. We have to determine some experimental conditions in order to satisfy the qualities required by the combustion phenomenon and especially the homogeneity of the block. The second part consists in one hand on the characterization of propellant systems by Crawford apparatus for determination of burning rate versus pression to establish combustion laws and adiabatic calorimeter for the calorimetric investigation.

Influence of isothermal ageing on the mechanical properties of HTPB-bonded composite rocket propellants expressed as master curves of torsion DMA measurements

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Keywords: composite rocket propellant; ageing; dynamical-mechanical analysis; shear modulus; master curves; shift factors; time-temperature-superposition.

Composite rocket propellants (CRP) have an elastomer as binder for the two types of solid fillers, which serve as oxidizer and fuel. Elastomers are as a whole not linear elastic in behaviour as metals or glasses. Their behaviour as function of temperature is named visco-elastic, to incorporate the feature of the glass-to-rubber transition in going from low temperatures to high temperatures. The distinctive property of the glass-to-rubber or vice versa rubber-to-glass transition is a dissipative energetic process, which causes the molecular rearrangements from 'ordered' configuration to 'disordered' configuration or vice versa. The ordered configuration appears at low temperatures and is called 'energy elastic' as metals and glasses are. The disordered configuration appears beyond the glass-to-rubber transition and is called 'entropy elastic'. The modules of visco-elastic materials are dependent on temperature and of the deformation rate. In case of thermo-rheological simple materials the effects of time and temperature on the material can be linearly superposed without loss in information. Time and temperature act 'orthogonal' on the material. This connection is also the base of the time-temperature-shift theorem according to Williams, Landel and Ferry. In other words a distinct correlation between modulus and temperature on one side and modulus and deformation rate on other side exists. From measurements at low temperatures the behaviour of the modules can be assigned to high deformation rates. One can establish so-named master curves to predict the material response at other load situations. Some artificially aged CRP were investigated by torsion DMA [1,2]. The temperature range was from about – 100°C to +40°C and higher with sinusoidial deformation at four frequencies in the range 0.1 to 56 Hz. The material properties storage shear modulus G', loss shear modulus G'' and loss factor tan(delta) obtained by torsion DMA behave with increasing deformation rate according to the visco-elasticity of the material. The ageing has distinct influence especially evident in the loss factor curves. The master curves and shift factors established from these data show the ageing infuence in transformed way, which can give some insides to better understand the behaviour of the materials on the molecular base.

The alternative mechanisms of thermal destruction of nitrotoluenes

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Keywords: quantum chemical investigation; o-nitrotoluene; 2,4-dinitrotoluene; 2,6-dinitrotoluene; 2,4,6-trinitrotoluene; mechanism of thermal decomposition; enthalpy of activation.

The alternative mechanisms of primary act of thermal gas-phase decomposition of o-nitrotoluene, 2,4- and 2,6-dinitrotoluenes and also 2,4,6-trinitrotoluene were considered in the article. It is proved, that the most energetic advantageous primary act of decomposition of o-nitrotoluene is connected with the formation of its aci-form. Another alternative proc-esses have the activation barriers with the significant exceed of experimental estimation. For 2,4- and 2,6-dinitrotoluenes and also for 2,4,6-trinitrotoluene the realization of alternative schemes of decomposition, first of all the processes of formation of their aci-forms and bi-cyclic intermediates of substituted (6S)-6-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxide and (6R)-2-methyl-7-oxa-8-azabicyclo[4.2.0]octa-1(8),2,4-triene 8-oxide is possible. The secondary processes are the limiting stages for thermal decomposition of nitro-toluenes; these stages are connected with the process of transfer of hydrogen atom from hy-drogen-containing substituent to nitro group. Additionally, the values of relational enthal-pies of activation for the chains of sequential reactions show that the further development of process is different, as compared with offered earlier in printed publications. For o-nitrotoluene the development of process is significantly determined by the alternative chan-nels of isomerization of HONO group – by the transfer of hydrogen atom between oxygen at-oms of by the rotation of the whole group. For substituted nitrotoluenes the final mechanism of thermal decomposition can be described only after the detailed research of secondary processes for all alternative schemes.

Thermal analysis of urethane copolymers of 3,3-bis(azidomethyl) oxetane and 3-azidomethyl-3-methyloxetane

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Keywords: thermogravimetric analysis; thermomechanical analysis; differential scanning calorimetry; 3,3-bis (azidomethyl) oxetane and 3-azidomethyl-3-methyloxetane copolymers.

In the present work of 3,3-bis (azidomethyl) oxetane (B) and 3-azidomethyl-3-methyloxetane (A) with different ratio of oligomeric units and type of molecular structure such as B(AB)n, A(AB)n and (AB)n were studied. Mechanical-deformational and relaxation behavior, structuring and decomposition processes of copolymers were investigated using thermogravimetric, thermomechanical analysis and differential scanning calorimetry.

The efficiency and safety increment of the BC-I-HS construction

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Keywords: non-primary explosive blasting cap; confinement; secondary explosives; metal cylindrical confinement; RDX; TNT; petn; HMX; lead azide; retarded high explosives.

For the high-safety instant action electric blasting cap (BC-I-HS) with no primary explosives in construction the application of the inner cant in the axis channel of the metal cylindrical confinement (MCC) was offered. It was experimentally proved that the application of the MCC with the cant can improve the efficiency of the BC-I-HS. This improvement makes it possible to use more nonhazardous high explosives than the RDX as the main charge of the BC-I-HS.

New explosive compositions based on triaminoguanidinium azotetrazolate

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Keywords: triaminoguanidinium azotetrazolate; explosive compositions.

The interest in high nitrogen explosives is a result of the increase in the safety of manufacture, storage and use of explosive materials in civilian and military technology. The explosion of a cartridge can stimulate the detonation of other missiles, and finally lead to the destruction of the entire warehouse or the vehicle. Therefore scientists are looking for high-performance substances which are insensitive to shock wave, mechanical and thermal stimuli. An example of such material is triaminoguanidinium azotetrazolate (TAGAZ). The aim of this work was to develop new explosive compositions based on TAGAZ which contain RDX or HMX. As a result we obtained compositions with reduced sensitivity to different types of stimuli and with high detonation parameters.

Polyglycerol as enviromental frendly binders for explosives

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Keywords: plastic bonded explosives; polymer; binders.

In the biodiesel production process, technical glycerin is one of the waste products. Due to the commercial scale of its production, possible ways of technical glycerin utilization are being explored. Polycondensation is the typical way of glycerin processing. As a final product of this process, the mixture of polyglycerols of linear, branched and cyclic structures is obtained. Relative fractions of these types of polyglycerols depend on reaction parameters. Products of different viscosities and colours (from yellow to brown) may be obtained depending on the degree of polycondensation. While physical and chemical properties of the product may be controlled, its low toxicity and cost-effectiveness are also an advantage. Therefore, in this study we made an attempt to use polyglycerols as binders for explosives. First, selected polyglycerols were mixed with Hexogen explosive. No problems in the formation of the mixtures were noticed. For selected mixtures, friction and impact sensivity and detonation velocity were measured. The promising results for the selected utilization properties, including detonation velocity, even for relative high polyglycerol fraction, are an encouragement to continue this field of study.

Research of a complex of characteristics of the firework and spark-forcing composites made by through passage pressing

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Keywords: colour spark-forcing composites; through passage pressing; burning rate.

The colour spark-forcing composites which are not containing perchlorates and chlorates which cause a hypersensibility of structures to mechanical influences and toxicity of the burning products are considered. Aluminium powders, that traditionally used for spark-formation, not always provide demanded entertainment effect because of incompleteness of burning of metal. Essential increase of an external friction at formation of such aluminized composites deteriorates their technological characteristics. Developed composites are processed in finished goods by a high-efficiency method of through passage pressing that causes necessity of detailed studying their rheologocal and technological characteristics. Compositions of colour fires (red, green and yellow) based on copolymer vinyl chloride with vinyl acetate VA-15, plasticized by dibutyl phtalate, and contained by oxidizers - nitrates of strontium, barium, sodium, are investigated. In quality of spark-forming the powdery titan of the various form and the size of particles are used. Influence of the composite features of structures, the constructive features of the forming tool, the temperature-time parametres of pressing on technological and operational properties (burning rate, sensitivity)of samples is established

Features of deflagration-to-detonation transition in primary explosive hexamethylenetriperoxide diamine

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Keywords: primary explosive; organic peroxides; deflagration to detonation.

The deflagration to detonation transition (DDT) in pressed samples of different porosity as well as large single crystals of a typical primary explosive from the organic peroxide chemical class, hexamethylenetriperoxidediamine (HMTD), was investigated in the interval of external pressures 0.1-30 MPa. The deflagration to detonation transition in HMTD single crystals at high pressures was found to occur easier than DDT in high density pressed samples. An important role of HMTD single crystal fracturing upon ignition was revealed. In all cases, the value of the predetonation column length decreased with the growth of external pressure. It has been shown that only quantitative differences exist between DDT processes in brisant and capable-to-combustion primary explosives.

Thermal decomposition of some N-nitrozo-N-alkyl(aryl)hydroxylaminates

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Keywords: N-nitrozo-N-alkyl(aryl)hydroxylaminates; thermal decomposition; mechanism.

The thermal decomposition of some copper(II) and nickel(II) N-nitrozo-N-alkyl(aryl)hydroxylaminates was studied by differential thermal analysis (DTA). The DTA curves consist of an endothermic effect in the temperature range from 90 to 150oC which corresponds to the absorption of 2 to 9 water molecules. The decomposition in the inert atmosphere is characterized by one or two exothermic peaks at 184-238oC. The value of the weight loss together with the quantum chemical modeling allows to propose the mechanism of the decomposition which depends on the nature of the alkyl (aryl) radical.

Effect of humidity and reaction atmosphere on the thermal safety of black powder

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Keywords: black powder; humidity; atmosphere; thermal safety.

The effect of humidity and atmosphere on the thermal decomposition of black powder was investigated by TG/DSC, and the thermal behavior of black powder under different conditions was analyzed. The kinetic parameters were calculated by Kissinger method. The results showed that the decomposition peak temperature and activation energy decreased with the increase of humidity level. On the other hand, the decomposition peak temperature and activation energy at air atmosphere decreased from 428°C to 420°C and 165kJ/mol to 135kJ/mol respectively compared with that under N2 atmosphere. Therefore, the thermal stability of black powder decreased by the effect of humidity and air atmosphere.

Organic explosive peroxides of acetone: enthalpies of formation

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Keywords: diacetonediperoxide (DADP); triacetonetriperoxide (TATP); enthalpy of formation.

Two explosive compounds, diacetone diperoxide (DADP) and triacetone triperoxide (TATP) were studied in respect to their thermodynamic properties. Gas-phase enthalpies of formation were calculated based on the total energies at the composite Gaussian-4 (G4) level. The energies of combustion were measured and the standard enthalpies of formation were derived using standard enthalpies of formation of the combustion products. The heat of explosion was measured for small pressed charges of the peroxides. The obtained enthalpies of formation of DADP and TATP were found to agree well with quantum chemical calculations and reasonably account for the observed derivative parameters: heats of decomposition, combustion, and detonation.

Thermal decomposition of onium 5,5’-azotetrazole salts

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Keywords: salt of 5,5’-azotetrazole; burning rate; temperature profiles; thermal decomposition; combustion mechanism.

Thermal decomposition and combustion of guanidinium, ammonium and melamine 5,5’-azotetrazole salts have been investigated. It was shown that combustion of salts obeys the condensed-phase mechanism. The kinetic parameters of the controlling chemical reaction have been estimated, and the detailed combustion mechanism of 5,5’-azotetrazole salts has been proposed.

Synthesis of azoxytriazolone by electrochemical reduction of nitrotriazolone in water/nitric acid system

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Keywords: azoxytriazolone; electroreduction; nitrotriazolone.

3-nitro-1,2,4-triazol-5-one (NTO) is an important and prospective compound due to their reduced sensitivity for mechanical and shock initiation. Many derivatives of NTO are described in last years, especially salts and complexes. Nitrotriazolone is also valuable substrate for synthesis of azo- and azoxy compounds. We present the results of systematic study on electroreduction of NTO in distilled water (nitric acid was used as the electrolyte). Electrosyntheses were carried out using standard DC power supply with 12V voltage and 4A effective current maximum. Graphite electrodes with surface area of 160 cm2 were used. Two series of experiments were conducted in laboratory scale. In the first tests reduction of NTO was conducted for 2-8h with mechanical stirring. Next each experiment were repeated with additional stirring time (18h) with no current. Solid products were collected by simple filtration, dried and weighed. The products were analyzed by using multinuclear NMR and DTA/TG techniques. Crystals shape were evaluated with images from optical microscope.

Modern nitramines TNAZ and CL-20 (HNIW): their electron accepting potency, enzymatic reactivity and cytotoxicity

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Keywords: high energy materials; strained cyclic nitramines; caged nitramines; TNAZ; CL-20; HNIW; RDX; BCHMX; TEX; peak potential; quantum mechanical calculation; toxicity; flavoenzymes; enzymatic reactions.

Energetic nitrocompounds are widely used in various industrial and military areas. Environmental contamination by these materials is an acute problem, and nitramine compounds are one of the major groups of such type contaminants. One of the initial stages of biodegradation and/or toxic action of such compounds is frequently related to their 1e-/2e-(4e-) reduction catalyzed by redox-active flavoenzymes. In this work the enzymatic reactivity of the newest nitramine compounds – TNAZ and CL-20 (HNIW) - was examined towards single- and two-electron transferring flavoenzymes and their electron-accepting potency was assessed by electrochemical and quantum mechanical methods. The standard nitramine RDX was also used in this work for comparison. The first peak potentials of voltammetric reduction (Ep,7) vs. Ag/AgCl of CL-20 and TNAZ were -612 mV to -390 mV, respectively, while Ep,7 of RDX was -554 mV. The same trend of the electron accepting potency of the compounds was obtained by means of quantum mechanical calculation. The enzymatic reactivity of the nitramines, expressed as apparent second-order rate constants (kcat/Km) of their reduction, towards single-electron transferring flavoenzyme P-450R as well as two-electron transferring flavoenzymes PETN-reductase (PETNR), nitroreductase (NR) and DT-diaphorase (NQO1) varied in the range of TNAZ > CL-20 ≥ RDX, and reac-tivity of TNAZ was almost one order of magnitude higher than that of CL-20 and RDX. This reactivity increased with an increase in the electron-accepting potency of the compounds. TNAZ and CL-20 were found to be much more toxic compounds for mice splenocytes than RDX; the CL50 values (the concentration of the compounds causing 50 % cell death) of TNAZ and CL-20 were defined to be equal to 15.6 and 21.9μM, respectively, while CL50 of RDX was 140 μM. The toxicity of the former compounds was much higher than that of relatively new nitramine representative TEX and bicyclic structure energetic nitramine BCHMX. This work demonstrates that the cytotoxicity of the compounds is caused mainly by their electron-accepting potency and might be influenced by their structural peculiarities.

4,5,6,7-Tetranitro-1,3-dihydrobenzoimidazol-2-one (TNBO): modified synthesis and crystal structure studies

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Keywords: benzimidazoles; nitrocompounds; 4,5,6,7-tetranitro-1,3-dihydrobenzoimidazol-2-one (TNBO); synthesis; X-ray diffraction; hydrogen bonding; density; high density material; high energy materials; HDEM.

4,5,6,7-Tetranitro-1,3-dihydrobenzoimidazol-2-one (TNBO) (molecular formula C7H2N6O9) has been selected in the present work for more detailed research. Two different methods of modified TNBO synthesis were developed (yields =76 and 89%). Two crystallohydrates of TNBO have been prepared and investigated by X-ray diffraction. Both these crystal materials conformed to triclinic systems and P-1 space groups; however, these forms exist in different crystal shapes and colour: TNBO semihydrate – consist of yellow prisms, while TNBO tetrahydrate (3TNBOx4H2O) is a pinkish-orange parallelepiped. The density of 2TNBOxH2O (semihydrate) is 1.878, while that of tetrahydrate - 1.821 g/cm3. Although the investigation of anhydrous TNBO is under way, it can be concluded that it will have even higher density (≥1.9 g/cm3). The data obtained in this work can also be useful for the investigation of the molecular structure of other heterocyclic polynitrocompounds and for the molecular design of new high density and energy materials (HDEMs). In general this investigation suggests that polynitrocompound molecules which are similar to TNBO and standard TATB and have NO2 and NH neighbouring groups in their structure are high energy materials with increased thermostability (decomp. >300 oC) and high density and these properties depend mainly on their hydrogen bonding ability.

Study of production method and phase diagram of MeNQ/NQ eutectic mixture

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Keywords: MeNQ-based eutectic; phase diagram; binary system; DSC.

Methyl-nitroguanidine (MeNQ) based eutectic mixture was thought as a potential substitution of TNT as the liquid carrier of cast explosive. And nitroguanidine (NQ) is a frequently-used component of mixture explosive and propellant. Phase diagram describe the dependence of composition and temperature. Studying phase diagram of MeNQ/NQ binary system has a very important meaning of designing the formula of MeNQ-based eutectic. There were two groups of samples of MeNQ/NQ binary system were produced in different methods, respectively. The first group was produced by heating the mixture of MeNQ and NQ and measured by Differential Scanning Calorimeter (DSC). Another group was produced by grinding the mixture and texted by melting point apparatus. The binary phase diagram of MeNQ/NQ with only one eutectic point can be constructed on the base of Van't Hoff's Equation and using melting temperature and composition of few points obtained by experiment. The two phase diagrams of different groups were approximate, their eutectic points are 0.315(mole fraction of NQ), 129.784°C and 0.304(mole fraction of NQ), 128.96°C respectively. This may give an evidence of that grinding is a new method of produce eutectic. The phase diagram with only one eutectic point indicated that there was no new substance in this system. And the results of XRD agreed with the phase diagram conclusion.

Optimization of solvent extraction method for gel permeation chromatography assay of polymeric modifier - polios 250 in smokeless powders

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Keywords: smokeless powder; Polios 250; extraction; gel permeation chromatography.

The quantification of Polios 250 - polymeric modifier of burning layer in smokeless powders was investigated. Different solvents and extraction parameters were used for selective separation of applied modifier. Two solvent extraction methods were compared e.g. with application of magnetic stirrer and ultrasonic-assisted. For quantification gel permeation chromatography (GPC) with UV-DAD detector was applied. The use of DAD detection at 320 nm with reference at 490 nm make possible optimal integration of Polios peak which is separated at a baseline level from peak of nitrocellulose and peak of low molecular stabilizer – diphenylamine. The obtained results proved that 80-95% of modifier deposited on powders surface was extracted.

Investigation of the reaction of energetic materials on jet impact

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Keywords: energetic materials; cumulative jet; improvised explosive devices.

The reaction of energetic materials closed in heavy enclosures on jet impact was tested. Non-ideal explosives, TNT and munitions secured by the police were chosen for investigations. A cumulative jet generated by applied shaped charges was characterized. Explosives were confined in steel tubes and their response was assessed by taking into account the number and size of fragments. Tests were carried out on a special set-up that allows the recovery of debris. Warfare agents were tested on the training range.

Study of features acid hydrolysis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane

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Keywords: 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane; decomposition rates; sulfuric acid; nitric acids.

The hydrolysis of the α, β and ε polymorphs of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20) was investigated in sulfuric acid and mixtures of sulfuric and nitric acids. It was found, that the decomposition rates of these three polymorphs are varied at the initial stage of the process in 92,4% sulfuric acid. Also, we have shown, that the rate of decomposition of HNIW is reduced with addition of small amount of nitric acid. By HPLC (High Performance Liquid Chromatography) it was shown that 2,4,6,8,10-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (PNIW) is formed in the systems containing 0,5 and 1,0 mol/l HNO3. The concentration of PNIW passes over a peak that proves that reaction is goes through a denitration stage.

Features of thermal decomposition of some explosive on the surface of porous carriers

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Keywords: RDX; thermal decomposition; differential scanning calorimetry; manometric method; topochemistry.

The influence of the surface of some porous carriers with specific surface from 5 to 650 m2/g on the decomposition of RDX at its concentration 0,8 - 2,0 % was studied by the method of differential scanning calorimetry and manometric method. Endotherms corresponding to melting of RDX were observed for carriers with low specific surface less than 10 m2/g. But they were absent for carriers with high specific surface more than 40 m2/g, that was explained by increased surface adsorption of the substance. The onset of decomposition and exotherms of RDX on the carriers with high specific surface were lower than on the carriers with low specific surface. The decrease at the temperature of the maximum heat flow was observed to be up to 20 ºS. A significant decrease in the activation energy of thermal decomposition occurred for each of the substances on the carriers with high specific surface. The significant growth of the initial rate of decomposition of RDX on the surface of carriers is accompanied with reduction of autocatalytic acceleration of decomposition and it becomes lower with high specific surface carrier.

Spherical PETN crystals obtained by crystallization from acetone-glycerol emulsions with additives

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Keywords: petn; RDX; crystallization; spherical; polymer.

PETN crystal samples were prepared by cooling of acetone solutions of PETN with glycerol content. Acetone and glycerol are only partially miscible and can form emulsion. Emulsion phase boundary helps to obtain relatively spherical and smooth crystals. The biggest crystals with highest bulk density were prepared with the help of ethylcellulose. This material is suitable for high filled level plastic explosives (experimental samples of Semtex 90). Most spherical crystals gave solutions containing pentaerythritol, fructose and polyvinylpyrrolidone. These materials will be tested for less sensitive applications with aim to replace more expensive and relatively toxic RDX.

Investigation of the optical properties of aluminum nanoparticles in PETN

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Keywords: laser; petn; explosive; nanoparticles.

Study of optical properties of metal nanoparticles is important in many technical applications, such as development of new energetic meterials, hyperthermia therapy carcinoma, creating new solar cells, etc. The problem is challenging because the nanoparticles both absorb and scatter light. The effect of multiple scattering occurs in many applications, so a comprehensive study that take into account the optical characteristics of individual nanoparticles and their mutual influence is necessary. Objective: To determine the characteristics of the absorption and scattering of light by metal nanoparticles in a transparent medium. Objects were PETN compressed tablets with additives of nano-sized aluminum (100 nm). Experimental measurements were performed using photometric sphere that allowed us to obtain the transmission coefficients and the sum of transmission and reflection coefficients varying the thickness of the sample and the mass fraction of the additives. The computer programs developed including the calculation of absorption and scattering cross sections and the scattering indicatrice in terms of the Mie theory with their reuse for solving the equation of radiative transfer with spherical harmonics approach. Fresnel boundary conditions were used. The simulation of light absorption and scattering was carried out. The increasing in the scattering coefficient comparing to the Fresnel value is shown. The dependence of the absorption coefficient on the concentration of inclusions is close to linear so the Beer's law is approximately applicable. The results compared with the experimental data at the wavelength of 643 nm, the refractive index obtained (1.280-5.899i) agrees well with the tabulated data. The values of true (0.661) and the apparent (1.640) coefficient of absorption efficiency determined in these conditions. It is shown that the energy absorbed by nanoparticles is higher than estimated with the geometrical cross-section because of the light scattering. The reported study was partially supported by RFBR, research project No. 13-03-98032.

Initiation of PETN by millisecond duration laser pulses

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Keywords: pentaerythritol tetranitrate; laser initiation; hot spots.

We propose a method to identify the thermal laser triggering mechanism, while the more efficient photochemical mechanism of initiation. The method relies on a different dependence of the efficiency of these mechanisms on the intensity and duration of the initiating radiation. The experimental verification of the method is carried out. It is shown that the threshold for initiation of thermo-chemical pure PETN with luminosity of about 10^4 W/cm^2 than 75 J/cm^2, the threshold for initiation of a thermo-chemical PETN with light-absorbing inclusions (0.1 wt%. Carbon black) drops to 14 J/cm^2.

Borehole velocity of detonation of ANFO and heavy ANFO explosives

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Keywords: velocity of detonation; ANFO; emulsion matrix.

ANFO is the most common explosive for civil use in the fields of mining and civil engineering. Satisfactory blasting performance, relatively low price, safety during blasting operations, a simple manufacturing process and the possibility of mechanical loading of boreholes are the main reasons for its frequent use. It has certain disadvantages, it is not water resistant and it has a relatively low velocity of detonation. It is possible to improve the properties like density, velocity of detonation and water resistance by mixing ANFO with emulsion matrix in certain proportions. This paper presents in situ measurement of detonation velocity of ANFO and ANFO explosives with certain proportion of emulsion matrix (heavy ANFO blends). Based on the measurement results, the dependence of the velocity of detonation on the percentage of added emulsion matrix was established.

Keyword Index

Author Index

The End