abstracts of the 11th seminar

New Trends in Research of Energetic Materials

NTREM

Pardubice, April 09–11, 2008

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

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New Trends in Research of Energetic Materials

held at the University of Pardubice

Pardubice, Czech Republic
April 09–11, 2008

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

This publication has not been submitted to language corrections and contributions have not been reviewed.

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532 10 Pardubice
Czech Republic

NTREM '08

Abstract proceedings of New Trends in Research of Energetic Materials

Jan Ottis, Jiří Pachmáň (editors).
Conference and proceedings number: 11.
Published by University of Pardubice.
Czech Republic, April, 2008.
138 pages.
Checked by editor, typeset and completed by Vít Zýka (www.typokvitek.com).

11th Seminar of the New Trends in Research of Energetic Materials

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Seminar is supported by:

U.S. Army Int. Technology Center (Atlantic)—European Research Office in London;
Office of Naval Research Global, Middlesex (only Session 3, see p. xii);
Schlumberger, Reservoir Characterization Group, Clamart Cedex, France;
Austin Detonator, Inc., Vsetín;
Indet Safety Systems, Inc., Vsetín, a member of Nippon Kayaku group;
Explosia, Ltd., Pardubice;
Faculty of Chemical Technology, University of Pardubice,
STV Group, Praha;
OZM Research, Hrochův Týnec;
BORGATA, Ltd., Praha;
Poličské strojírny, Ltd., Polička.

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Preface

This is the eleventh seminar *New Trends in Research of Energetic Materials (NTREM)* and jubilee the tenth in the series of seminars organised by the Institute of Energetic Materials (IEM) of the Faculty of Chemical Technology, University of Pardubice. It is held in year which is of the 55th anniversary of devolution of the Science & Technology of Explosives education from the present Prague's Institute of Chemical Technology in Prague to the former Institute of Chemical Technology in Pardubice (the present Faculty of Chemical Technology, University of Pardubice). Also the 45th anniversary of the IEM transfer from the main building of Faculty in the centre of Pardubice to the Pavilion of Special Production (nowadays Technological Pavilion in a village Doubravice) can be mentioned.

In the year that has passed from the tenth seminar, we lost some of the well-know figures in the international energetic community. The greatest loss for us is the demise of Prof. Anatoly Nikolaevich Dremin (Institute of Problems of Chemical Physics in Chernogolovka) in January 12, 2008. He appeared like a star amidst the 'cold war' around 1970 in the western world as a Russian ambassador of science. As an outstanding scientist he did thoroughly know the western work, and introduced his western colleagues in the long tradition of Russian related work in detonics. In the Eastern Europe he had a relatively close relation to the Research Institute of Industrial Chemistry (Explosia Co.) in Pardubice and after political transformation also to IEM at University of Pardubice. He was markedly influenced a teaching of Physics of Explosion at IEM. We will miss him as not only an excellent scientist but also a very good friend.

The international seminars NTREM belong among the most significant activities of IEM at present. The original purpose of these meetings was to teach young research workers how to present their results in front of scientific audience; therefore, they are first of all meant for undergraduates, PhD students, young workers in scientific research and university teachers in the field of energetic materials (research, development, production, handling, environmental issues, testing, application) and the therewith connected safety engineering. The safety engineering has an individually sponsored session in the framework of the 11th Seminar. The mentioned original purpose was later complemented by not only the exchange of findings and experience but in particular making friendly contacts between the members of the beginning young generation of experts in the area of energetic materials coming from many countries all over the world.

Realization of our seminars would never be possible without the generous support of many sponsoring institution. In the case of this eleventh Seminar very significant financial support has been regularly provided by the U.S. Army Int. Technology Center (Atlantic)—European Research Office in London, Office of Naval Research Global in Middlesex (it supports only session of safety engineering), Schlumbergerff-F˘s Reservoir Characterization Group in Clamart Cedexff-B (France), Austin Detonator in Vsetín, Indet Safety Systems, Inc. in Vsetín (a member of Nippon Kayaku group), Explosia Co. in Pardubice, Faculty of Chemical Technology in Pardubice, OZM Reasearch in Hrochův Týnec, BORGATA, Ltd. in Prague, Poličské strojírny in Polička and STV Group, Praha. 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 specifics of the previous seminars can be maintained. It would be quite unfair not to mention personal efforts of our foreign friends helping to find sponsoring institutions publicize the Seminar abroad and personally participate in organizing activities during the Seminar.

And what should I add on the occasion of this 11th NTREM Seminar? First of all, I would like to express the wish: May its proceedings be successful and may it bring inspiration and pieces of knowledge for use in further scientific research activities in the area of energetic materials, may it enable establishing of new contacts and deepening of the existing ones particularly between the young participants in this meeting, and may the participants feel at home throughout the Seminar. Finally, I wish to thank the

members of the Scientific Committee, the authors of all the submitted papers and, last but not least, you, the participants in this seminar, for its success and its influence on the continued success and growth of all future meetings at our University of young people and university teachers working in the field of all kinds of energetic materials.

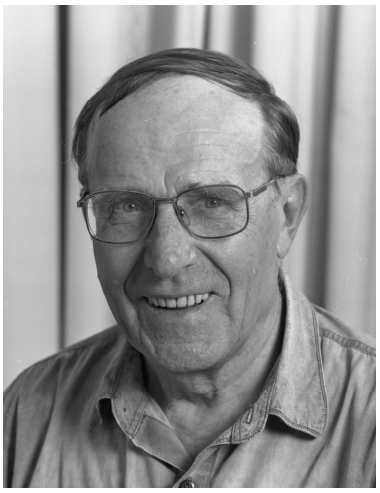
Pardubice, March 10, 2008

Svatopluk Zeman

Obituary

Professor Anatoly Nikolaevich Dremin

⋆1930-07-15, †2008-01-12



Professor Anatoly Nikolaevich Dremin, one of the founders of Institute of Chemical Physics (ICP), Russian Academy of Sciences (RAS) in Chernogolovka, a personality of outstanding merit in Russian science, a worldwide researcher in detonics, Doctor of physicalmathematical sciences died on January 12, 2008 after a serious and long illness at the age of 77 years.

Anatoly Nikolaevich started his scientific career at the ICP after graduating from Moscow Physico-Technical Institute (school of the Chemical Physics) in 1954. He was one of those young scientists whom Academician N. N. Semenov entrusted with highly important tasks connected with strengthening of defensiveness of the country. After 1958 he organized in ICP a group of young and talented co-workers and in 1960 founded a laboratory of physico-chemical properties and investigation of explosives. This laboratory became a basis for formation of Department of high dynamic pressures at the subsidiary of ICP RAS USSR in Chernogolovka: Anatoly Nikolaevich was head of this Department from 1989. The research conducted in the Department was highly appreciated both in Russia and abroad. Great contributions were made by him to the development of theory of detonation and physics of shock waves in condensed media. Dremin´s school gained authority and well-deserved acknowledgement in this scientific field both in this country and abroad. Anatoly Nikolaevich and his co-workers revealed the phenomenon of instability of detonation front in a number of explosives, which allowed formulation of new ideas and development of theory of critical diameter of liquid explosives and understanding special features of detonation. Beside his many publications he summarized the results in two monographs [1,2].

A very important and natural role of Anatoly Nikolaevich was in overcoming of political barriers: he appeared like a star amidst the ‘cold war’ around 1970 in the western world as a Russian ambassador of science. He offered more basic understanding versus ‘straight forward’ interpretations and stimulated new research also in the West. As an outstanding scientist he did thoroughly know the western work, and introduced his western colleagues in the long tradition of Russian related work in detonics. Quite naturally beside his teaching activities he organized meetings, and symposia, was in related Committees and the editorial boards of Combustion and Explosion Physics, and for point of time also Propellants, Explosives, Pyrotechnics. No wonder that his contributions and discussions had been highlights of such meetings. As a university teacher he prepared many specialists in the area of physics of explosion; his results and activities markedly influenced teaching of Physics of Explosion at the Faculty of Chemical Technology in Pardubice.

Anatoly Nikolaevich was a highly understanding man in his relation towards other people, kind-hearted and magnanimous. However, in science he was highly demanding and uncompromising. If he expressed his opinion, one could be sure that it was supported by extensive study in every context. He had a number of very good friends in the Czech Republic, who highly appreciated his excellently logical way of thinking, his ability to connect theory with experimental results, and his original approach to dealing with fundamental problems of detonation. They also appreciated his extensive and complex knowledge in the area of world painting. The important point is that Anatoly Nikolaevich was not only an important

researcher, he was a WONDERFUL Human Being. All those who had the fortunate opportunity to get more deeply acquainted with him will miss him and will often cast their minds back to meeting him.

[1] Dremin, A. N.; Savrov S. D.; Trofimov, V. S.; Shvedov, K. K. *Detonation Waves in Condensed Media*. NAUKA, Moscow, 1970. Edited translation: Sechovicz, J. Translation Division, Foreign Technology Division, WP-AFB, Ohio FTD-HT-23-1889-71, 1972.

[2] Dremin, A. N. *Toward Detonation Theory (High Pressure Shock Compression of Condensed Matter)*. Springer, New York, 1999.

Dr. Carl-Otto Leiber
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Recent and Current NATO RTO Work on Munitions Disposal

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Keywords: environment; munitions; disposal; demilitarisation;.

The environmentally acceptable disposal of surplus munitions has become a major problem for NATO and others. The NATO Research Technology Organisation carried out a study of the problems and tried to identify both gaps and possible research directions to fill these. It covered not only disposal but also land contamination and included a Workshop in Sofia in September 2007. The conclusions and recommendations will be outlined.

A New Look at Evaluating Shock Sensitivity by Gap Tests

Ruth Doherty, Harold Sandusky, Richard Granholm, Joshua Felts

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Keywords: shock sensitivity; gap test; PBXN-109; SDT.

Measurement of the shock sensitivity of PBXN-109 using three different gap tests has revealed unexpected behaviour in the growth of reaction in the acceptor charges as a function of the length of the gap. Addition of instrumentation to the gap tubes and post-test recovery of the tube fragments showed that, for gaps slightly longer than the critical gap, a reactive wave with a nearly constant shock velocity somewhat higher than the sound velocity propagates through the acceptor charges. This phenomenon is observed over a range of gap thickness that is dependent on the quality of the RDX used in the PBXN-109. The results also showed a transition to detonation at a much greater distance from the gap than had previously been expected.

Blast – Fragment Loads

Manfred Held

TDW

Keywords: improvised explosive; blast.

Improvised explosive devices can exist from a large number of different ammunition types. Very usually are blast charges in nearly all quantities. Now the question arises, are the impulses against target structures reduced or increased by casings or fragments around the charges. First the expansion of blast waves will be explained, generated by the detonation of a high explosive charge. Then will be shown the time differences of blast and fragment impacts as function of distances and with the charge sizes as parameter. Finally were given rules, where additive effects of blast-/fragments have to be considered on targets

Basic Safety ABC

Hans Pasman

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Keywords: accident investigation; cause-consequence; safety management.

Preventing accidents pays good dividend. Safe working is a matter of culture but also of systematic approach. A Safety Management System (SMS) has been developed based on experience in accident investigation and quality assurance. Such systems became widely introduced after the Piper-Alpha offshore platform disaster in the North Sea in the early nineties of last century. The paper will describe and elucidate briefly the elements of an SMS.

Relationship between the Compaction Reponse and Morphology of RDX and Its Shock Semsitivity

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Keywords: RDX; mechanical properties; sensitivity; specific area; particle sizing.

Using small-scale gap-testing a sensitivity scale has been determined for a variety of class sizes and types of tapped granular RDX. The chosen materials cover a large range of particle sizes (10–1600 μm) and a wide range of crystal shapes, void contents and surface qualities. In this paper the effect on the sensitivity of individual particle morphology and the response of the material to compaction are explored. The compaction response is determined at two widely differing loading rates – 4 mm/min in an Instron mechanical testing machine and 3 m/s in a drop-weight facility. It is found that there is a large difference in the response between the two compaction rates, but that there are no obvious correlations between the resistance to compaction and the sensitivity. Particle sizing of the tested and untested materials demonstrates a considerable amount of particle fracture, the extent of fracturing occurring being comparable between the two rates. Image analysis performed on optical microscope micrographs was used to obtain detailed information on the morphology of individual particles in each batch. It is found that the sensitivity of the materials within a given class appears to decrease as a greater fraction of the total projected area is contributed by larger particles. In three dimensions this would correspond to the sensitivity increasing with the specific area.

Inhomogeneous Ageing of a PBX

Mark Ashcroft, Simon Torry, David Tod

QinetiQ, Kent

Keywords: PBX; inhomogeneous ageing; diffusion limited oxidation; NMR; FTIR microscopy.

Energetic materials tend to degrade with time, which can lead to a decrease in safety margins, increases in whole life cycle cost and loss of overall effectiveness of the munition. An important aspect of both propellant and polymer bonded explosive ageing processes is diffusion-limited oxidation. Ageing trials normally ignore the fact that most ageing processes are inhomogeneous. That is to say, the rate of degradation is dependent on the distance from the energetic materials free surface. The ageing behaviour is also different at interfaces such as between the insulating liner and the energetic material. In this work, the heterogeneous ageing chemistry of a plastic bonded explosive (PBX) was studied using nuclear magnetic resonance spectroscopy, infrared spectroscopy, dynamic mechanical analysis and chemical analysis techniques. As in large web propellants, PBXs can develop oxidation profiles during ageing processes. A diffusion-limited oxidation model was invoked to explain some aspects of the heterogeneous oxidation profiles in the PBX. However, the basic model was unable to account for some oxidation profile characteristics. Differences were observed between the ageing characteristics of polybutadiene/ammonium perchlorate based propellants and the PBX.

Calculation of Detonation Parameters of RDX Mixtures with Inert Additives

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Mendelejev University of Chemical Technology

Keywords: RDX; inert; calculation.

Analysis of works concerning to metal working by explosion shows, that the range of detonation pressure of explosives charges for this purpose is P=0.3–10 GPa. Experimental investigations show that RDX mixtures with sodium chloride meet the requirement. Heat of explosion of such mixtures, that formats their velocity and pressure of detonation can change in a wide range. These mixtures are applied for measuring of minimal initiation pressure of dangerously objects in the practice of industrial safety investigations. Computer codes for calculation of detonation velocity and pressure are unsuitable for mixtures containing less than 30
our paper is elaboration of a method of calculation of detonation parameters of RDX/inert additives mixtures and estimation of its efficiency. The results of experimental measurement of detonation parameters of such systems, that had been carried out in Mendeleev University in 70-th years, were taken into account. Experimental results of a detonation pressure measurement are compared with computation ones at constant and at variable (vs. density of explosive) polytropic exponent. The good agreement turns out in a second case. Detonation of RDX/inert powder mixtures is possible as particles of additives have not time to warm up in detonation wave. However at firing of such mixtures particles warm up and burning process damps. Such peculiarity, ability to detonation and inability to burning and therefore to deflagration to detonation transition, excludes its accidental explosion at use.

The Two-Stage Detonation Propulsion Model: Further Exploring 1st Stage Performance Effects by a Look Backward at the Model's Basis

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Keywords: explosive performance; detonation modeling.

The goal of this paper is to describe to students and young researchers issues that are rooted in the original data forming the basis for the Two-Stage Detonation Propulsion Model and that might be explained through new experimental work.

An oral presentation is preferred; but a poster presentation would also provide a suitable forum in which to convey the paper's message.

The Two-Stage Detonation Propulsion Model was presented at the 9th NTREM as a means to identify, model, and explain effects occurring during the detonation of a condensed heterogeneous explosive that affect the explosive's measured and modeled performance. At the 10th NTREM, the model was used to reveal issues well established in experiments described in scientific publications that now could be explored differently through new experiments guided by the model's methodology.

The proposed paper reexamines the experimental data from which and upon which the Two-Stage Detonation Propulsion Model was constructed in order to offer students research areas in which new experiments and scientific study might provide fresh insight into important explosive-driven effects such as: • How an air gap between an explosive and a boundary material affects modeling an explosive's performance and the material's propulsion, • How the direction of a detonation wave may affect both the throw direction and final velocity of propelled materials, and • How 1st propulsion stage effects may be principal factors deciding detonation propagation throughout an explosive charge.

Impact Testing of RDX; the Effect of Crystal Quality

Richard Bouma, Antoine Heijden, A. Boluijt, H. Verbeek

TNO Defence, Security and Safety,
Protection, Munitions and Weapons

Keywords: RDX; impact sensitivity.

The effect of RDX crystal quality on the shock sensitivity of RDX-based plastic bonded explosives has been extensively studied internationally, as significant differences in shock initiation pressures had been observed. The RDX crystal itself can be visualized, but a unique and also easily quantifiable property of the crystal related to shock sensitivity, is still missing. In an international round-robin test a.o. the impact sensitivity of RDX has been measured. Standard impact testing thereby focusses on the determination of the dropheight corresponding to a 50 % initiation propability. However, no correlation with shock sensitivity has been found. In this paper results will be presented on impact testing of various RDX samples using the Ballistic Impact Chamber (BIC). The pressure evolution in the BIC is measured. Numerical simulations have been performed to guide the experimental design and explain the observed phenomena in the measured pressure evolution. The experimental results obtained with the BIC are compared to the RDX crystal quality as observed by optical microscopy and SEM. The reactivity of RDX in the impact testing with the BIC does correlate to this crystal quality and opens up the possibility of achieving a quantitative determination of crystal quality.

Correlation of Structure and Sensitivity in Inorganic Azides

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Keywords: inorganic azides.

Abstract The sensitivity of explosives is a subject of keen interest to all those involved in the handling of these materials. Current ability to predict sensitivity is based on a series of empirical rules for different classes of explosive compounds. Whilst these may be valid for organic classes, inorganic materials do not conform to any of these patterns. This study examines the structure of a number of inorganic azides using a molecular mechanics based on a Universal Force Field (UFF) approach. The process was successfully validated for KN3, RbN3, CsN3, TlN3 and AgN3. These azides showed RMS deviations of between 0.07 and 0.11Å from the original crystal structure following operation of the minimisation technique for a disordered arrangement with the constituents atoms displaced from their known positions by around 0.25Å RMS deviation. The structures of the inorganic azides were examined and compared with their impact sensitivity. A very good correlation was found between impact sensitivity and the minimum non-bond nitrogen to nitrogen distance across a wide variety of azides. This correlation is likely to be the result of minimising the atomic movements required to produce the reaction products. Using the UFF, appropriate point defects (Schottky and Frenkel pairs) were modelled for these azides under conditions of the maximum and minimum achievable pair separation. The maximum limit on pair separation was a result of the explicit modelling being limited to a 3 x 3 x 3 unit cell matrix. The results showed that the minimum non-bond nitrogen to nitrogen distance narrowed in the presence of defects for all azides. A greater difference was found in TlN3 compared with the other azides. This may indicate that the sensitivity of TlN3 is greater than the ideal crystal structure would suggest.

Properties of Lead-Free Primers – Development of a Testing Facility at the Cavendish Laboratory

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Keywords: primers; ignition; test methods; green energetics.

Small calibre ammunition performance is strongly influenced by primer and propellant characteristics. While the technology for propellant characterisation has been developed, primer performance has received less attention. This paper describes the development of a system which directly measures primer combustion parameters to aid development of heavy-metal-free primers, and primary explosives. A small, light gas gun propels a projectile down a 150 mm barrel towards a percussion primer, igniting it on impact. Gases evolved expand into a 104 mm3 cavity, and a high-speed (1 μs rise time) ballistic pressure gauge measures the pressure profile along the impact axis. Preliminary pressure profiles of three primer compositions are presented. Further instrumentation can be added, (e.g. thermal and spectral measurements) such that many properties of new, greener primers can be measured.

Characterization of High Calorific Fe-KClO4 Mixture

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Keywords: heating mixture; Fe/KClO4 system.

High calorific mixtures are used as a heating source for technical installations This paper discusses properties of two components mixture consisting of iron power and potassium chlorate(VII). Its characteristic features are: low gases emission and high heat conductivity, which allows storage of excess energy produced in the first phase of its ignition as well as low electric resistance. It was observed that the influence of iron powder type, percentage and specific volume palletized components of the mixture on the specific caloric value and burning rate. Moisture present in iron powder significantly decreases its burning rate as well as the caloric value. This review discusses also the influence of storage conditions on the above parameters. In addition, burning rate of the mixture directly influences activation time and its readiness for the practical use. Properties of iron powder used for pallets' production reflect its burning rate as a high calorific mixture. The most important of all are impure metallic element cumulated on the surface of the pallets as well as phase oxides composition. The reactivity of particular samples with different oxides phase composition was measured by the degree of potassium chlorate (VII) conversion. The remaining (not reacted) amount of KClO4 underwent decomposition but did not react with iron, and the oxygen liberated on the decomposition was released to the atmosphere. In our study we argues that an increase of KClO4 in a mixture significantly increases calorific properties and burning rate reducing at the same time the amount of oxygen reacting with iron powder. It is observed that decreasing the specific volume of pallets results in an insignificant decrease of burning rate. In addition, the paper describes the influence of storage conditions and its ageing hasten in 130oC at lower pressure on its burning rate.

Urban-Module for Explosive-Tests

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Keywords: Urban-Module; blast; closed Rooms.

In 2007 a new urban-module was build in the test-area of Meppen. The module has eight rooms and a corridor. The rooms are 5 metres long, 4 metres wide and 2.5 metres high. Some rooms have windows and doors, other rooms have only doors. With this module we will investigate the effects of explosives and the behaviour of explosive fumes in rooms. After tests it is possible to change the walls and the ceilings of the rooms.

Dynamics of Explosive Fumes

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Keywords: fumes; simulations; AUTODYN; SIBEX; shockwaves; closed space.

The first task was to simulate the afterburn effect of SIBEX (Shock Insensitive Blast enhanced EXplosives) with the simulation-software AUTODYN 6.1z, but AUTODYN 6.1z has no material data and EOS of SIBEX in its own library. The analysis of literature and measured pressure-curves shows that in the period to approx. 15 ms after the detonation the pressure behaviour of SIBEX is nearly the same as HE (example TNT). After approx. 15 ms the afterburn effect seems to appear (fumes-reactions, subsonic, no shock wave, only explosion). With AUTODYN 6.1z we simulate only TNT-fumes in the period of max. 15 ms after the detonation in various environments. The results of TNT-fumes-simulations show: Near reflective surfaces (walls, bottom and/or ceiling) the fumes have a dynamic movement as a result of pressure-reflection (exchange/transfer of momentum). The beginning of the fumes-reactions (max. 15ms after the detonation) will probably be observed in the middle of the room independent of the place of detonation in the room (with or without windows/doors). The fumes-reactions/dynamics in open air and rooms are not the same. As a result of pressure-reflection the reaction process (afterburn) in the fumes gets an additionally influence (coupling of shock-wave-pressure and combustion-pressure of the fumes in rooms). The verification of the simulated fumes-dynamics and of the beginning of the fumes-reactions is necessary.

The Quantitative Risk Assesment of Civil Facilities Handling Explosives

Milos Ferjencik

University of Pardubice

Keywords: risk assessment; explosives handling; computational tool; demil; safety culture.

The paper summarizes the author's experience with the quantitative risk assessment (QRA) within explosives handling facilities. Relevant QRAs are required by the Czech law that implements the Seveso II directive. Author presents applied approach to the QRA and a computer tool that enables the realisation of approach. He explains that results of the QRA may support motivation for safety culture in the facility. Unresolved tasks are identified and possible ways to their solution are described in the paper.

Development and Testing of High Density Energetic Materials Containing Superior Amounts of Oxygen

Michael Göbel, Thomas M. Klapötke

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Keywords: energetic materials; high oxygen explosives.

Trinitroethanol (TNE) (1), bis(2,2,2-trinitroethyl)amine (BTNA) (2), bis(2,2,2-trinitroethyl)carbonate (BTNEC) (3), N1-(2,2,2-trinitroethyl)-1H-tetrazole-1,5-diamine (TTD) (4) as well as N1,N5-bis(2,2,2-trinitroethyl)-1H-tetrazole-1,5-diamine (BTTD) (5) have been synthesized and characterized using vibrational spectroscopy (IR, Raman), mass spectrometry, multinuclear NMR spectroscopy and elemental analysis. The thermal decomposition was monitored using differential scanning calorimetry (DSC). Some of these high-crystal-density polynitro-group containing compounds show available oxygen in amounts never before attained in solid explosive compounds. The crystal structure analysis of 1-5 using single crystal X-ray diffraction was accomplished as a preliminary step in an investigation of the relationships between structure and crystal density in energetic substances.

Software for the Computation of Activation Energy from Differential Scanning Calorimetry and Related Safety Parameters of High Energetic Materials

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Keywords: differential scanning calorimeter; time-to-thermal-runaway; Cook-off temperature; thermal hazard potential.

The kinetics of exothermic reactions is important in assessing the thermal hazard potential of energetic materials. In view of this, a software package, named LION-Kins- version 1.0 is developed to perform the computation of activation energy, Arrhenius pre-exponential factor and rate constant of a system from differential scanning calorimetry data based on ASTM E698-05, followed by computation of thermal hazard potential of energetic materials such as 1) Time-to-thermal-runaway, 2) adiabatic decomposition temperature rise, 3) explosion potential, 4) shock sensitivity, 5) critical half thickness, 6) Critical (cookoff) temperature, 7) Instantaneous power density and 8) NFPA instability rating. An iterative algorithm is incorporated to vary surrounding initial temperature with predefined steps to compute initial environmental temperature vs Time-to-thermal-runaway. Successive approximation type of iterative algorithm is incorporated in the software package for the computation of cook-off temperature / critical temperature. The internal computed values during the computation of cook-off temperature can be directly exported in Excel format to view the effective convergence of iteration by successive approximation. The software package developed in the present work - LION-Kins can be installed in Windows 98, 2000, Me, XP and Vista. Keywords: Differential Scanning Calorimeter, Time-to-thermal-runaway, Cook-off Temperature, Thermal hazard potential.

Influence of [equiv.NCO/equivOH] on cross-link density

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Keywords: stress-strain; HTPB.

Polyurethanes based on Hydroxy Terminated Polybutadiene (HTPB) are most suitable binder systems for composite solid propellants as they are helpful in increasing performance by offering excellent flow properties, high solid loadings, aging stability, hydrolytic stability, and good low temperature mechanical properties. They are extensively used in the development and manufacturing of composite solid propellants due to their excellent reproducible curing mechanism and easy control of mechanical properties. The focus of this paper is to study the stress-strain behavior of polyurethane networks in relation to kinetic theory of elasticity. Hydroxy Terminated Polybutadiene (HTPB) based urethane networks were prepared by reacting HTPB with Toluene Diisocynate (TDI) at various equivalent ratios (R) of (NCO/OH). Curing was done at 50 C for 168 hours. Mechanical properties were tested on INSTRON and cross-linking density was measured by swelling method. From results, it was observed that stress varies directly with the cross linking density where as an opposite relation between stress and molecular weight between cross-links was observed. Experimental stress-strain curve showed excellent agreement with theoretical stress-strain curve at low strains.

Overpressure Calculation of Gas Explosion in Tunnels

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Keywords: gas explosion; deflagration; overpressure; tunnel.

Gas explosions in coal mines are serious problem for long decades and thousands of people have been killed during those accidents. Decrease in coal production caused also decrease of research institutes interest in gas explosions in 1-D geometry. Therefore consequence assessment techniques for this kind of explosion are not very advanced. There is a simple code ”Plyny“ used for overpressure calculation in Czech coal mines. Results of ”Plyny“ calculation were compared with experiment together with CFD simulations by AutoReaGas code. The comparison was also done for classical TNT method found in literature. The use of particular methods is proposed.

A Novel High Energy Density Material Compound 3,4-Bis(nitrofurazano)furoxan:Synthesis, Characterization and Properties

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Keywords: high energy density material compound; 3, 4-bis (nitrofurazano) furoxan; synthesis; characterization; properties.

A novel high energy density material compound 3,4 - bis (nitrofurazano) furoxan (BNFF) was synthesized using 1,3-dicyanopropane as initial material through four steps. An organic compound possessing a new chemical molecular structure was founded. The synthetic process of BNFF was discussed at length. This paper also reports the properties of BNFF and its intermediates such as melting point, 5s explosion point temperature, and sensitivity (friction, impact and electrostatic spark). Quantum chemistry and BKW calculations were conducted on them, too. The theoretical and experimental studies show that BNFF is a novel high energy density material compound with its energy some higher than that of HMX, approaching that of CL-20 and mechanical sensitivity some lower than that of HMX.

Computer Program of Designing Drilling and Blasting Works on Open Cast Mines

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Keywords: computer program; blasting works.

Designing a complex of drilling and blasting works on open cast mines is made by considering an economic expenditure of material and monetary resources, maintenance of set granulometric composition and the convenient form of disorder of the blown up mountain weight, and also a high level of safety of works. The program enables to choose an optimal type of en explosive for the given mining-geological conditions, to calculate mass of borehole charges and to ascertain parameters of their arrangement. It also calculates combined charges, chooses optimum schemes of explosion and intervals of delays between explosions and calculates radiuses of dangerous zones. Parameters which should be entered into the program (Microsoft Visual Fox Pro) include information about geological and mine technical conditions and also market price of comparing explosives. Considering the circumstance that some of the entrance parameters may not be known in advance, in the program there are entered help data from which the user can choose value of the missing parameter corresponding concrete object. The program is appropriate for different quarries of Georgia with absolutely different mining-geological conditions.

Decomposition Chemistry of Crystalline DADNE

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Keywords: DADNE; organic molecular crystals; energetic materials; explosive decomposition.

In this study, the thermally activated decomposition chemistry of crystalline 1,1-di- amino-2,2-dinitro-ethylene (DADNE) is modeled by means of an Embedded Cluster Method with Density Functional Theory. Our primary goal is to understand initiation mechanisms in solid explosives and ultimately to learn how to predict and control both the sensitivity to initiation and the performance of the energetic materials at large. Our first principles calculations show that the response of an explosive solid to external stim- uli is essentially a cooperative phenomenon, which strongly depends on the interplay of molecular and crystalline structures of materials under study. The research also revealed that mechanisms of initiating chemistry in bulk crystals may differ significantly from those in gas phase molecules despite the molecular nature of the energetic materials, and, therefore, a special attention should be paid to develop further solid state models of initia- tion and performance. Relevant decomposition reactions in DADNE are discussed and analyzed.

Synthesis, Structure and Properties of Some New Nitro- and Oxo-Derivatives of Pyridine

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Keywords: 2,3,5,6-tetraoxo-4-nitro-pyridine; 4,6-dinitro-2-ethoxy-3-hydroxy-pyridine.

Ammonium 2,3,5,6-tetraoxo-4-nitro-pyridinate (I) and 4,6-dinitro-2-ethoxy-3-hydroxy-pyridine (II) were obtained as products of catalytic oxidative nitration of 2-amino-3-hydroxy-pyridine. The features of their crystalline structures were determined by X-ray method. The studies of the above substances showed that the thermal decomposition of I is in accordance with the radical mechanism as far as the mechanism of decomposition of is the molecular one.

Advanced Concept of the Phenomenon of Negative Erosion at the Energetic Materials Unsteady Combustion

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Keywords: solid propulsion systems; combustion instability; negative erosion; solid propellant energetic performances.

Combustion instability represents one of the most complex engineering problems yet confronted in the solid propulsion system development.

The phenomenon of reduction of the burning rate as a result of blowing of the propellant burning surface with small velocity of the combustion products of the same composition refers to as the effect of "negative erosion". The phenomenon of "negative erosion" is one of typical anomalies of burning.

In the paper the new concept of the phenomenon of negative erosion is suggested.

Interaction of the blowing flow with wandering micro-torches on the burning surface causes excitation of the micro-vortex cells - periodic toroidal vortex micro-structures. Excitation of the periodic toroidal vortex micro-structures above the burning surface causes increase of the heat flow from the gas phase into the burning surface and, as a result, local increase of the burning rate. Besides, each of toroidal vortex micro-structures creates effect of the "Thermal Pipe" by means of which is provided heat-transfer enhancement to the burning surface. At increase of the blowing velocity occurs destruction of the micro-vortex toroidal structures that leads to reduction of the heat supply to the burning surface. In these conditions the intensity of thermo-electric convection decreases and influence of the "negative erosion" increases. Accordingly it leads to reduction of the burning rate that can lead to extinction of the energetic material.

The phenomenon of "negative erosion" is the most frequently observed in the solid propulsion systems with the charges having two and more coaxial channels. In the paper the mechanism of excitation of the phenomenon of negative erosion in the solid propellant charges having coaxial channels is considered.

The phenomenon of negative erosion will reduce the solid propellant energetic performances. Hence, development of technologies which can reduce influence of this phenomenon, has great importance. For improvement of the solid propellant energetic performances and for exception or minimization of the phenomenon of gas-dynamic closing of the channel the new technology of control by the existential instability of the electro-physical fields and spatial-periodic micro-structures in the burning wave of the energetic material is suggested.

Bridged-Bistetrazole Derivatives

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Keywords: hydrazinebistetrazole; guanazinium; azotetrazolate; hydrogen-bonding; stability; detonation parameters; propellant.

Large scale syntheses of nitrogen-rich 5,5´-hydrazinebistetrazole (HBT) and bis(3,4,5-triamino-1,2,4-triazolium) 5,5´-azotetrazolate (G2ZT) with high yields and purities on a multigram scale are introduced. DSC analysis showed good thermal stabilities for both materials (>200 °C) and their long-term stabilities were assessed by TSC (Thermal Safety Calorimetry). Since molecular structures play an important role in the properties of an energetic material, hydrogen-bonding in both compounds is described in terms of graph-set analysis. The extensive hydrogen-bonding in the structures seems to account for their relatively high densities (HBT: ρ = 1.841 g cm-3 and G2ZT: ρ = 1.708 g cm-3). The heats of combustion of the two compounds were measured using bomb calorimetry (ΔcU°(HBT) = -2990(40) cal g-1 and ΔcU°(G2ZT) = -3380(80) cal g-1) and combined with the experimentally determined densitites (X-ray) and the molecular formulas to calculate the detonation pressures (P) and velocities (D) using the EXPLO5 computer-code (HBT: P = 36.7 GPa, D = 9463 m s-1 and G2ZT: P = 27.7 GPa, D = 8702 m s-1). The sensitivity of both materials to shock, friction and electrostatic discharge was assessed using standard BAM tests, revealing very stable compounds (HBT: Shock >30 J, friction >108 N and G2ZT: Shock >30 J, friction >360 N) with no sensitivity towards an electrostatic discharge of 20 kV. In addition, the explosion/decomposition gases were experimentally measured by means of IR spectroscopy and mass spectrometry and are compared with the explosion/decomposition gases calculated using the ICT thermodynamic code. With high nitrogen contents (80%), the reported bistetrazoles are prospective new, environmentally friendly, high-performance energetic materials/ingredients with low sensitivities and good thermal stabilities

An Analysis of Test and Assessment Methods on Chemical Compatibility of Primary Explosives

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Keywords: chemical compatibility; primary explosives; test and assessment methods.

It was done an analysis in the frame of test and assessment methods on material compatibility (mainly expressed by chemical reactivity) of primary explosives applied in initiation devices like detonating squibs or firing primers, igniters and fuses (fusing systems) filled with such primary explosives as mercury fulminate, lead azide, lead trinitroresorcinate (lead styphnate) and tetrazene. This analysis was realized on the basis of available scientific and technical literature sources including NATO and USA standardization documents. From above analysis, it appears that the most often used test and assessment methods on chemical compatibility of primary explosives are: Vacuum Stability Test (VST) measuring quantity (optionally volume, pressure) of gaseous reaction products released during thermal decomposition at 100 oC or 120 oC for 40 h or 48 h, heat isothermal tests at 75 oC or 100 oC on mass loss of tested sample due to 48 h or 96 h heating, and thermal analysis methods comprising Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) usually determining onset of peak of thermal decomposition temperature, comparative titration analysis and non-contact methods on assessment of metal corrosion.

Continuous Aerobic Degradation of Dinitrotoluenes by Immobilized Mixed Microbial Population

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Keywords: biodegradation; dinitrotoluenes.

This study describes biodegradation characteristics of the individual 2,4-DNT and 2,6-DNT by a defined mixed culture in packed bed bioreactor. The reactor was packed with poraver. All continuous degradation procedures were carried out at excess of oxygen that enabled to achieve the complete pollutant mineralization. The loading characteristics proved higher biodegradation rate and efficiency of 2,4-DNT than for 2,6-DNT.

Liability of Some Ammonium Nitrate Mixtures

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Keywords: ammonium nitrate; safety hazards; accidents.

Ammonium 2,3,5,6-tetraoxo-4-nitro-pyridinate (I) and 4,6-dinitro-2-ethoxy-3-hydroxy-pyridine (II) were obtained as products of catalytic oxidative nitration of 2-amino-3-hydroxy-pyridine. The features of their crystalline structures were determined by X-ray method. The studies of the above substances showed that the thermal decomposition of I is in accordance with the radical mechanism as far as the mechanism of decomposition of II is the molecular one.

Safety Evaluation of Detonation Parameters for Hydrogen-Methane-Air Mixtures During Transport in Pipelines, Based on Experimental Study

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Keywords: detonation; hydrogen-methane-air mixtures; explosion hazard in pipelines.

Paper presents a computational study of the fundamental detonation parameters of stoichiometric hydrogen-methane-air mixtures based on Chapman-Jouguet theory, ZND model and detonation wave cell size calculations. Methane-hydrogen mixture is used at different combustion devices like spark ignited engines, gas turbines, different kind of burners with premixed and diffusion flames. A series of calculations on detonation parameters of stoichiometric hydrogen-methane-air mixtures were made with different H2 contents in the mixture, from 10% up to 100% of hydrogen. The effect of the initial composition of the mixtures as well as initial pressure on the detonation velocity and cell size were investigated.

Energetic Materials based on 5-Aminotetrazoles

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Keywords: energetic materials; 5-aminotetrazole; nitration; diazotation; cycloaddition.

5-Aminotetrazole (1) is an unique starting material for synthesis of new energetic materials with high nitrogen contents. In this work different reaction pathways and selected compounds are presented. For all this reactions 5-aminotetrazole or its methyl derivatives 1-methyl-5-aminotetrazole (2) and 2-methyl-5-aminotetrazole were used as the precursors. Available are next to tetrazolium and tetrazolate salts of 1 – 3, 5,5'-azotetrazoles, 5-azidotetrazoles, 1,5-bistetrazoles, 5,5'-bistetrazolylamines, 5-nitriminotetrazoles, bistetrazolyltriazenes, 5-nitrotetrazoles, 5H-tetrazoles and many more energetic derivatives. Each kind of these classes originate valuable energetic materials, which can be used for primary and high explosives, propellants or as coloring agents in pyrotechnic compositions. Nearly all compounds were characterized by standard chemical analytic methods (X-ray, IR and Raman Spectroscopy, multinuclear NMR spectroscopy, elemental analysis, mass spectrometry) as well as methods with regard to their energetic properties (differential scanning calorimetry, bomb calorimetry, thermal safety calorimetry, impact and friction test).

Detonation Parameters and Blast Wave Characteristics of Nitromethane Mixed with Particles of an Aluminium-Magnesium Alloy

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Keywords: heterogeneous explosives; detonatioon performance; blast waves.

In this work the investigation of detonation parameters and blast wave characteristics of the mixtures of nitromethane and particles of an aluminium and magnesium (Al3Mg4) alloy was carried out. The mixtures of gelled nitromethane containing 15, 30, 45 and 60 wt. % Al3Mg4 were tested. Measurements of detonation velocity and Guerney energy were performed. Parameters of blast waves produced by charges of the investigated explosives were measured.. Thermochemical and gasdynamical calculations were also performed. A degree of combustion of the metallic addition with the gaseous products during detonation and expansion is discussed.

Experimental Assessment of the Detonability of Ammonium Nitrate

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Keywords: ammonium nitrate; detonation; confinement.

Application of Nanotechnology Techniques to Non-Ideal Emulsion Explosives

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Keywords: nanotechnology; emulsion explosive; non-ideal explosive; aluminum particles; thermal properties.

Abstract. Ammonium nitrate emulsion explosives are non-ideal explosives that may be made more effective for certain applications by controlling the energy it releases. One means of adding overall energy to the basic emulsion explosive is through the addition of aluminum particles. It is well known that the size of the aluminum particles affects the reaction rate of the explosive. What is not so well known is that the control of the properties of the oxide coating on the aluminum particles controls manner in which the energy is released. Modeling of the burning of aluminum particles in an emulsion explosive shows that the thermal and mechanical properties of the oxide coating on the aluminum particles controls the amount of the overall energy that is released as shock energy and the amount of energy that is released that does not support the shock wave. Nanotechnology techniques may be used to control the coating properties, such as its thermal conductivity and specific heat. Whether the coating remains an oxide coating or is replaced by non-oxygen based coating it is these two properties of the coating that controls the split of energy from the explosive. By modeling this split of the output energy one may use the cheaper non-ideal explosives in applications normally thought to be effectively filled only by ideal explosives.

Nanometer Detonation Soot at Low Temperature

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Keywords: weak detonation; slurry explosive; detonation soot; parameter predicting.

The methodology assumes that the heat of detonation of an explosive com-pound of composition CaHb-NcOdLieMnf can be approximated as the differ-ence between the heats of formation of the detonation products and that of the explosive, divided by the formula weight of the explosive. For the cal-culations in which the first set of decomposition products is assumed, pre-dicted heats of detonation of slurry explosives with the product H2O in the gas phase have a deviation of 866 kJ/kg from results with the product H2O in the liquid state. Fine-particle lithium manganate has been prepared by the detonation of slurry explosives of the metal nitrates, M (NO3) x (M = Li, Mn) as oxidizers and glycol as fuels, at high temperature and short reaction time. The detonation products were identified from X-ray pow-der diffraction (XRD) patterns, and scanning electron microscopy (SEM) measurements. XRD analysis shows that nanoparticles of Lithium Manganate can be produced from detonation of slurry explosives due to fast quenching as well as appropriate detonation velocity, pressure and temperature.

Variation Analysis Of Propellant Mechanical Properties

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Keywords: solid propellant; mechanical properties; variation.

Approving the mechanical properties of solid rocket motors is usually done by testing the mechanical properties of specimens from molds which are casted in parallel to the casting of motor. However, statistical analysis of the properties shows high variation of up to 30% in batch to batch and within the same batch. The object of this work was to find the causes of the variations in the mechanical properties and to minimize them. The research included 3 parts: monitoring of the variation sources, statistical analysis of the gradient in the mechanical properties and reducing it by design of experiments (DOE) method. This research included all propellant production steps (raw material treatment, mixing, casting, curing and lab tests) and proved that the variation is attributed mainly to the propellant casting step. Because of the temperature difference between the propellant and casting facilities (molds and funnel), a temperature gradient exists during the casting, which is suspected to be the cause of variation in mechanical properties. Reduction of the temperature difference between the propellant and casting apparatus reduced the variations in the mechanical properties. Tests of propellant samples which were taken from 2 full scale motors indicate that there is also variation in their mechanical properties. The conclusions are: - Part of the variation in the mold may be explained due to casting conditions such as temperature distribution between the propellant and the casting equipments, temperature difference in the mold itself - bottom versus top. - Casting with a heated funnel and heated molds reduces the variation in mechanical properties. This may be attributed to a uniform temperature profile in the propellant and hence less difference in reaction rate within the mass of propellant. The variation in a full scale motor requires further research.

Could be the simple methods of overpressure calculation during vented gas explosion universally use for various conditions?

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Keywords: vented gas explosion; deflagration; overpressure.

Proper design of gas explosion mitigation measures e.g. bursting discs cannot be done without knowledge of object internal blast loading. This question is also important in connection with European directive 1999/92/EC known as ATEX 137. Empirical, semi-empirical and theoretical methods could be used for generated maximum overpressure calculation or venting area calculation. Computational fluid dynamic used in sophisticated software codes is other possibility. There is comparison of some empirical and semi-empirical relations in the paper. Results of calculations are compared with experimental results published by various authors who used various geometrical configurations and various mixtures. There are recommendations for use of relations listed in paper.

Synthesis of 1,2,3-triazole Derivatives from 3-azido-1,3-dinitroazetidine

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Keywords: α-nitroazides; 1,3-dipolar cycloaddition; 1,2,3-triazoles; nitro esters; azidomethyltriazoles.

The synthesis of 1,2,3-triazoles via 1,3-dipolar cycloaddition of α-nitroazides to propargyl alcohol, 2 butyne-1,4-diol and 4 (2 nitrovinyl)morpholine is reported. New energetic 1,2,3-triazole derivatives have been synthesized from product of these addition

Analysis of a Curve of Relative Frequency for Explosions of Hexogen

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Keywords: sensitivity; hexogen; a curve of relative frequency for explosions.

On the basis of deformation model of destruction an high-explosive (HE) charge at impact and probability-theoretic representations about distribution of variate values of charges strength at its manufacturing the calculations of a curve of relative frequency for explosions of hexogen, turning out at standard tests HE for sensitivity to mechanical actions are executed. For the analysis of behaviour of a frequency curve the method of strenghten D-diagrams by means of which the explanation is given to prominent features of theoretical and experimental dependences, including numerical values of the lower limits of explosions frequency and energies of impact, corresponding to 50 %- probabilities of explosion is used.

Explosion Hazard of Aromatic Organic Compounds Containing One or Two Nitrogroups

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Keywords: nitroderivates;azoderivates; toluene; benzene.

Aromatic compounds containing one or two nitrogroups use in chemical industry commercially in the first place there are mono- and di- nitroderivatives of benzene and toluene. There are some industrial incidents at heat selfignition of them, and explosive properties of them were discussed in literature. This investigation deals with explosion hazard of less investigated in this regard class nitrocompounds – azo-dyes. All azo dyes contain azo or amino groups, two benzene circles with substituents. Some of them contain one or two nitrogroups. Nitro- and azo- groups can give explosion hazard to organic substance. Temperature of fast decomposition beginning at heating and kinetic parameters of slow decomposition was experimentally measured for ten of them. The enthalpies of formation were measured experimentally, and explosion parameters were calculated for three of them. These results effort an opportunity to calculate the temperatures of heat explosion on a base of fundamental theory of heat explosion at convection heat transfer with environment. It was found that calculated temperatures of heat explosion good agreed with experimental temperatures of fast decomposition beginning at heating, the divergence was 4% on average. Thus it was shown that investigated azo dyes were the weak explosives, and theory of heat explosion could be quite applied to them.

Forensic Investigation of some Peroxides Explosives

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Keywords: acetone peroxide; hexamethylenethreeperoxidediamine; forensics.

A number of organic peroxides are applied in chemical, polymer, pharmaceutical and some other branches of industry. Some of peroxides are produced in fair quantities. Explosion properties of benzoyl peroxide, cyclohexanone peroxide and cumene hydroperoxide were investigated in preceding papers and were discussed on NTREM seminars. The elaboration of safety handling rules of them was a main goal of these works. However unexpected need of enlargement peroxides row has occurred. It connects with increase in relative frequency of caption of improvised explosive devices that were equipped with them. Acetone peroxide (AP) and hexamethylenethreeperoxidediamine (HMTD) belonging to these substances are the main objects of this investigation. The intimate knowledge of properties and of methods of analysis of them is necessary for low machinery for carrying of investigative action and for working up of competent indictments. Various methods of analysis of these substances both in bulk quantities and in traces were investigated. The limits of analysis in traces were found. The recommendations about treatment of sites of occurrence with aim conservation of traces of explosive components of improvised explosive devices were made. Detonation velocities at poured density at initiation by flame were measured by means of streak camera. It was shown that detonation impulse of HMTD suffices to initiate powdery TNT.

Cast Porous Charges on a Base of Ammonium Nitrate-Urea Eutectic

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Keywords: eutectic; ammonium nitrate; urea; fusion diagram; detonability; detonation velocity.

There are great number tasks of explosive technique, requiring the charges with low pressure and detonation velocity. Powerful tool of regulation of these parameters is lowering of charge density. The main goal of this work is elaboration of technology of manufacture and investigation of explosive properties of charges on a base of eutectic ammonium nitrate-urea mixtures (AN/UR) that have melting point Tm<1000C. The physico-chemical properties of these mixtures were investigated by means of DSC method and fusion diagram of them was plotted. The composition AN/UR 80/20, that has Tm=80-900C was chosen for subsequent investigation. The molten composition was mixed with fine aluminum powder, portion of it was placed into paper tube. The level of a liquid was less than length of the tube. Crystallization of melted mixtures was carried out in vacuum chamber, the level of liquid increased at pumping because of expansion of air bubbles introduced with aluminum particles and reached the upper cork of tube. In such a way porous charges were formed. The dependence of charge density vs. population of tubes by melted mixtures was plotted. Calculated heat explosion of mixtures at content of aluminum Al=10-15% is Qv=4.5 – 5.3 MJ/kg, calculated detonation velocity at density ρ=0.5 – 1 g/cm3 changes from D=3.2 to 5.2 km/s. Detonability of charges was investigated experimentally. Failure diameter (df) of detonation was measured, it was df = 22 mm (ρ=0.6 – 0.7 g/cm3) for charges without confinement at initiation by means of booster or blasting cap.

Thermodynamic Calculation of Detonation Parameters of TNT/Al Mixes

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Keywords: detonation; performance; aluminum; trinitrotoluene.

Introduction of aluminum powder into explosives can improve their detonation performance, significantly increase heat of explosion, enhance air blast, increase bubble energies in underwater weapons, raise reaction temperature, and create incendiary effects. On the other hand, it is generally known, that introduction of aluminum into high density explosives decreases detonation velocity (D), and pressure (PCJ), and the effect is more appreciable for fine Al. The objective of current paper is to study the effect of aluminum in Trinitrotoluene (TNT) mixes. Fundamental investigations have been shown, that introduction of aluminum powder and flake (10-15%) into TNT increases Qv, decreases D, and reduces critical diameter of detonation in particular at low charge density. Recently P. Brousser et al found, that nanometric aluminum (Alex) increases D, and Qv of TNT/Al mixes. The increase of detonation velocity was more pronounced at small charge diameters close the critical diameter. Alex was shown to decrease significantly critical diameter of TNT mixes. In current work detonation parameters of aluminized composite explosives were calculated by means of SD (Shock and Detonation) computer code. Computations were performed for complete oxidation of Al within the reaction zone of a detonation wave and nonreacting Al. The effect of phase transition C-graphite → C-diamond was into account too. Detonation parameters of TNT mixers with 10-30% Al at charge density 1 – 1.7 g/cm3 were computed and calculation results were compared with experimental data on detonation.

On the Reaction of Trinitroaromatic Compounds with 4-amino-1,2,4-triazole

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Keywords: trinitrophenyl compounds; nucleophilic substitution; vicarious replacement.

Treatment of some 2,4,6-trinitrophenyl compounds with 4-amino-1,2,4-triazole in the presence of sodium methoxyde in Me2SO leads to competing reactions of nucleophilic aromatic substitution and vicarious replacement of hydrogen. Formation of 4-(2,4,6-trinitrophenyl)amino-1,2,4-triazole and polyamino trinitrobenzene derivatives is observed. Influence of the nature of the substitute on speed and direction of the reaction is considered.

Theoretical Study on Structures and Properties of Nitroimidazole Compounds

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Keywords: energetic materials; theoretical studies; structures and properties; nitroimidazole;detonation velocity.

Abstract: 10 nitroimidazole compounds have been investigated by density functional theory. Their optimized geometry, electronic structures, heats of formation and densities were calculated at the B3LYP/6-311G(d,p) level. Results show imidazole ring has some aromaticity. VLW equation was used to calculate detonation velocity and C-J pressure. They are good candidates for energetic materials.

Calculation of Thermochemical and Explosive Characteristics of Furoxanes

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Keywords: furoxanes; benzofuroxanes; high-power energetic materials; heat of detonation; detonation velocity; detonation pressure.

Search of high-power energetic materials is one primary line of development of chemical-physics of combustion and explosion. Yield of such materials is usually very small, and its cost is very high. Calculation of unknown characteristics and properties is the only way out from this situation. There're different methods today that allow calculating unknown detonation per-formance and some of physico-chemical properties. Examination of calculated detonation performance of furoxanes and benzofuroxanes compounds that are not enough investigated is presented in this work. These compounds are new high-power energetic materials. Influence of error in enthalpy of formation of these compounds on theirs detonation performance is also exam-ined in this work. Furoxanes plays particular part among energetic materials. They are convenient blocks of molecules of high-power energetic materials. Joining of ex-plosiphorus cluster of atoms reduce to obtaining of number of high-performance compounds. It is caused by flatten structure of furoxane ring, that provided high density and characterized by high and positive value of enthalpy of formation. Detonation performance of furoxanes wasn't study practically. That's why 10 furoxanes have been chosen as object of study (see Nomenclature). 7 of 10 studied furoxanes have anomalous elemental composition, because they are hydrogen-free. In order to evaluate possible error in computational detonation performance, ex-plosive characteristics of 6 hydrogen-free energetic materials with known experi-mental data have been calculated.

New Ingredients for CMDB Propellants

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Keywords: azides; nitramines; nitrocellulose based propellants.

Research for more stable and efficient propellant ingredients represents a stimulant challenge in the development of safe ammunition. In this paper we present our preliminary results on the synthesis and characterisation of an energetic filler, N,N´-dinitropiperazine (DNPZ) and an energetic plasticizer, 1,2-bis(2-azidoethoxy)ethane (TEGDA) as promising candidates for use in NC based powders. Analyses of these new ingredients in terms of their sensitivity, thermal stability and compatibility were performed by standard methods

Synthesis of New Modification of Aluminum Oxide and Iron Aluminates by Impact of Explosive

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Keywords: synthesis; oxides; impact.

Synthesis of new high-strength superdispersed materials by use of detonation and shock waves is developing branch of recent technology. Diamond, metal oxides, nitrides, and many other substances are produced and find industrial application. The objective of current work was synthesis new modification of aluminum oxide and iron aluminates. For the synthesis initiation of explosion of aluminized composite explosive by impact was firstly used. Experiments carried out by use K-44-II impact machine in the tool #1. Falling weight is M=10 kg, its height of falling down is H=50 cm, the mass of the sample is m=0.05 g, density of sample was 0.9 g/cm3. X-ray diffraction analysis of the condensed residue after experiments carried out by Huber Imaging Plate Guiner Camera. X-ray diffraction examination shown, that iron aluminate with cell parameter, a=8,090(4) Å, cation-defective iron aluminate Fe0,5Al2,33O4 with a=8,002 Å, and new modification of aluminum oxide occurred in explosion products. Aluminum oxide may crystallize in the form of hexagonal syngony primal lattice with a=9,151(1) Å, c=7,945(2) Å, V=576 Å3, or trigonal syngony primal lattice with a=7,941(2) Å ic=4,575(1), V=288 Å3.

Some Properties of 1-(tetrazol-5-yl)-2-nitroguanidine

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Keywords: high explosives; nitroguanidine; nitrimines; tetrazoles; thermal explosion; impact sensitivity.

Some properties of 1-(tetrazol-5-yl)-2-nitroguanidine (TetrNQ) was investigated. The sensitivity to explosion by heat was determined as the temperature of flash and time to explosion delay. The impact sensitivity of TetrNQ was defined with the help of fallhammer test. Energetic and detonation parameters of TetrNQ were estimated using thermodynamic method with BKW equation of state and by simple correlation methods.

The Synthesis and Some Chemical Transformations of Alkylnitroamino-polynitromethyl-1,3,5-triazines

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Keywords: N-nitration;alkylnitroamino-1,3,5-triazines.

The N-nitration of alkylamino-1,3,5-triazines which contain polynitromethyl group as a substituent in a system «acetic anhydride-nitric acid» leads to the formation of alkylnitroamine derivatives of 1,3,5-triazines. Denitration of alkylnitroamino-trinitromethyl-1,3,5-triazines goes selectively on trinitromethyl group. The functional derivatives on dinitromethyl group can be synthesized on the basis of alkylnitroamino-dinitromethyl-1,3,5-triazine salts. The structure of 2-metoxy-4-methylnitroamino-6-chlorodinitromethyl-1,3,5-triazine was investigated by X-ray analysis.

A New Synthetic Route to LLM-105 (2,6-Diamino-3,5-dinitropyrazine 1-oxide)

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Keywords: LLM-105; synthesis.

A new synthetic route to LLM-105 (2,6-diamino-3,5-dinitropyrazine 1-oxide), involving direct nitration of 2,6-diaminopyrazine 1-oxide, is described. 2,6-Diaminopyrazine 1-oxide was synthesised by either N-oxidation of 2,6-diaminopyrazine or condensation of iminodiacetonitrile with hydroxylamine. The nitration of 2,6-diamino- and 2,6-diacetamidopyrazine has also been studied as a source of 2,6-diamino-3,5-dinitropyrazine for use in the usual route to LLM-105.

Abnormal Dependence of the Kinetics of Thermal Decomposition of HMX on Particle Sizes

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Keywords: thermal decomposition; HMX.

Reducing of particle sizes of organic energetic materials usually insignificantly increases rates of their thermal decomposition. This little effect is connected with the fact that the surface quote of the substance is small even for fine-disperced powders. So, the effect may be appreciable only for substances with a large retarded effect of lattice (REL), such as RDX. But even for this substance the above effect is observed only on early steps of the reaction of thermal decomposition. Small crystals grow very soon to form large bubbles. The value of the surface energy then diminishes and the rate of the reaction decreases to a usual level. During experiments with HMX at elevated temperatures the time of polymorphous transition equals the time of heating. The value of REL is not enough for significant increasment of rates of thermal decomposition with reducing of particle size. Really, we observe the decreasment in rates of thermal decomposition with diminishing of crystal sizes by any method (grinding, pressing, re-crystallization and so on). Additional experiments show that the observed effect is provoked by auto-catalysis in the condenced phase. The appearence of autocatalytic substances is followed by a sharp growth of the rate. Appearing in one place, the zone of auto-catalysis quickly spread around the whole crystal. For fine dispersed crystals the effect is so significant that can be of a practical use.

Thermal Stability of Emulsified Ammonium Nitrate Containing Cooling Agents

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Keywords: emulsion explosive; thermal stability; activation energy.

In the paper results of thermal stability of emulsified ammonium nitrate formulations containing sodium chloride, ammonium chloride or chlorinated parafin are presented. Thermal analyses by combined TG/DSC techniques were performed at different heating rates. The results obtained were used to evaluate the influence of the type and concentration of an additive on the decomposition course. Charasteric temperatures of the decomposition process were determined and apparent activation energies were calculated using Kissinger method. It was staded that the additives do not cause thermal destabilization of the emulsions.

Oxides Layer Study onto Fine-Grained Iron Powders

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Keywords: iron powder; energetic mixtures.

Iron powders are obtained as result of reduction of iron compounds by hydrogen, of thermal dissociation of ironpentacarbonyl or di-iron-nonacarbonyl, by the electrolytic process, and water gas atomisation. Full determination of the bulk and surface properties of iron powders is necessary for assessment of the use of a given powder as a component of the high energetic mixtures. The same problem occures in the case of aluminum and zirconium powders. The grain sizes of the iron powder samples were measured by the laser light scattering method. The results of measurements are presented in the form of volumetric and numeric distribution as a function of diameter particles and particle size concentration. Nitrogen adsorption and desorption were carried out in the relative pressure range p/po= 0-1. The BET equation was used to calculate the specific surface area. It has been shown that the samples obtained by water gas atomization characterized higher amounts of impurities such as Mn and Cr, which are present mainly on the surface and close to the surface layers rather than inside the iron powder grains. For qualitative determination of the oxides occurring on the surface of the iron powder samples and estimation of the thickness of the layer they form on the surface of the gains, the measurements by the temperature-programmed reduction by hydrogen were applied. On the surface of the tested samples the dominant phases are Fe2O3 and Fe3O4, present in comparable amounts and the phase FeO occurs in trace amounts. In the case of samples obtained by water gas atomization and thermal dissotiation of ironpentacarbonyl or di-iron-nonacarbonyl methods, after their treatment of the surface by hydrogen there were observed little less Fe3O4 phase even after reduction in 500oC.

Disposability of the energy produced in shock tube

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Keywords: shock tube; detonator; fuse head; energy.

Measurement process and result of measurements of the available energy of shock tube after conversion are described in the paper. Energy of shock wave in shock tube was converted in electrical energy through the electrical induction in spool. Disposability and amount of energy are calculated in way to determinate possibility to initiate electrical fuse head of detonator. Conversion of energy is achieved by flying magnet in spool. Tests are carried out in purpose to estimate basics for function of inductive detonator powered with shock tube.

Determination of additives explosive materials from various matrices

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Keywords: extraction; GCMS; explosives.

The contamination of explosive in soil and groundwater represents a significant in-ternational environmental problem because of their toxic and recalcitrant proper-ties. These compounds are found in environmental, because of the manufacturing and manipulation with army munitions. Explosives are labile in the environment, they can be transformed by sunlight or soil microflora and then can migrate through subsurface soil to cause groundwater contamination. Some nitro com-pounds are moderately to weekly soluble in water, toxic, health hazard and sus-pected mutagen. The widely extensive explosives are nitrate esters (nitroglycerine, ethylenglykoldinitrate) or polynitroaromatic compounds (2,4,6-trinitrotoluene and other). To be able to determine the type and concentration of explosives and their by-products in different soil environments, a comprehensive analytical methodol-ogy of sample preparation, separation and detection in thus required. The choice of the apposite extraction technique is one of the most important pa-rameters in the analysis of various environmental samples. This preconcentration step is able to remove matrix interference and enhance sensitivity of the determina-tion. The extraction techniques are widely used for the isolation of analytes from water samples (liquid-liquid extraction, solid phase extraction and solid phase mi-croextraction) or soils (pressurised fluid extraction, ultrasonic extraction and su-percritical fluid extraction).

Characterization of Two Dinitropyrazoles

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Keywords: energetic materials; synthesis; characterisation; thermal stability.

In the quest for new energetic materials with low sensitivity and high thermal sta-bility, several structural features can be imagined. Alternating electron donating groups and nitro groups seem to reduce the sensitivity of energetic compounds, e.g. TATB and FOX-7. One way to increase the nitrogen content and the enthalpy of formation is the use of a heterocyclic core, e.g. NTO. These observations prompted us to prepare and evaluate two compounds with a pyrazole nucleus in terms of their thermal stability and sensitivity to mechanic stimuli. The first, 4-amino-3,5-dinitropyrazoles, has alternating electron donating and withdrawing groups. It was previously prepared by other methods. It indeed exhibits excellent thermal stabil-ity, no sensitivity to friction and moderate sensitivity to impact. The second, 3,4-dinitropyrazolin-5-one, could be considered an analogue of NTO, with nitrogen be-ing exchanged for a carbon. However, the dinitropyrazolinone is hygroscopic, prone to hydrolysis and thermally unstable, which indicates limited aromaticity. These properties made us discard any further evaluation of this compound.

Applicability of Thermal Methods for Identification of Homogeneous Propellants

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Keywords: thermal methods; homogeneous propellants; identification; differential scanning calorimetry; thermogravimetry.

Methods of thermal analysis are nowadays widely used experimental techniques in various fields of research. Besides the more ”chemical“ areas, such as polymers, fine organic chemicals and pharmaceuticals, they have applications in electronics, in construction, engineering – generally in the field of characterization and investigation of materials. Thermal methods can provide information, such as quality, lifetime and safety during usage and storage of energetic materials. Thermal methods are mostly used for the investigation and determination of the thermal properties of energetic materials (e.g. melting process, polymorphic transformations, temperature of initiation, etc.), as well as to estimate thermal stability, and to study thermal decomposition. Furthermore, thermal methods can be also used for analytical purposes, such as identification of some commonly used high explosives, determination of their purity, determination of phlegmatiser content, etc. The aim of this work was to examine the possibility to apply differential scanning calorimetry (DSC) and thermogravimetry (TGA) for the identification of the homogeneous propellants type. It has been found out from the shapes of DSC and TGA thermograms, i.e. from the position of some characteristic points on the theromograms that it is possible to distinguish clearly between nitrocellulose and double based propellants. Also, from the TGA thermogram the content of nitroglycerine in the double based propellants could be roughly determined. The presence and amounts of additives, such as stabilisers, modifiers of ballistic properties etc., cannot be identified and determined reliable by thermal methods.

The Catalytic Effect of Nano Fe2O3 on Burning Rate of an Aluminized PBAN/AP/HMX Composite Propellant

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Keywords: nano Fe2O3; aluminized composite propellant; catalytic effect; burning rate.

In the present work aluminized PBAN/AP/HMX composite propellants containing nanometer- and micrometer-sized Fe2O3 as well as ferrocene as catalysts were tested. Fe2O3 nanopowders were prepared by the sol-gel auto-combustion method using polyvinyl alcohol as a gelating agent (and fuel) and iron nitrate as an oxidizer and a precursor of iron oxide. The morphology and microstructure of the components and propellant samples were determined. Thermodynamic calculations were performed and burning rates were measured using the Crawford strand burning technique. It was stated that the catalytic effect of the F2O3 nanopowder on the burning rate is comparable with that of ferrocene.

Influence of Nitrocompounds on Aluminized Composite Propellants

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Keywords: PBAN-base composite propellants; DNT; TNT; RDX; thermodynamic calculations; burning rate.

Thermodynamic parameters of combustion of aluminized composite propellants has been predicted. Calculations were carry out in the ICT – Thermodynamic Code. Basic components of the tested samples were ammonium chlorate(VII), PBAN-based binder and aluminum powder. Influence of 2,4-dinitrotoleuene (DNT), trotyl (TNT) and hexogen (RDX) on the results of calculations has been presented. For the presented above components, burning rate was determined in Crawford bomb, in the range (2.0 ÷ 6.0) MPa. Decreasing of RDX content from 19% to 15% with simultaneous increase of content of aluminum powder from 8% to 12%, caused significant lowering of burning rate. There were no significant changes in burning rate, if such a decreasing of RDX content was achieved by increasing ammonium chlorate(VII) content, from 58% to 61%. Changes in burning rate of samples with addition of (2 ÷ 4)% of DNT were meaningless. Replacement of DNT by TNT cause lowering of burning rate.

Determination of Thermal Diffusivity of HTPB/AP/Al Composite Solid Propellant

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Keywords: solid propellant; diffusivity.

Hydroxy terminated polybutadiene based composite solid propellants are extensively used in propellant industry due to their remarkable mechanical properties, and ageing characteristics. Certain performance parameters of composite solid propellants like working pressure and burning rate are strongly dependent on their thermal behavior. Similarly thermal properties have a significant effect on the processing technology, especially during heating and cooling stages. In the thermal analysis of composite solid propellant, thermal diffusivity is an important parameter, which determines the temperature distribution through a material in un-steady state conditions i.e. when the material is being heated or cooled. The focus of this paper is to determine the thermal diffusivity of composite solid propellant and to study the influence of temperature on thermal diffusivity of composite solid propellant by applying thermal analysis techniques. The experimentation was carried out on Hydroxy Terminated Polybutadiene (HTPB) based composite solid propellant using tri-model Ammonium Per chlorate as oxidizer and Aluminium powder as metal fuel. Propellant ingredients were thoroughly mixed in a 5L vertical kneading mixer by fixing solid loading at 86% and NCO/OH ratio at 0.79. Curing was done at 50 C for 168 hours. Thermal diffusivity, thermal conductivity, and specific heat were measured by Laser Flash Method. From the results, it was found that a quite low value of thermal diffusivity was obtained for HTPB/AP/Al composite solid propellant. Low value of thermal diffusivity reflects that this propellant behaves almost as an insulator. From analysis, it was also observed that thermal diffusivity varies directly with thermal conductivity and has opposite relation with heat capacity.

The synthesis of N-nitroamino-1,3,5-triazines with polynitromethyl and other explosophoric groups

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Keywords: N-nitration;polynitromethyl-1,3,5-triazines.

The N-nitration of amino-1,3,5-triazines which contain trinitromethyl and fluordinitroethoxygroups in 98% nitric acid media, in the mixture of nitric and sulfuric acid media, in the mixture of nitric acid and acetic anhydride media was studied. N-nitrated products were obtained in the mixture of nitric acid and acetic anhydride media. According to 1H NMR spectra these products have N-nitroimine structure with a proton in the 1,3,5-triazine cycle. According to 14N and 13C NMR spectra these products furnish silver salts on introamine group. The alkylation of these salts with methyl iodide leads to the formation of N-methylnitroamino-1,3,5-triazines which contain trinitromethyl and fluordinitroethoxyl groups.

Ammonium Nitrate Phase State Control By Intermolecular Interaction between Nitrate Anion and Organic Modifiers Built into the Ammonium Nitrate Crystal Lattice

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Keywords: ammonium nitrate; phase transitions; stabilization.

Using quantum-chemical calculations, X-ray, X-ray phase analysis, UV, IR-spectroscopy the influence of small additions (2-10%) of modifiers on mechanism of ammonium nitrate (AN) phase state has been investigated. The modifiers are selected from among N-heterocycles containing amino- or iminogroups, and carbonyl groups. Earlier the main principles for stabilizers of AN phase state have been formulated, and basing on these principles a set of the most powerful stabilizers has been selected (uric acid, aminouracyl and derivatives of 1,3,5-trihydroxyisocyanuric acid). Even being in small amount all these substances stabilize ammonium nitrate in temperature range between -50 and +100°C, that is instead of three phase transitions in ordinary product the stabilized samples have only one phase transition (at 55-60°C). Structures of the following substances have been studied: ammonium salt of trihydroxyisocyanuric acid, 4-aminouracyl, and the hydrate of the last one. In these structures the combinations of two or three molecules with highest intermolecular interaction are found. Basing on non-empirical quantum-chemical calculations of the energies of one molecule and two interacting molecules the energy of two molecules interaction has been determined. Its value (-18 kcal/mol) is comparable with the lattice energy value. The results of these calculations help to understand the nature of interaction between molecules of modifier and the nitrate anions. It means that the plane NO3– has twice degenerated binding orbital of pi–type and non-binding orbital of n–type, these orbitals lie in the anion plane, the under vacant orbital is of the pi–type as well. Considering the electron structure of NO3– it is rather possible that by interaction with the modifier molecule the nitrate anion can serve as the donor as well as the acceptor of electrons. In the alloy of ammonium nitrate with a modifier strong intermolecular interactions may appear besides of strong intermolecular hydrogen bonds. UV and IR investigations confirm the existence of a new net of hydrogen bonds in the alloys, and the existence of orbital interactions pi*(NO3–) -> pi*(C=O), that stabilize the ammonium nitrate phase state. It was found that in some conditions modified AN samples can become subject to further crystal transformation forming ultradisperse roentgen-amorphous product, having no phase transitions in the temperature range from -50 up to +100 °C. UV and IR spectra of these samples showed considerable changes in the nature of intermolecular interactions and hydrogen bonds in comparison with initial product

Bond Dissociation Energies for Nitrgroup Scission in Molecules of Various Classes of Explosives

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Keywords: quantum-chemical calculation; molecule; nitrogroup; dissociation energy.

Results of quantum-chemical calculations for about 70 molecules of various nitrocompounds, most of which are classical and new high explosives, are presented. Calculations were carried out in the density functional theory approach with the use of the Gaussian 98 program. The basic theory level B3LYP/6-31+G(d) was used in calculations. In many cases smaller and larger basis sets were also used for comparison. Dissociation energies for the C-NO2, N-NO2 and O-NO2 bonds were calculated first of all. Influence of several chemical and geometrical factors, such as concrete nitrogroup position, presence and disposition of other nitrogroups and presence and disposition of other functional group, such as CH3, NH2 and OH, was detected and analysed. As a result of such an analysis some common tendencies were revealed and empirical relations describing them were constructed. Qualitative explanation of these relations was given on the basis of consideration of results on electron density distribution in examined molecules.

Influence of Ionization and Excitation on Initial Stage of Decomposition of Simple Nitro Compounds

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Keywords: quantum-chemical calculation; ionization; decomposition; dissociation energy.

Results of quantum-chemical calculations for molecules of three simple nitro com-pounds and several their methyl derivatives are presented. The most simple of nitro compounds are considered, initial stages of decomposition for which are charac-terized by dissociation of C-NO2, N-NO2 and O-NO2 molecular bonds. They are ni-tromethane CH3NO2, nitramide NH2NO2 and nitric acid HONO2. Calculations were carried out in the density functional theory approach with the use of the Gaussian 98 program. The basic theory level B3LYP/6-31+G(d) was used in calcu-lations. Dissociation energies for the mentioned bonds were calculated for the molecules in the stationary basic and triplet states as well as for the positive and negative molecular ions. The NO2 radicals being generated at scission of the bonds are also considered in the basic and ionized states. Similar results were also ob-tained for the trinitrobenzene, cyclotrimethylenenitramine and pentaerythritol tetranitrate molecules with the use of the smaller 3-21G basis set.

Quantum-Chemical Calculations of Properties of Several Light-Sensitive Molecular Complexes

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Keywords: quantum-chemical calculation; molecular complex; light-sensitive explosive.

Results of quantum-chemical calculations for several energy-intensive molecular complexes of metal perchlorates with tetrazole derivatives, which can be used as light-sensitive explosives are presented. Calculations were carried out in the density functional theory approach with the use of the Gaussian 98 program set. The combined B3LYP functional and the 3-21G, 6-31G(d) and LANL2DZ basis sets were used in calculations. Such complexes as perchlorate (5-cyanogentetrazole-N2)pentaaminecobalt(III) (the СР substance), perchlorate tetraamine-cis-bis(5-nitrotetrazolato-N2)cobalt (III) (the BNCP substance), perchlorate di(3-hydrazine-4amine-1,2,3-triazole)copper(II)) and perchlorate (5-hydrazine-1Н-tetrazole)mercury(II)) were examined. Some geometrical and energetical charac-teristics were determined for optimized structures of the complexes. Bonds disso-ciation energies for such functional groups as ClO4, NO2, HClO4 and NH3 were calculated first of all. Infrared spectra of characteristic vibrations of the complexes were calculated too.

From Molecular Structure to Explosive Performance Parameters: Properties of the Homologous Series of Guanidinium Salts of 3,5-diaminopicric Acid

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Keywords: 3,5-diaminopicric acid; x-ray diffraction.

The molecular and crystal structures of guanidinium 3,5-diaminopicricate (GDAP), aminoguanidinium 3,5-diaminopicricate (AGDAP), diaminoguanidinium 3,5-diaminopicricate (DAGDAP) and triaminoguanidinium 3,5-diaminopicricate (TAGDAP) have been determined using single crystal X-ray diffraction as a preliminary step in an investigation of the relationships between crystal density and explosive performance parameters such as velocity of detonation or detonation pressure. Their heats of combustion were measured using bomb calorimetry and their heats of formation calculated. Analytical data such as multinuclear NMR spectroscopy, vibrational spectroscopy (IR, Raman), mass spectrometry, elemental analysis, thermal decomposition (DSC) as well as their impact sensitivities have been measured.

Some Aspects Regarding the Influence of Chemical Catalysts on Combustion of Rocket Solid Propellants

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Keywords: catalysis; rocket; propellant.

In this paper it is presented some aspects concerning the mode how it is influenced the combustion of rocket solid propellants by different chemical substances. In the case study it is analyzed the influence of a chemical catalyst on flame at exit section of nozzle, in order to reduce it. The reduction of flame at exit section of nozzle is beneficial for protection of aircraft, in the case of aviation missiles and for diminution of thermal signature, in the case of rocket launched from land.

Green Pyrotechnic Compositions

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Keywords: pyrotechnics; copper complex; red; green.

Pyrotechnic compositions which are used for producing a green flame contain barium salts. Due to the toxicity of barium a huge consent to substitution of these heavy metal salts exists. Therefore, several copper complexes with energetic anions are tested in consideration of their applicability as green flame colorant and if possible also as oxidizer. Another poisonous chemical widely used in pyrotechnic compositions, as additive especially for red flame colors, is potassium perchlorate. An alternative oxidizer could be potassium permanganate. Furthermore, strontium salts with energetic anions could be both oxidizing and coloring agent in red pyrotechnic compositions.

Safety Testing of Protective Gloves

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Keywords: gloves; injury; protection; fragments.

When working with explosive materials, the worker's hands are usually the most exposed body part and highly endangered by fragmentation effects. Several kinds of protective gloves are available. Existing standards describe testing procedures for the testing of protective gloves for mechanical risks, but seem to not realistically simulate fragmentation effects. An experimental setup was developed to test the performance of protective gloves under conditions similar to exploding glass ware in direct vicinity to the protected hand. The test should take the effects of fragments and shrapnel on the protected hand into account and be fairly reproducible.

A Study of Alkyl and Cycloalkyl Nitrates and Polynitrates

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Keywords: alkyl nitrates; X-ray crystallography; sensitivity.

Several alkyl and cycloalkyl nitrates were synthesized. The cyclopentyl derivative 1,1-bis(nitratomethyl)cyclopentane was isolated for the first time. All compounds were compared in terms of their chemical and physical properties. Especially long term stabilities, impact and friction sensitivity, additionally spectroscopic and structural data were collected.

The Nitration Kinetics of 6-hydroxy-2-methylpyrimidine-4(3H)-one in Sulfuric-nitric Acid Mixtures

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Keywords: nitration; 6-hydroxy-2-methylpyrimidine-4(3H)-one; FOX-7; kinetics.

6-Hydroxy-2-methylpyrimidine-4(3H)-one is known to be used as a precursor in the synthesis of FOX-7 via nitration reaction. In this connection we studied the nitration kinetics of 6-hidroxy-2-methilpyrimidine-4(3H)-one in sulfuric-nitric acid mixtures. A by-product reaction leading to a decrease in the yield of 2-(dinitromethylene)-5,5-dinitropyrimidine-4,6(1H,3H,5H)-dione was revealed. The data obtained allowed a scheme of the nitration process, which included three consecutive reactions. The reaction rate constants were obtained for each of the stages.

Closed Vessel Experiments - Investigation of Ignition Phase

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Keywords: internal ballistics; closed vessel tests; burning rate low; ignition.

Different ignition systems have been used for the characterization of ignition phase in closed vessel tests. Basic closed vessel experiments were carried out in a con-ventional closed vessel of 200 cm3. Ignition systems with various mass of black powder were used. Comparable experiments were carried out in a micro-closed vessel (MCV) of 1,786 cm3, constructed on the basis of 7,62-mm machine gun bar-rel that was cut down to reduce the internal volume. In this case standard primer ignites the propellant. Pressure-time data from the both closed vessels firing were used to calculate experimental vivacity and burning rate behaviour of some con-ventional single-base tube propellants with different dimensions of grains. It was observed that dynamics of propellant burning not only depend on the size and shape of the propellant grains, the web thickness but also depend on parameters of ignition system and loading conditions. Good reflection of pressure-time curve of a gun system requires not only adequate burning rate form in the fundamental pe-riod of propellant combustion but also requires specific burning rate form in the ignition period of combustion.

Some Anomalies in the Dependence of Specific Impulse of Energetic Compositions on the Aluminum Content

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Keywords: specific impulse; aluminum; flourine; energetic compositions.

If one begins to introduce aluminum into an energetic composition basing on C, H, N, and O elements it usually increases the specific impulse (Isp) until aluminum content reaches 16-24%, then after having achieved the maximal value the Isp decreases with the further aluminum content rising. Studying energetic parameters of the compositions containing additionally fluorine it was found that for some compositions the Isp value begins with the decrease while introducing aluminum into, and only after having achieving the local minimum on the curve describing the dependence of the Isp value on the aluminum content (at the last one being between some tenths of a percent and a few percents) the Isp begins to increase with the further aluminum content rising. This phenomenon was not known earlier and this presentation is aimed to investigate its nature. It was found that the reason of this phenomenon is a considerable complication of high temperature equilibrium between gaseous and condensed Al-containing combustion products in fluorine presence: when the fraction of gaseous Al-containing combustion products is rather high the Isp decreases. The variation of Isp value at Al content increase depends strongly on the formation enthalpy of the system (that is on the combustion products temperature), on the content of fluorine and hydrogen. The role of each factor affecting on the dependence of the aluminum content on the Isp value is studying out. Increase of the fluorine content or the formation enthalpy of the composition as well as the decrease of the hydrogen content increases equilibrium content of gaseous Al-containing products and therefore amplifies the anomaly. It was found that even in compositions with no fluorine this anomaly intervenes, but in this case it may be noticed at too low aluminum content only

New Variant of 1,3,3-trinitroazetidine Synthesis

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Keywords: 1,3,3-trinitroazetidine; TNAZ; synthesis.

1,3,3-Trinitroazetidine (TNAZ) has wide-ranging potential as a possible casting explosive as well as a casting matrix for other explosives owing to its low melting point, high stability in liquid phase within a broad temperature interval and rather low sensitivity. More than 14 variants of TNAZ synthesis were described. To prepare TNAZ in this work new method for the synthesis of the 3-hydroximino-1-(p-toluenesulfonyl)azetidine (3-hydroximino-1-Ts-azetidine) 1 and new variant of its transformation were developed. Dichloro- and dibromoacetone ketals 2a,b were applied as precursors of oxime 1. The cyclization of ketals 2a,b into ketals of 1-Ts-azetidin-3-one 3a,b was performed by an interaction with TsNH2 sodium salt in dipolar aprotic solvents. The maximum yield (65%) was reached for the dibromoacetone ketal 3b. The hydrolysis and an interaction with hydroxylamine of the ketal 3b resulted in 3-hydroximino-1-Ts-azetidine 1. The oxime 1 under the action of 1 mol of HNO3 in CHCl3 gave the 3-nitro-3-nitroso-1-Ts-azetidine as dimer 4 and the dezoxymation product – 1-Ts-azetidin-3-one. The latter was converted into oxime 1 in quantitative yield. TNAZ was obtained by an oxidation of nitroso group in dimer 4 with peroxytrifluoroacetic acid (PTFA) followed by substituting nitration of Ts group in good yield.

Kinetics of Nitroglycerine Evaporation in Double Based Rocket Propellants

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Keywords: activation energy, double based rocket propellant, kinetics of evaporation, nitro-glycerine, thermogravimetry.

Double based rocket (DBR) propellants are composed of two basic compounds: nitrocellulose (NC) as matrix and nitroglycerine (NG) as blasting oil and plasticiser at the same time, and of additives such as stabilizers, burning catalysts, modifiers of ballistic properties, etc. In the course of time, a number of chemical and physical processes, such are: stabilizer consumption, migration and evaporation of NG, decomposition of NG and NC, etc., take place in the propellant grain. Consequently, physical, chemical, thermal, ballistic and mechanical properties of the propellants change with time. This will result in the decrease of propellant's performances and reduction of the propellant's safe service lifetime. Standard methods for the determination of propellant stability are mostly based on following of stabiliser consumption. However, experience has shown that the mechanical properties can be a crucial factor in the case of double base rocket propellant's safe service lifetime. Since amount of NG in the propellant strongly influences the mechanical stability, the aim of this work was to study kinetics of evaporation of nitroglycerine in a double base rocket propellant. The kinetics was studied from the following experiments: a) following the mass loss of the propellant sample (10 g) subjected to accelerated thermal degradation in thermostat (isothermal method) for a different period of time, 2) following the mass loss of the propellant sample (4 mg) as a function of time of heating, applying isothermal TG analysis (isothermal method), and 3) following the mass loss of the propellant sample (2 mg) as a function of temperature applying dynamic TG analysis (isoconversional method). It was found out that the sample mass loss during the early stage of evaporation could be described by the potential kinetic model ( ), while the sample mass loss for the whole range of NG evaporation could be described by the nth-order kinetic model ( ). The non-isothermal TGA experiments were treated by the Flynn-Wall isoconversional method. The activation energy of evaporation of NG was calculated to be from 77 to 110 kJ/mol, while the pre-exponential factor ranges from 2.5•107 to 2.5•108 s-1.

Comparison of 3,3'-Bis-1,2,4-oxadiazol-5-one and 5,5'-Bis-1H-tetrazole

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Keywords: explosives; 5,5'-Bis-1H-tetrazole; 3,3'-Bis-1,2,4-oxadiazol-5-one; structure; density.

3-substituted-1,2,4-oxadiazol-5-one derivatives may replace or complement tetrazole derivatives as pyrotechnics and propellants. As oxadiazolones have better oxygen balances (-47 % compared to 57% for tetrazole), both generate the same amount of gaseous products per molecule. Comparison of 3,3'-Bis-1,2,4-oxadiazol-5-one (H2OD) with 5,5'-Bis-1H-tetrazole (H2BT) shows some simi-la-ri-ties and some differences which are discussed. The H2OD decomposes at 376 °C and has a density obtained from x-ray diffraction of 1.90 g cm-3. H2BT already decomposes at 254°C and has a density of only 1.74 g cm-3.

5,5´-Hydrazinebistetrazole and Its Metal Salts: Promising Propellant and Pyrotechnic Ingredients

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Keywords: hydrazine; tetrazoles; energetic; crystal structure; pyrotechnic mixtures.

5,5´-Hydrazinebistetrazole (HBT) is a nitrogen-rich (83.4% N) energetic material with a high performance, low sensitivity and interesting properties for use as pro-pellant. However, the synthesis and properties of its metal salts remain largely un-investigated. Here we would like to report on the synthesis and full characteriza-tion by spectroscopical and analytical methods of salts of HBT with alkali (Li-Cs) and alkaline earth (Mg-Ba) metals. The compounds are insensitive to friction, shock and electrostatic discharge (BAM testing) but react vigorously in the flame giving the characteristic flame color for the metal atom. Differential scanning calorimetry (DSC) measurements showed strong bonding of the crystal water and great thermal stabilities as indicated by the high decomposition points. Lastly, due to the prospective interest of metal salts containing the HBT2- anion as energetic materials the constant volume energies of combustion were measured experimen-tally using bomb calorimetry and their heats of formation were back-calculated ac-cordingly. With high nitrogen contents and great thermal stabilities the new com-pounds are prospective candidates for use in pyrotechnic mixtures. Keywords: Hydrazine, tetrazoles, energetic, crystal structure, pyrotechnic mixtures

Energetic Salts with the Guanylurea Cation

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Keywords: Guanylurea; FOX-12; energetic; X-ray; detonation parameters.

Reaction of cyanoguanidine (1) with hydrochloric acid yielded guanylurea chloride (2). 2 was reacted further to form a new family of energetic salts based on the guanylurea cation and azide (3a and 3b), 5-nitrotetrazolate (4), 5-aminotetrazolate (5), picrate (6) and 5,5´-azotetrazolate (7) anions. All materials were fully charac-terized by analytical and spectroscopic methods. Additionally, the crystal struc-tures of 2 and 3a were determined. The thermal behavior of 3-7 and their constant volume energies of combustion were assessed by DSC and bomb calorimetry measurements, respectively and their sensitivity to shock, friction and electrostatic discharge was measured by submitting the compounds to standard tests. In addi-tion, MP2 calculations were used to predict the energies of combustion and we calculated the detonation pressures and velocities of the compounds using the EX-PLO5 code. The new compounds have performances in the range of commonly used energetic salts qualifying the compounds as new insensitive low-energy monopropellants. Keywords: Guanylurea, FOX-12, energetic, X-ray, detonation parameters

Numerical Study of Two Dimensional Gaseous Detonation in a Channel

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Keywords: numerical simulation; LS-DYNA code; gaseous detonation; cellular structure.

In this paper we use an adaptive second-order Godunov scheme with front tracking algorithm to carry out two-dimensional numerical simulation in a channel. For this simulation, we had used LSDYNA-code. Also the chemical kinetics, a single-step Arrhenius law is utilized. Initiation of detonation performs with a one dimensional planar blast wave as an initial condition. The one dimensional detonation is perturbed by placing a disturbance in the initial density. The structure of the front appears as detonation propagates in the channel. The front structure, that includes triple point, transverse wave. Incident shock, and Mach stem, is investigated in this study. Cellular structure of detonation that is created by tracking of the triple point, is observed. In long time propagation, only one cell across the channel, with a cell size 10 units length, is formed. The convex curvature of the first half of a cell, as well as the concave curvature in the second half, is also observed in the present simulation.

Energetic Possibilities of Compositions Basing on Polynirous High Enthalpy Substances

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Keywords: high formation enthalpy; polynitrous substances; energetic abilities.

The investigation is aimed for the estimation of the possibilities of superhigh enthalpy polynitrous substances as potential compounds of highly energy compositions. Development of quantum-chemical methods of molecular structure and intermolecular interactions energy calculation have been ingenerating a real boom in the sciences of the energetic materials, the main question is if it is possible to obtain real substances constructed almost exclusively basing of nitrogen atoms and having formation enthalpy appreciably higher than +2000 kcal/kg. It is too hard to suppose that such substances would be gotten anywhen, at least, definitely they would be very sensible to impact and friction, and would be rather unstable. Anyway theoretical estimation of energy possibilities of such substances is rather useful because it allows to understand at least where the energetic limit of compositions using the stored chemical energy is hidden. In the investigation the analysis of energetic parameters of solid and liquid systems is presented for compositions in which superhigh enthalpy polynitrous substances serve as the only component as well as in mixture with other substances, that must be introduced for obtaining other necessary properties besides energetic ones. The comparison of these energetic systems with the best real ones has been proceeding. Mainly, the following substances were selected as the objects of the investigation: tetraazatetrahedran N4, octaazacubane N8, trioxyhexazine N6O3, bipentazole N10, octanitrocubane C8N8O16, 1,3,5,7-tetranitro-2,4,6,8- tetraazacubane C4N8O8, derivatives of pyrroles, pyrazoles, triazoles, tetrazoles and other polynitrous high enthalpy substances

Crystallization of 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0.5,903,11] dodecane

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Keywords: crystallization; TEX.

In this paper, the methods of synthesis and crystallization of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclo[5.5.0.0.5,903,11] dodecane (TEX) are presented. The aim of the work was to obtain cubic crystals of TEX. Several solvents for crystallization of TEX were checked. The fuming nitric acid and mixture of dimethylsulfoxide/glycerine as solvents to crystallization were the best. The influence of various parameters on crystallization process was investigated. The particle size distribution and the density for the obtained crystals are presented.

Synthesis of 3-amino-6-nitro-1,2,4,5-tetrazine and Its 2,4-dioxide

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Keywords: 3-amino-6-nitro-1,2,4,5-tetrazine; 2,4-dioxide; synthesis.

According to calculated data the 3,6-dinitro-1,2,4,5-tetrazine (1) (if it could be prepared) is highly energetic compound with zero oxygen balance, however all attempts to synthesized this compound failed. In this work we succeeded to prepare a possible precursor of the 3,6-dinitro-1,2,4,5-tetrazine (1) – the 3-amino-6-nitro-1,2,4,5-tetrazine (2) by a diazotization of one of amino groups in the 3,6-diamino-1,2,4,5-tetrazine (3) followed by Sandmeyer reaction with NaNO2. The method for the synthesis of compound 2 was optimized and its yield was 62 % counting on diamine 3 entering in reaction. The structure of compound 2 was estimated by spectral data and X-ray analysis. Melting point of compound 2 is 206-208 oC and density (X-ray) – 1.811 g/cm3. This compound was oxidized into 3-amino-6-nitro-1,2,4,5-tetrazine 2,4-dioxide (4) under the action of peroxytrifluoroacetic acid (PTFA) in yield 65%. Compound 4 was described in literature.1 The physicochemical characteristics of dioxide 4 (density, 1H, 13C and 14N NMR and UR-spectral data) were similar to that obtained in work1 and Tdecomp. was 191 °C.

Energetic Polymers Based on 2,4-dinitrostyrene: Synthesis, Characterization and Unexpected Sensitivity to Impact

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Keywords: energetic polymers; dinitrostyrene.

Energetic polymers based on 2.4-dinitrostyrene were synthesized from monomers and characterized by elemental analysis. The polymer was then tested by DSC and the sensitivity to impact was tested. It was found, that the polymer has the impact sensitivity between HMX and HNS

Effects of Computed Electric Fields upon the Properties of Nitromethane and Dimethylnitramine

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Keywords: electric field; dipole moment; impact sensitivity; nitromethane; dimethylnitramine.

We present an overview and summary of the computed effects of electric fields of various strengths and directions upon the properties of nitromethane and dimethylnitramine. We discuss geometries, polarities, energies, molecular electrostatic potentials and the C-NO2 and N-NO2 stretching vibration frequencies. Fields that reinforce and increase the natural polarities of the molecules, which are essentially along the C-NO2 and N-NO2 bonds, also lower their energies and increase the C-NO2 and N-NO2 frequencies, presumably strengthening these bonds. The relationship of energetic materials' sensitivities to molecular surface electrostatic potentials and other molecular properties is discussed.

Comparison of Perfluorinated Tetrazolate Salts

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Keywords: 5-perfluoroalkyltetrazolate; crystal structure; vibrational spectroscopy; multinuclear NMR spectroscopy.

The stoichiometric syntheses of trifluoroacetonitrile, pentafluoropropionitrile and heptafluoro¬butyronitrile using mild reaction conditions from readily available starting materials are described. Furthermore, the reactions of the nitriles with sodium azide forming the corresponding sodium 5 perfluoroalkyltetrazolate salts in acetonitrile were carried out. The guanidinium 5 perfluoroalkyltetrazolate salts were synthesized via metathesis reactions using the silver 5 perfluoroalkyltetrazolates. The guanidinium salts were all characterized including vibrational (Raman and infrared) and multinuclear NMR spectroscopy, differential scanning calorimetry, elemental analysis and X-ray diffraction.

Study Regarding Effectivness of Stabilizer "Revival" Process on Old Artillery Propellants

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Keywords: nitrocellulose; propellant; simple base; diphenylamine; stabilizer.

The paper deals with some experimental investigations performed in order to evaluate some safety and performance characteristics of old simple base propel- lants for large calibre ammunition, after a ”revival“ process consisting in supple- mentary DPA addition. The revived propellants were tested comparative to new and old propellants of similar composition and geometry.

QSARs in the Reductive Denitration of Organic Nitrate and N-nitramine Explosives by E. Cloace PB2 PETN Reductase

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Keywords: trinitroglycerol; PETN; RDX;.

Enterobacter cloacae PB2 NADPH:PETN reductase (PETNR) performs the reductive denitration of explosives PETN and glycerol trinitrate (GTN), which may be an important step in the biodegradation of the above explosives. We examined the PETNR-catalyzed reduction of PETN, GTN, their aliphatic nitroester analogues, and non-aromatic N-nitramine explosives (RDX, HMX, EDNA, DINA, nitroguanidine)(n = 14). The reduction of PETN, mannitol hexanitrate and inositol hexanitrate was accompanied by the formation of > 2 mol nitrite/mol compound, and the reduction of TNG was accompanied by the formation of > 1 mol nitrite/mol compound. The rate constants of the reduction of nitroesters by PETNR exhibit a complex dependence on their steric parameters (a parabolic reactivity dependence on the VdWvol of compounds, and a negative linear dependence on their VdWvol per nitrate group). The discrimination of N-nitramines vs. nitroesters is caused by the electronic effects. Both groups of compounds are modestly toxic towards mammalian cells.

Safety Assessment of Composite Propellants Manufacturing Processes According to TEMCLEV-Ex Method

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Keywords: safety assessment; TEMCLEV-Ex; manufacturing of composite propellants.

Some examples of significant breakthrough in the field of novel kinds of chemicals which can be apply in manufacturing processes of composite propellants (CP) has been analyzed. The analysis was carried out with special emphasis on the question, how to cross between development in optimizing characteristics of a given CP system and a need to use more and more safety technologies. In a few past years, hazard assessment method for assessment of explosion and fire hazard in manufacturing of explosives, called TEMCLEV-Ex, has been worked out. It has been shown in this paper, how TEMCLEV-Ex can help to make different manufacturing methods of CP more safety. The assessment procedure of TEMCLEV-Ex was practically presented on the example of laboratory-scale process unit.

Analysis of Residues in the AESTUS Engine for the ATV Mission

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Keywords: AESTUS; restart; methylhydrazine (MMH); nitrogen tetroxide (N2O4); residuals.

The restart of the AESTUS engine after a ballistic phase (vacuum conditions) using monomethyl hydrazine (MMH) / dinitrogen tetroxide (NTO) might possibly be negatively influenced due to the formation of residuals during the shut-down phase. In previous investigations possible residues of this hypergolic mixture were determined. Sublimation and evaporation rates of residuals were collected by different temperature and pressure experiments. To figure out the quantities of residuals gas - gas and liquid - liquid MMH / NTO reactions were performed.

Ammonium Salts of Some Oxynitrogen and Oxyhalogen Acids: a New View on the Combustion Mechanism

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Keywords: combustion; decomposition, mechanism, kinetics.

Ammonium salts of oxygenated acids such as HNO3, HNO2, HClO4, HClO3, HIO4 and HIO3 are energetic materials and there is a heat release at their decomposition. Earlier the combustion of these compounds was studied in a wide pressure interval of and it was shown that their burning rates are very varied, that was explained by different oxidation properties of acids which are included in a composition of salts. However, such explanation implies that leading reactions of combustion are the oxidation-reduction process into combustion wave. At the same time it is known now that at least burning rates of two salts - ammonium perchlorate and nitrate are determined by kinetics of their decomposition. In this connection the purpose of the present work was the analysis of the existing data for salts with determination of their combustion mechanism. As a result of the conducted analysis is was shown that the burning rates of two ammonium salts (NH4NO2, NH4ClO3) are determined by kinetics of their decomposition. The kinetic data of the decomposition have been obtained, based on burning-rate and thermocouple data.

Sensitivity of CL-20 to External Stimuli Related to the Shapes and Size of

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Keywords: CL-20; crystallization; grain shape and dimensions; friction and impact sensitivity.

A total of nine CL-20 crystal samples obtained by crystallization conducted in a solvent/ nonsolvent system under variable process parameters such as: solvent kind, time of nonsolvent addition, stirrer speed, were studied in the aspect of their sensitivity to stimuli. As the result of the crystallization processes performed, CL-20 crystals were obtained that differed in their appearance and size. The CL-20 crystals of relatively small size and with rounded shapes. which were in part single crystals, exhibited the least sensitivity to friction or impact, whereas the crystals of irregular shape were sharp-edged agglomerates which exhibited the highest friction and impact sensitivities. Likewise, the large-size CL-20 crystals measuring ca. 200 mm, despite being rounded-shape single crystals, showed a high friction and impact sensitivities.

Structure and Spark Sensitivity Relationships Modeling by QSPR-methods

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Keywords: computer modeling; structure-property relationships.

One of the most difficult for theoretical estimation of energetic materials (EM) physical-chemical properties is their sensitivity to different actions. In the study we investigated one form of sensitivities – the spark sensitivity - using Quantitative Structure Property Relationships (QSPR) methods: our original Chemical Structure Matrix (CSM) method and Artificial Neural Networks (ANN). We investigated structure-spark sensitivity relationships for some data base and elaborated models for estimation and prediction this characteristic. The high prediction capability in spark sensitivity estimation was achieved for compounds of different chemical classes.

Synthesis and Characterization of Nitrogen Rich Energetic Polymers

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Keywords: tetrazoles; polymeric precursor; energetic polymers; nitrogen rich polymer.

Nitrogen rich, energetic polymers were obtained by polycondensation of bifunctional tetrazoles using diisocyanates, dicarbon acid dichlorides, or the tetrazoles themselves. The polymers were characterized by vibrational spectroscopy and the energetic properties were determined.

Thermal Decomposition of Some 4-substituted 3-methylfuroxans

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Keywords: 3-methylfuroxans; thermal decomposition; kinetics.

The thermal decomposition kinetics of 4-substituted 3-methylfuroxans are investigated by the manometric method. On the strength of the IR-spectroscopic analysis of condensed decomposition products the limiting stage is identified. The thermal decomposition activation parameters in gaseous and condensed phase are defined.

Nitrogen Rich Dinitramides - A Class of Energetic Compounds with a well balanced Oxygen Content

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Keywords: energetic materials; dinitramides; azides, oxygen balance; X-ray; calorimetry.

The highly energetic compounds azidoformamidinium dinitramide (1) and triamino-guanidinium dinitramide (2) were synthesized by the reaction of potassium dinitramide and azidoformamidinium perchlorate and triaminoguanidinium perchlorate, respectively. A full characterization of the chemical properties (single X-ray diffraction, IR and Raman spectroscopy, multinuclear NMR spectroscopy, mass spectrometry and elemental analysis) as well as of the energetic characteristics (differential scanning calorimetry, bomb calorimetry, impact and friction tests, Koenen test) is given in this work. The detonation parameter of compounds 1 and 2 were calculated using the EXPLO5 software resulting in auspicious values for potential applications as high explosives.

N-Rich Salts of 1-Methyl-5-nitriminotetrazolate – An Auspicious Class of Thermal Stable High Explosives

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Keywords: 1-methyl-5-nitriminotetrazolate; DSC; calorimetry; X-ray; Koenen test.

1-Methyl-5-nitriminotetrazole (1) is formed by nitration of 1-methyl-5-aminotetrazole, which is obtained by methylation of sodium 5-aminotetrazolate. 1 was deprotonated using potassium hydroxide forming the corresponding potassium salt (2), which can be transferred into silver 1-methyl-5-nitriminotetrazolate (3) by the reaction with silver nitrate. Ammonium (4), guanidinium (5), aminoguanidinium (6), diaminoguanidinium (7), triaminoguanidinium (8) and azidoformamidinium (9) 1-methyl-5-nitriminotetrazole were prepared by metathesis reaction either using 2 and guanidinium perchlorates or 3 and guanidinium chlorides under the precipitation of KClO4 and AgCl, respectively. All compounds were fully characterized by single crystal X-ray diffraction, vibrational spectroscopy, multinuclear NMR spectroscopy, elemental analysis, DSC as well as bomb calorimetry. In addition the sensitivities were tested using the BAM drop hammer and friction tester. With regard to develop new high explosives triaminoguanidinium 1-methyl-5-nitriminotetrazolate shows the most promising detonation parameter using the EXPLO5 software and was therefore successfully tested in a Koenen Test using a hole width of 10 mm.

Toxicity of Small Cartridges

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Keywords: after-shot emissions; toxicity of cartridges.

Presently, toxicity of small cartridges is adjudicated mainly from the view of the content of heavy metals and some gaseous emissions, which are disengaged into air during a gunshot. Of course, the own problem of toxicity of small cartridges is much vaster. It contains especially regularities of solely part reactions, passing a gunshot and which are functions of individual constructional parts of the cartridge (for example: primers, propellants..), physical conditions and the production of the cartridge itself. This work is aimed at the cartridge 9x19 mm Luger. We have chosen this cartridge, because it belongs to the most widespread cartridges in the world and its use values are the topic of an eternal development.

Combustion Synthesis of Multiwalled Carbon Nanotubes

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Keywords: carbon nanotubes; nanostructures; combustion synthesis.

Mixtures of calcium carbide with different oxidizers, such as C2Cl6, C6Cl6, (C2F4)n and (CF)n were investigated. Reactions between these substrates in the presence of sodium azide are exothermic enough to proceed in a high temperature, self-sustaining regime. Combustion of the tested mixtures was performed in the presence of ferrocene (or without it) as a catalyst of nanostructures growth. Heat effects accompanying the reactions were measured and the solid reaction products were analyzed. SEM and TEM observation revealed the presence of multi-walled carbon nanotubes in combustion products of CaC2/C2Cl6/NaN3/Fe(C5H5)2 mixture. Exfoliated graphite was observed in solid combustion products when (CF)n was an oxidizer. In others systems soot like morphology dominated.

Quantum Chemical Studies on Nitroethylnitramine (NENA) and its Charged Forms

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Keywords: NENA; charged forms, DFT.

In this study, the neutral and various charged forms (±2, ±1) of NENA (nitroethylnitramine, an energetic plasticizer) have been considered for their relative stabilities to investigate whether the charged forms play any role in the explosion process. Additionally, some tautomers and conformers (s-cis and s-trans) of NENA have been investigated. The explosive properties of NENA compounds strongly depend on their energetic nitramino and nitrato groups, where the latter are often responsible for an elevated sensitivity and a reduced stability. In the present study also, the relationship between structure of the main skeleton of the NENA and properties of known NENA compounds have been compared. Moreover, the thermal stabilities have been evaluated from the homolytic bond dissociation energies of N-NO2, C-NO2, C-C, C-O, C-N bonds and heats of formation values for NENA. All the calculations have been made by using various basis sets at the levels of ab initio and DFT methods.

Theoretical Treatment of Some Novel Nitropyrimidines

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Keywords: nitropyrimidines; density functional theory.

Mono, di, tri, tetra nitro substituted pyrimidine derivatives have been subjected to theoretical analysis at semi empirical (PM3) and density functional theory (DFT) B3LYP/6-31G(d, p) levels. The structures are geometry optimized with both closed and open shell calculations. Certain properties have been theoretically obtained (quantum chemical properties, aromatic character and vibrational spectra). The molecular orbital calculations reveal that all the compounds studied are stable but endothermic in nature. To find out whether the structures are potential candidates for novel explosive materials, the homolytic bond dissociation energy (for C-NO2 bond) calculations have been carried out. The results revealed that the bond dissociation energy for the tetra nitro derivative is the minimum among the group and it is followed by 4,5,6 and 2,4,5-trinitro and 4,5-dinitro derivatives. The tetra nitro derivative also has the maximum heat of explosion and pressure of explosion values among the series of compounds studied.

Is it possible to find a gunshot residues on the shooter´s hand after shooting with Nontox ammunition?

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Keywords: ammunition; primer composition; gunshot residue; GSR.

The paper presents a short review of the chemical composition of sinoxid and sintox primer composition of different ammunitions. In connection with production of a new kind of non-toxic primer composition called Nontox, it was investigated the chemical composition of inorganic particles originated from this primer composition befor and after shooting by using SEM/EDX method. At the same time was investigated the possibility of proof of these particles on the shooter´s hand and their distinguishing from environment particles. Gas chromatography and mass spectrometry methods were used to investigate the possibility of proof of traces originated from organic components of primer composition on the shooter´s hand.

Modeling of Non-Linear Properties of Solid Propellant

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Keywords: solid propellant; mechanical properties.

Typical experimental research related to energetic materials, where solid rocket fuels are typical examples, is quite analogous to experimental methods of solid materials. It generally aims in determining the main mechanical and physical properties of specially performed testing specimens. Characteristic features of solid rocket fuels, from the mechanical point of view, are: Young modulus (E), Poisson ratio (ν), glass transition temperature, coefficient of thermal expansion and others. Those parameters influence on application possibilities of solid rocket fuels in driving elements. Determining of mechanical response of previously mentioned energetic materials on mechanical and thermal loading is of first importance. It is particularly dangerous when on the surface of solid rocket fuel a crack occurs. Even 0,1 [mm] crack or delamination observed between crystal and binder may cause engine explosion due to increasing of the combustion surface, and in consequences, uncontrollable pressure buildup. Standards in experimental methods in mechanics of solid rocket fuels are still insufficient. They mainly consist in measurement and detections of cracks already occurred on surface of materials. Typical applied methods are: visual measurement using movable microscope, measuring magnifier, visual measuring on the crack surface, crack length determining basing on the observed spacing. For establishing a suitable constitutive model for solid rocket fuels in the first step mechanical properties of the testing samples have to be investigated. Also focus should be placed on the strain rate and temperature effects on these materials under typically observed deformations. In this study typical experimental results from uniaxial tension are presented. A phenomenological constitutive law (Chaboche's model) is adopted to model these materials. Validation of the constitutive model is also described. It has to be pointed out that this paper is just an initial probe of adaptation the typical viscoplastic model, built for metals, for describing non-linear properties of solid rocket fuels. On this stage only uniaxial results have been taken into consideration. Advanced experimental research such as tensile tests under various strain rates, impact of temperature effects, hydrostatic compression, shear tests etc. have been totally neglected in this study.

Unconventional Nano-Balls from Ion Reaction

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Keywords: nanostructures; lithium compounds; weak detonation.

This paper describes a new method for prediction of the Chapman–Jouguet detonation parameters of CaHbNcOdLieMnf explosives for mixture of some of critical detonation explosives at $\rho 0$ = 1000 kg/m3. Detonation Temperatures of slurry explosives and explosive formulations are predicted using thermochemistry information. The methodology assumes that the heat of detonation of an explosive compound of products composition H2O–CO2–CO–Li2O–MnO2–Mn2O3 can be approximated as the difference between the heats of formation of the detonation products and that of the explosive, divided by the formula weight of the explosive. For the calculations in which the first set of decomposition products is assumed, predicted temperatures of detonation of slurry explosives with the product H2O in the gas phase have a deviation of 98.18 K from results with the product H2O in the liquid state. Lithium and manganese oxides have been prepared by the detonation of slurry explosives of the metal nitrates, M (NO3) x (M = Li, Mn) as oxidizers and glycol as fuels, at relative low temperature. We have also used the Dulong-Petit's values of the specific heat for liquid phase H2O. Lithium manganese oxide powders with chrysanthemum-like morphology secondary particles, but with smaller primary particles of diameters from 5 to 50 nm and a variety of morphologies were found. The oxides produced by this cheap method affirmed the validity of detonation synthesis of nano-size materials for lithium ion batteries.

Quadrate Crystal from Green Chemistry

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Keywords: emulsion explosive; layered texture; zinc and lithium oxides.

The present situation of detonation synthesis and emulsion explosives both at home and abroad is summarized in this paper. To solve the problems in research for lithium ion batteries, we suggested that zinc and lithium oxides should be used as cathode materials for lithium ion batteries. So, we design special emulsion explosives, and synthesize zinc and lithium oxides from an emulsion explosive. It is concluded that nanoparticles of lithium zincate can be synthesized from the unconventional emulsion explosive. Unconventional emulsion explosives for synthesis of zinc and lithium oxides are designed firstly. Furthermore, we succeeded in synthesizing nano-powders of zinc and lithium oxides by explosion at the fist time in the final analysis. Zinc and lithium nanooxides are successfully collected and validated by XRD, FTIR, and TEM.

Fast Reaction and Nanometer Products

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Keywords: weak detonation; water-gel explosive; detonation; parameters.

Nanoproducts spherical spinel lithium manganese oxide (LiMnO) with about 20nm in diameter was synthesized by explosive method. The growth of lithium manganate via detonation reaction was investigated with respect to the presence of an energetic precursor, such as the metallic nitrate and the degree of confinement of the explosive charge. The detonation products were characterized by scanning electron microscopy. Powder X-ray diffraction and transmission electron microscopy were used to characterize the products. Lithium manganate with spherical morphology and more uniform secondary particles, with smaller primary particles of diameters from 10 to 30 nm and a variety of morphologies were found. Lithium manganate with a fine spherical morphology different from that of the normal spinel is formed after detonation wave treatment due to the very high quenching rate. It might also provide a cheap large-scale synthesis method. Explosive detonation is strongly nonequilibrium processes, generating a short duration of high pressure and high temperature. Free metal atoms are first released with the decomposition of explosives, and then theses metal and oxygen atoms are rearranged, coagulated and finally crystallized into lithium manganate during the expansion of detonation process.

Fast Reaction and Nanometer Products

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Keywords: Nanoproducts;lithium manganese compounds; detonations.

This paper describes a new method for prediction of the Chapman–Jouguet detonation parameters of CaHbNcOdLieMnf explosives for mixture of some of critical detonation explosives at $\rho 0$ = 1000 kg/m3. Detonation Temperatures of slurry explosives and explosive formulations are predicted using thermochemistry information. The methodology assumes that the heat of detonation of an explosive compound of products composition H2O–CO2–CO–Li2O–MnO2–Mn2O3 can be approximated as the difference between the heats of formation of the detonation products and that of the explosive, divided by the formula weight of the explosive. For the calculations in which the first set of decomposition products is assumed, predicted temperatures of detonation of slurry explosives with the product H2O in the gas phase have a deviation of 98.18 K from results with the product H2O in the liquid state. Lithium and manganese oxides have been prepared by the detonation of slurry explosives of the metal nitrates, M (NO3) x (M = Li, Mn) as oxidizers and glycol as fuels, at relative low temperature. We have also used the Dulong-Petit's values of the specific heat for liquid phase H2O. Lithium manganese oxide powders with chrysanthemum-like morphology secondary particles, but with smaller primary particles of diameters from 5 to 50 nm and a variety of morphologies were found. The oxides produced by this cheap method affirmed the validity of detonation synthesis of nano-size materials for lithium ion batteries.

1,1-Di(methoxy-NNO-azoxy)ethene as a Perspective Source for Synthesis of New Energetic Substances

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Keywords: alkoxy-NNO-azoxy substances; 1,1-di(methoxy-NNO-azoxy)ethene; synthesis; X-ray analysis.

Alkoxy-NNO-azoxy substances (AAZ) R-N(O)=N-O-R; are known since the end of the XIX century. Last 25 - 30 years some representatives of this poor studied class have attracted attention as perspective energetic compounds because ADO have the same element formula as secondary nitramines, but AAZ have a bit higher enthalpy of formation. Besides usually AAZ are more thermostable and chemicaly inert. Before 1969 unsaturated AAZ were not known yet. For obtaining many new AAZ derivatives the synthesis of unsaturated AAZ would be rather useful because the C=C bond is rather reactive especially when it is enhanced by the conjugation with the electron-acceptor -N(O)=NO-group. Unknown earlier high reactive AAZ-olefin, 1,1-di(methoxy-NNO-azoxy)ethene (DMAE) has been synthesized and separated in pure form. DMAE has been obtained by the reaction of methansulphonate of 2,2-di(methoxy-NNO-azoxy)ethanol with diisopropilethylamine. Yield of DMAE is 65 %, C4H8N4O4, m.p. 63.5-64.8°C. The structure of DMAE has been determined with X-ray analysis, Dx = 1.436 g.cm-3. DMAE may become starting substance for synthesis of new AAZ because of high reactivity of DMAE with nucleophiles (Mikael reaction). For example DMAE reacts easy with nitroform forming 1,1-di(methoxy-NNO-azoxy)-3,3,3-trinitropropane in qantitative yield, C5H9N7O10, m.p. 107-107.5°C.

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