

Schedule & Abstracts



Time

October 5 – October 7 2020

4- 6:45 pm (CEST) daily

via CISCO-Webex

SCHEDULE

MONDAY October 5 2020

EDT 10:00 AM / CEST 4:00 PM Introduction
EDT 10:15 AM / CEST 4:15 PM **Prof. Dr. Edward Dreizin**, NJIT, Newark, NJ, USA
Metal-Metal Fluoride Reactive Composites and Reactions Leading to their Ignition
EDT 11:30 AM / CEST 5:30 PM **Prof. Dr. Michelle Pantoya**, TTU, Lubbock, TX, USA
Ignition Mechanisms for Fuel Particles in Energetic Composites
EDT 12:45 PM/ CEST 6:45 PM End of first day

TUESDAY October 6 2020

EDT 10:00 AM / CEST 4:00 PM Introduction
EDT 10:15 AM / CEST 4:15 PM **Prof. Dr. Steven Son**, Purdue, West Lafayette,
IN USA Impact Ignition of Energetic Materials
EDT 11:30 AM / CEST 5:30 PM **Prof. Dr. Jan Puszynski**, IMP, Rapid City, SD, USA
Ignition of Energetic Materials: Mechanism, Theory and Modeling
EDT 12:45 PM/ CEST 6:45 PM End of second day

WEDNESDAY October 7 2020

EDT 10:00 AM / CEST 4:00 PM Introduction
EDT 10:15 AM / CEST 4:15 PM **Dipl.-Ing. Volker Weiser**, FhG-ICT, Karlsruhe, BW, DE
Experimental investigation and modelling of the ignitor plume/propellant interaction
EDT 11:30 AM / CEST 5:30 PM **Prof. Dr. Bill Proud**, Imperial College, London, UK
Impulsive Loading of Detonation Trains
EDT 12:45 PM/ CEST 6:45 PM Summary and End

Metal-metal fluoride reactive composites and reactions leading to their ignition

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Most of the recent developments in reactive composite materials focused on thermites combining metals with metal oxide oxidizers. The interest in thermites was renewed due to rapid progress in preparation of nanocomposite materials. When the scale of mixing of metal and oxidizer is refined, the reaction rates accelerate rapidly. High reaction rates extend the range of possible applications of nanothermites from selected pyrotechnic systems to explosives and propellants. However, nanothermites are very sensitive to electrostatic discharge (ESD) making them difficult to store and handle. Combustion products of most thermites are condensed species; this restricts their use in energetic systems requiring increased pressures and expanding gases. This talk will discuss how replacing metal oxides with metal fluorides combined with metal fuels on the nanoscale can alleviate both of the above issues. The resulting metal/metal fluoride composite reactive materials are ESD insensitive, they burn generating gaseous products, and they exhibit short ignition delays and high burn rates comparable to or exceeding those reported for their nanothermite analogs.

Fluorinated oxidizers have certainly been explored in the past in many reactive and energetic formulations [1]. However, most work was focused on fluoropolymers with little attention paid to reducible metal fluorides. Recently, both aluminum and boron were combined with several such metal fluorides to form new reactive composite materials. All prepared materials were fuel-rich, so that once ignited, they could use oxidizer from the environment. For aluminum-metal fluoride thermites, ignition was explored for Al-CoF₂ and Al-BiF₃ nanocomposites [2]. The exothermic reactions started at lower temperatures than in any previously prepared reactive nanocomposites based on aluminum. Redox reactions in Al-CoF₂ and Al-BiF₃ nanocomposites started around 200 and 250 °C, respectively. These initial reactions were rate-limited by the decomposition of fluorides. In the oxygenated environments, metallic Co and Bi generated by reducing the starting fluorides oxidized readily. Becoming shuttle catalysts, oxidized Co and Bi were rapidly reduced by excess aluminum, causing rapid heterogeneous oxidation of aluminum at low temperatures. The low-temperature thermally activated reactions led to low ignition temperatures for these materials (ca. 450 and 490 °C for composites with CoF₂ and BiF₃, respectively). Despite the low ignition temperatures, aluminum-metal fluoride composites were relatively insensitive to ignition by ESD, likely due to their high ionic conductivity preventing the formation of hot spots by the passing current. The combination of low ESD sensitivity with reduced activation energy for thermally activated ignition makes aluminum-metal fluoride composites attractive components for advanced energetic formulations.

For composite powders based on boron, also combined with CoF₂ and BiF₃, low-temperature reactions occurring just above 100 °C upon heating were catalyzed by hydrated boron oxide [3]. These reactions led to formation of gaseous boron fluorides. At high heating rates, such reactions caused ignition at very low temperatures (increasing from ca. 250 to 500 °C, with heating rates

raising from 2,500 to 23,000 K/s). The same exothermic reaction kinetics and ignition temperatures were observed for composite powders with both CoF_2 and BiF_3 serving as oxidizers. This confirmed that decomposition of the hydrated boron oxide was the rate-limiting reaction. Additional composite materials were prepared with boron, for which the hydrated surface oxide was removed. This was achieved by washing boron in acetonitrile. For such materials, exothermic reactions began at higher temperatures, causing also higher ignition temperatures. For composite powders using washed boron, both kinetics of the exothermic reactions and ignition temperatures were affected by the type of fluoride: materials using BiF_3 reacted and ignited at temperatures lower by about 100°C than those using CoF_2 .

The talk will further discuss the effect of the composite structure and metal/fluoride ratio on their ignition and combustion behaviors [4-8].

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Scratching beneath the surface of aluminum fuel powder ignition and combustion

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Fuel particles have a multi-layered, complex architecture that includes a crystalline core surrounded by a native oxide shell barrier that is further surrounded by a hydroxylated outer structure. For aluminum (Al) particles each layer plays an important role. The core contains an abundance of stored chemical energy waiting to be harvested. The metal oxide shell provides strength, thermal insulation, and is a mass transport barrier protecting the pyrophoric metal core from spontaneous combustion. The hydrated surface structure can be exploited for its catalytic properties that allow engineers to tailor surface chemistries that tune particle compatibility within a composite or tune the overall combustion performance.

As the advent of nanotechnology swept the globe, researchers from nearly every country explored the attributes of nanoparticle fuels and gained new appreciation for the properties of the shell and outer hydroxylated layers. At the nanoscale, the surface area to volume ratio is so high that the shell composition becomes a significant fraction of the overall powder content. New ideas for reaction mechanisms were introduced, and attempts to extend the new nanoscale derived knowledge towards small micron-scale particles show potential. Also, an appreciation for the distinction between burning behaviors that are a function of fuel particle size were rekindled with technology that helped us 'see' the ignition and combustion process of single particles at spatial and temporal scales never before observed. The observations were compelling and even inspiring. New ideas on how to harness the chemical energy stored within fuel particles began to emerge.

This presentation will review strategies that have been used to manipulate the surface structure of fuel particles and their resulting effect on fuel particle ignition and combustion. We will start with surface functionalization strategies that employed self-assembled monolayers (SAMs). Vapor deposition processes will also be highlighted that effectively capped particles with a coating in intimate proximity to the fuel for enhanced diffusion reactions. Plasma surface modifications will also be presented as well as general wet chemistry approaches for modifying the particle's multi-layer chemical and physical architecture toward tailored reactivity. In addition to the chemical modifications reviewed, we will also highlight physical alterations to a spherical particle induced by annealing and quenching treatments. The process of annealing and quenching has been shown to delaminate the core from the shell of the particle. The gap generated at the core-shell interface also influences reactivity and could provide additional insight into reaction mechanisms that are a function of ignition condition.

The objective of this presentation is to identify processes occurring during ignition and oxidation of surface altered aluminum particles. Then, identify how the surface alterations affect reaction mechanisms. In some cases, particles experience a multi-stage ignition processes, sometimes called pre-ignition reactions (PIR). Surface modifications can also induce different reaction pathways owing to the temperature of combustion and product species recovered. Other effects include higher or controlled energy release rates. All of these behaviors will be reviewed and predictions on how these treatments may influence reactivity in other fuels will be discussed.

Impact Ignition of Energetic Materials

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Impact-induced reaction is a complex and technically rich topic. In this overview talk, I will highlight some of our recent work that includes shock and non-shock ignition that highlights two applications: shock assisted synthesis and the impact ignition of an aluminum-fluorinated acrylic. Some background fundamentals will also be reviewed, focusing on what affects impact ignition. Mechanical initiation of reactions in powder systems involve complex interactions that can yield unexpected results. Two materials that exhibit similar thermal responses can behave very differently under the same loading conditions due to differences in their mechanical properties. Reactive composite powders with small characteristic dimensions can exhibit short ignition delays and reduced thermal ignition thresholds; however, a full understanding of the response of these powders to rapid mechanical loading is still unclear. Shock induced reaction synthesis is a complex, scientifically rich field with the potential to produce novel materials with unique properties. An example will be presented of the synthesis of cubic boron nitride through shock induced reaction synthesis. The direct synthesis of cubic boron nitride through shock loading of 3B+TiN composite particles. It was found that reduction of the diffusion distance through high energy ball milling before loading was critical for success, with unmilled powders showing no evidence of reaction after recovery. The results show the possibility of rapid reaction occurring in a condensed phase system at microsecond timescales. As a result, optimization of this process may provide a route for the fabrication and discovery of other advanced compounds. Recently, we extended this work to shock-induced reactions to boron (B) - metal nitride (MeN: Me=Ga, Zr, Cr) exothermic systems. All considered powder mixtures were again mechanically treated in a high-energy ball-mill to fabricate B-MeN nanostructured composite particles, which were subsequently shock loaded using an explosive charge. The structures of these materials were analyzed by conventional and synchrotron X-ray diffraction, Fourier transform infrared spectroscopy, and transmission electron microscopy. It was discovered that shock-induced reactions in the GaN+B system resulted in the formation of the metastable wurtzitic form of boron nitride (w-BN). This directly implies that ultra-fast (0.5-5 ns) reactions took place under the high-pressure conditions of the shock wave, which was a surprising result.

The second example presented is tailoring the reactivity of an aluminized fluorinated acrylic (AlFA) nanocomposite to an impact. The reliability of impact ignited reactive materials continues to be an elusive challenge. Ideally, a sensitizing agent is preferred over device or reactive ingredient modification. Here, I present an impact study of aluminized fluorinated acrylic (AlFA) and material sensitization via the introduction of inert particles. Initial impact testing of neat AlFA50 samples yielded a general baseline for material ignition at approximately 120 m/s for the configuration considered. Ignition was observed to occur on the far wall or in corners indicating that a pinching mechanism may be responsible. A modified experimental setup was used to image the response of a designed pinch point. Based on insights from these experiments, AlFA50

samples were prepared with 15% glass beads by volume and were impacted at high and low velocities. Ignition events were then observed at velocities at least as low as 35 m/s (lowest impact speed achievable currently) and originated promptly in the region of the face of the plunger rather than in corners, indicating the ignition event was much more independent of the geometry used. Further experiments with varying concentrations of the glass bead additives (between 10-30%) showed that the concentration could alter the level of sensitization of the material to low-speed impacts. The addition of glass micro-balloons, as used to sensitize explosives, was also considered but found to be less effective than glass beads. These results show that the impact sensitivity of these AIFA50 materials can be tailored by the addition of inert beads, such as the glass beads used here, to create multiple pinch points in the reactive that can result in ignition.

The work presented here serves to increase the understanding of the ignition response of reactive materials, such as aluminum-fluorocarbon materials, to mechanical stimuli, as well as shock-assisted combustion synthesis.

Ignition of Energetic Materials

Mechanism, Theory, Modeling, and Sensitivity Testing

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Theories of ignition and reaction front propagation in energetic materials have been of interest to energetic materials community for many years, but significant advances have been made during the past twenty years. Energetic materials (EM) are traditionally comprising of: i) explosives; ii) propellants; and iii) pyrotechnics. Primary and secondary explosives react within few microseconds releasing large quantity of gases and generating shock waves. Propellants are designed to react in less violent matter (milliseconds), and they are used for acceleration of flying objects e.g. rockets, bullets, etc. or for special fact mechanical actions, e.g. cutting, inflation, etc. Pyrotechnics, in general, are used to produce smoke, light, noise, and slow gasless propagations, e.g. time delays, with reaction times from milliseconds to several minutes.

There are different ignition mechanisms of energetic materials but in principle any ignition process relies on the transformation of any kind of energy, e.g. mechanical, thermal, light, and electrostatic, to the formation of "hot-spots". However, the precise mechanism of EM initiation is still discussed by the scientists.

The focus of this presentation will be on:

1. Mechanism of ignition of energetic materials;
2. Theory of thermal ignition;
3. Mathematical modeling of initiation by different energy means;
4. Mathematical modeling of reaction front propagation in condensed phase systems;
5. Sensitivity testing techniques for impact, friction, and electrostatic discharge.

Experimental investigation of the ignitor plume/propellant interaction

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The ignition of gun propellants is still a challenging task that requires igniter compositions optimized to each type of propellant. Propellant ignition is mainly dominated by the local heat transfer to the propellant that must be large enough to initiate a self-sustaining reaction with a heat release which overcomes all internal heat loss. In the case of pyrotechnic ignition, heat transfer from the ignitor plume to the propellant's body works in combination of different mechanisms as convection from hot gases, conduction of hot impinging and penetrating particles or condensing metal vapors on the propellant surface as well as heat radiation from the plume.

Normally, the performance of an igniter mixture is characterized by ballistic closed-bomb tests under isochoric conditions measuring the ignition delay time by analyzing the pressure time curve. This method validates the applicability of a selected mixture but does not give any hints to understand the individual mechanism of ignition process. This may help to optimize the ignition mixture. This presentation introduces a method to investigate simultaneously some performance data of the igniter mixture and the ignition process using a chimney-type window bomb under isobaric conditions but on different pressure levels (0.1 to 10 MPa N₂). A small amount of igniter mixture is filled in a vertically positioned polymer tube and ignited using a melting wire. In a defined distance that may vary between 5 and 30 mm above the upper tube edge, a single propellant grain is fixed in horizontal position. The expanding igniter plume and its interaction with the propellant grain is observed simultaneously using a color high-speed camera and a fast NIR emission spectrometer with 660 spectra/s.

This enables to measure expansion speed and temperature of the plume as well as profiles of temperature and species emission during the interaction with the propellant grain and the ignition delay time. Besides these technical data, the visual analysis of the movie results in additional qualitative but highly interesting information e.g. on the effect of penetrating particles on ignition (Figure 1).

To measure ignition delay time, both the video signal and the series of species spectra were analyzed. In some cases, e.g. when the combustion of igniter takes longer than the ignition delay time, only the species spectra results in a quantitative value. In this case, the first appearance of a typical propellant combustion product as e.g. water is used to define propellant ignition (Figure 2). When both signals can be analyzed the ignition delay times coincide fairly in an order of the standard deviation of repeated measurements (Figure 3). In summary the ignition behavior is characterized using the ignition delay times as a function of the pressure level usually best depictable in a log-log-diagram (Figure 3). The absolute value of ignition delay time varies with the formulation of ignitor mixture and the type of propellant. This ranking corresponds with ballistic measurements which were performed with selected igniter mixtures and propellants. As expected, the ignition delay times decrease drastically with pressure. Only sometimes the pressure dependence can be described with a linear plot. But depending on temperature, particle and metal vapor content, the ignitor plume of some mixtures shows different effectivity at low pressure (<1 MPa) or medium pressure >4 MPa. Also, such pressure effects are difficult to measure with ballistic tests.

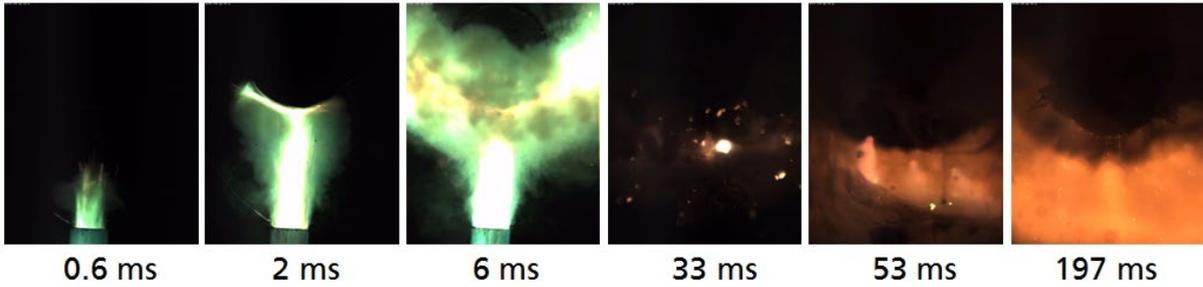


Figure 1: Interaction of B/KDN igniter plume jet with a JA-2 propellant grain during an isobaric ignition test at 2 MPa.

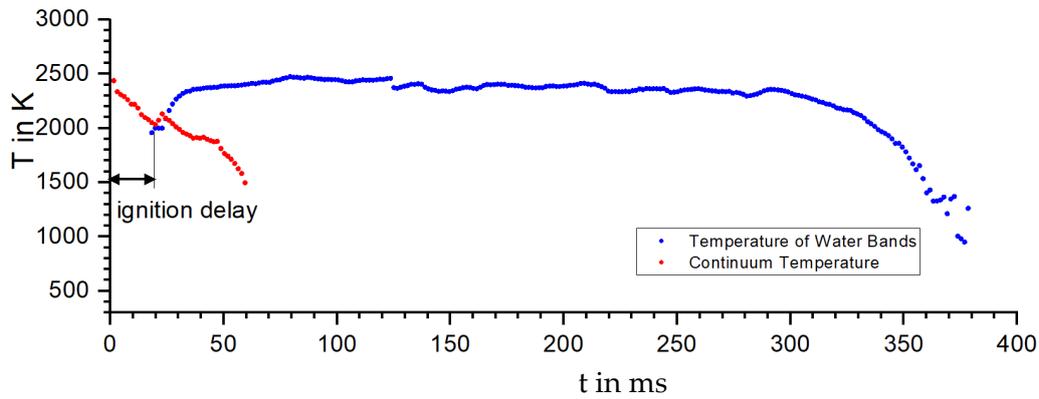


Figure 2: Temperature profile of continuum emission (red) and water band emission (blue) achieved from an ICT-BaM evaluation of a spectra series.

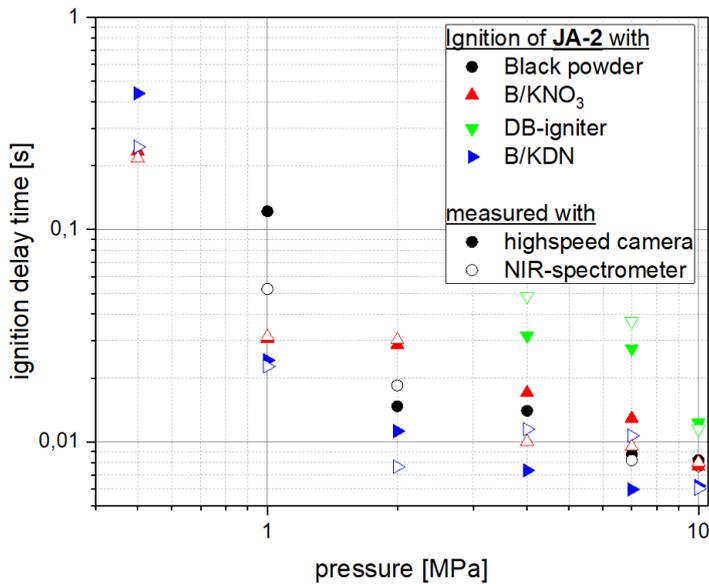


Figure 3: Ignition delay times of JA-2 with various igniter compositions as a function of pressure analyzed from high-speed movies and NIR-spectra.

Detonation and Barriers

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A number of drivers exist for munition systems regarding stewardship, function and safety. Advances in material processing and manufacture offer a seeming panacea of bespoke functionality, while the demands for modularisation of munition systems would seem to be best addressed with a more general system. Stewardship and its associated costs, require a system which has few long-term monitoring requirements and is impervious to environmental conditions, both thermal and mechanical. The increasing urgency of environmental concerns implies materials that are 'green' at the point of manufacture and systems which can be recycled, thus reducing the need for consumption of new resources. These drivers can be seen as pulling research in numerous directions.

This presentation will focus on the effects of modularity and physical barriers on the transmission of detonation from a detonator to a main charge. It will consider theories such as the James Criteria, the use of safety data from the gap test, and the use of functionally graded materials.

The presentation will draw on a number of current research topics and give an overview of the relevant literature. This will include examples taken from gap tests.

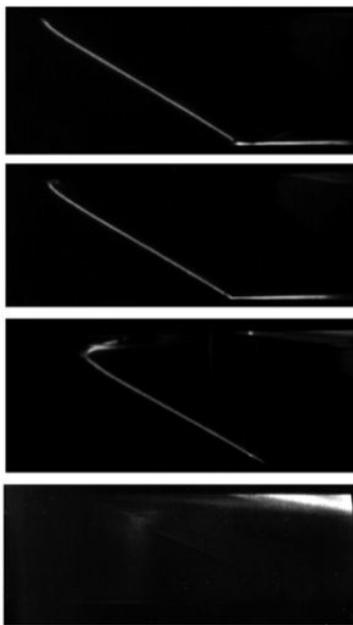


Figure 1. *Streak records of gap tests on fine-grained PETN 90% TMD. Gap thickness; top - 3.53 mm, second - 3.63 mm, third - 3.67 mm, bottom - 3.71 mm*

The high-speed streak images in figure 1. The streak records from a series of experiments on 90% TMD fine grain size PETN. The field of view is 30 mm and the top of the image corresponds to the bottom of the gap. The gaps used were 3.51, 3.63, 3.67 and 3.71 mm thick. In the top image the detonation is prompt and slightly overdriven. The detonation velocity settled down within 5 mm of column length. The second image shows slight hooking due to the detonation starting a short distance down the column, indicating a longer initiation time. With the 3.67 mm gap the hooking is severe, detonation breaks out ~8 mm down the column. Finally with a 3.71 mm gap there is no detonation. The brass witness plate indicated a detonation pressure in all cases except for the 3.71 mm gap where only a small dent was found indicating the more modest pressure associated with deflagration [1]. This research has been progressed through functionally grading the recipient material.

Progress in the processing of materials, such as resonant acoustic mixing has produced materials in batches, allowing for variations of composition to be produced in a rapid fashion. While this has great advantages for the researcher or designer who wishes to study such variations, it can also present issues involving reproducibility. Such issues have always existed, even in continuous production methods. However, as designers and manufacturers materials to the extreme minor variations and processing flaws can become more critical. A recent comparative study has shown for some material compositions this is not significant issue [2] regarding detonation properties. Questions regarding long-term stability of such materials remain relatively open.

In function, the energetic system and it's the arming unit may be subject to violent acceleration/deceleration. This can affect the electronics of the system, but also result in material compaction or separation due to local structures in the system. The need for a timed trigger, combined with survivability and function of the energetic presents the researcher with the task of designing appropriate, instrumented test vehicles and providing data on high rate mechanical properties for use by designers.

The overall aim of this presentation is to show how the need to propagate a detonation wave through a mechanical barrier can be used as an exemplar of the variety of driver in the science and industry of energetic materials.

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ERNST-CHRISTIAN KOCH

HIGH EXPLOSIVES, PROPELLANTS, PYROTECHNICS

This dictionary contains 740 entries with about 1500 references to the primary literature. Details on the composition, performance, sensitivity and other pertinent properties of Energetic Materials such as High Explosives, Propellants, Pyrotechnics, as well as important ingredients such as Oxidizers, Fuels, Binders, and Modifiers are given and presented partly in over 180 tables with more than 240 structural formulas .

In detail the dictionary gives elaborate descriptions of

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- 170 Pyrotechnic Compositions
- 360 High Explosive and Propellant Formulations

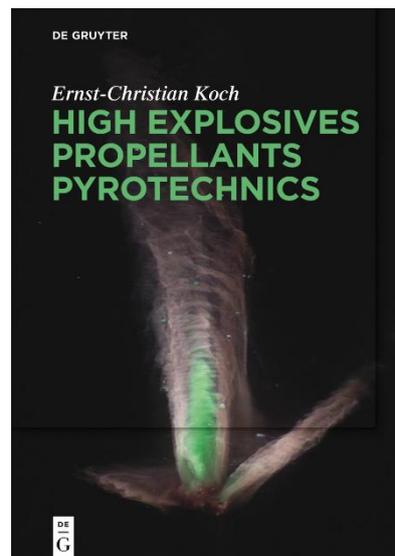
In addition, the basic physical and thermochemical properties of 435 pure substances (elements & compounds) typically occurring as ingredients or reaction products are given too.

150 Figures, schemes and diagrams explain Applications, Test methods, Scientific phenomena, Research facilities, and finally Individuals closely tied with the development and investigation of Energetic Materials.

The book is intended for readers with a technical or scientific background, active in governmental agencies, research institutes, trade and industry, concerned with the procurement, development, manufacture, investigation and use of Energetic Materials, such as High Explosives, Propellants, Pyrotechnics, Fireworks and Ammunition. The book serves both as a daily reference for the experienced as well as an introduction for the newcomer to the field.

The author

Dr. Ernst-Christian Koch, FRSC, studied chemistry and completed his dissertation at the Technical University of Kaiserslautern, Germany. He has been active in the field of research and development of Energetic Materials for over twenty years. Dr. Koch is owner of Lutradyn - Energetic Materials Science & Technology Consulting, Germany.



Review of the second German edition:

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