Energetics Science and Technology in Central Europe

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Science and Technology
in Central Europe

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Preface

Energetics Science and Technology in Central Europe is one book in a series of Center for Energetic Concepts Development books on Energetics Science and Technology in different parts of the world. This book is the 2nd in a planned series of six volumes. Each volume covers a different region of the world. The motivation for this series is to provide a comprehensive collection of information on this critical technology and identify the energetic materials science and technology being conducted across the globe.

The first book started with the discovery of gunpowder in China, where energetics (in the form of fireworks) originated. Knowledge of fireworks, gunpowder and other forms of energetic materials flowed out of China and into Europe in the 13th Century along routes such as the Silk Road.

Since European scientists were the first to improve on gunpowder and create an array of imaginative uses, for both civilian and military purposes, we selected Central Europe to be 2nd in the series. European contributions are too many to capture in a single volume. Contributions from elsewhere in Europe will be included in another of the six volumes.

Among the first uses of gunpowder in Europe was its appearance during a defense of Prague in 1420, at Vitkov Hill in what is today the Czech Republic. Since that time the countries in this region of Europe have sought to improve energetics for both peaceful (e.g., coal mining) and military purposes. Since the end of the Cold War, there has been an increased transparency into the energetics and research capacity in this section of the world. The increased transparency makes possible this volume.

An important example of Central European energetics research capacity is the Institute of Energetic Materials at the University of Pardubice (http://www.upce.cz/en/fcht/uem.html). Annual seminars open to a worldwide audience began at the University of Pardubice in 1998.

The seminars have come to be known as NTREM—New Trends in Research of Energetic Materials. The seminars are specifically designed to be a part of the study curriculum of Pardubice students. NTREM is one of the first ways energetics research capacity in this section of the world was made known to Western Nations.

As the quality of the NTREM presentations increased since its 1998 inception, the organizers sought a process for timely publication of the research findings. The solution was the founding of a new scientific journal. The *Central European Journal of Energetic Materials* first appeared in 2004. The Institute of Industrial Organic Chemistry in Poland publishes the journal (http://www.wydawnictwa.ipo.waw.pl/).

The editors designed the book to be a collection of chapters by energetic scientists living in and near Central Europe. We started by inviting scientists historically associated with NTREM.

We invited chapters from the NTREM Chairman, Svatopluk Zeman of the Czech Republic; Scientific Committee Chairman, Adam Cumming of the United Kingdom; Scientific Committee members from Poland, Andrzej Maranda; Germany, Thomas Klapötke; Russia, David Lempert and Tatyana Pivina; and Turkey, Lemi Türker.

We also invited Wanda Karaś, Managing Editor of the *Central European Journal of Energetic Materials*, Poland; Manfred Bohn, Germany; Aleksandr Smirnov and Vladimir Klimenko, Russia. Joining Klimenko writing one of his two chapters are Ronald Armstrong and Davinder Anand of the United States.

We are releasing this book to the public during the *15th International Seminar on New Trends in Research of Energetic Materials*, held at the University of Pardubice, April 18-20, 2012. Analogous to Energetics Science and Technology in China, it is our hope this book will also provide an impetus for the editors, authors, and readers doing energetics research to reach out and connect directly for the purpose of research collaboration.

We thank Ania Picard for designing the cover and preparation of the final product; and Eric Hazell for copy editing each of the eleven chapters.

The Editors

Executive Summary

A selected synthesis is presented of organizational and current research activities reflective of the considerable effort being devoted in Central Europe to the development of improved energetic material formulations for military and industrial uses. The listed descriptions of (1) Svatopluk Zeman's annual seminars on "New Trends in Researches on Energetic Materials"; (2) Andrzej Maranda and Wanda Karaś's *Central European Journal of Energetic Materials*; and, (3) Vladimir Klimenko's "International Conferences on New Models and Hydrocodes for Shock Wave Processes in Condensed Matter", are shown in each case to involve significant outreaches to the international community of researchers on the topics of energetic materials and their properties. Additional research articles provided by these article contributors and additional colleagues of theirs establish bibliographically the international character of associated researches on the comprehensive range topics: energetic molecule syntheses; compilation of the material properties, particularly relating to energetic components of propellant formulations; chemical decompositions that occur both on molecular and crystal lattice scales; the consequent material responses under impact and more extreme loading conditions; the important viscoelastic properties of binder material in formulations; and, explosive uses in industrial mining applications.

Chapter 1. Professor Zeman provides a brief history of teaching the chemistry and technology of energetic materials at the University of Pardubice, especially as connected with his development over ~15 years of the annual seminars on "New Trends in Research of Energetic Materials". The seminars have been directed towards university students and recent graduates. An important outreach effort has been to have invited lecturers from the international energetics community.

Chapter 2. An elaboration is provided by Dr. Adam Cumming, DSTL, UK, of organizational support and scientist participations provided by Western European agencies for the NTREM activity, in particular, and for cooperation of Western-Eastern European research activities. Comment is provided on Romanian and Bulgarian connections in the Central European community.

Chapter 3. Professor Andrzej Maranda, co-founder and Chairman of the *Central European Journal of Energetic Materials* joins with the journal's managing editor, Ms. Wanda Karaś, in a discussion of the topics covered in the journal. The journal, based in the Institute of Industrial Organic Chemistry, Warsaw, provides an authoritative outlet for publication of articles presented at the NTREMs, particularly those first presented as poster presentations and for the plenary lectures.

Chapter 4. A description is provided by Dr. Vladimir Klimenko, Institute of Chemical Physics, Moscow, and colleague Professors Ronald W. Armstrong and Davinder K. Anand, of the University of Maryland, Center for Energetic Concepts Development (CECD) of the “International Conferences on New Models and Hydrocodes for Shock Wave Processes in Condensed Matter”. The conferences are devoted to development of more accurate physically-based material models for material behaviors to be employed in the next generation of hydrocode computations for extreme material loading conditions. The approximately biennial conferences have been ongoing from an initial meeting in St. Petersburg in 1995 and followed up with meetings at the UM CECD and other venues. The conferences have importantly involved research presentations from scientists at the former closed cities such as Arzamas and Chelybinsk.

Chapter 5. Professor Thomas Klapötke, Ludwig-Maximilian University, Munich, describes researches on the synthesis of new molecules covering: high-energy-density munitions, oxidizers, high-nitrogen propellants, pyrotechnics, and primary explosives. The researches are connected with activities of government establishments, such as Institut Chemische Technology, Fraunhofer Institute, Pfintzal, and private companies such as Diehl BGT Defence, Rheinmettall Defence, Rheinmetall Nitrochemie, DYNA Energetics and Bayern Chemie.

Chapter 6. For more than three decades scientists have sought simple correlations of chemical, physical, and detonation properties of energetic materials. Professor Lemi Türker of Turkey's Middle East Technical University offers a curious, almost linear, relation between density and the total energy and molecular weight of an explosive material.

Chapter 7. Compilation of polynitrogen energetics is provided by Drs. Aleksander Smirnov, David Lempert and Tatyana Pivina, representing research institutes in the Nizhny and Moscow Regions of Russia. The aim of such researches, described in relation to current property levels, is to achieve nitrogen allotropes with an advantageous density of ~2.0 g/cm^3, enthalpy of 6800 kJ/kg, detonation pressure of ~50 GPa, significant metal acceleration performance and tolerable sensitivity to initiation.

Chapter 8. The sensitivity of energetic materials at the molecular level via fragmentation of isolated molecules is described by Professor Zeman. There is remarkable connection between such evaluated molecular stability against decomposition and the bulk material sensitivity as measured by mechanical loading by impact, even up to generation of shock pressures, and to electrical stimuli.

Chapter 9. Sensitivity to mechanical initiation is addressed at the crystal lattice and meso-mechanics scale by Dr. Klimenko. In particular, the role of dislocation mechanics based plasticity is addressed for creation of hot spots leading to initiation of explosion.

Chapter 10. Dr. Manfred Bohn, ICT Fraunhofer Institute, describes important mechanical aspects of polymer binder materials as employed in current propellant formulations. In this case, for both material processing and use, the aim is to prevent an unwanted transition to a brittle glassy structure.

Chapter 11. Professor Andrzej Maranda, Military University of Technology, PO, describes the important use of explosives for mining. Emphasis is on safety issues regarding the explosives themselves and on their initiating elements, not unlike the situation for military concerns.

Author Biographies

Davinder K. Anand is Professor of Mechanical Engineering and Director of the Center for Energetic Concepts Development, both at the University of Maryland, College Park. He received his doctorate from George Washington University in 1965. Dr. Anand was Senior Staff at The Applied Physics Laboratory of the Johns Hopkins University from 1965-1974. From 1991-2002, he chaired the Department of Mechanical Engineering at College Park. He has served as a Director of the Mechanical Systems Program at the National Science Foundation, and his research has been supported by NIH, NASA, DOE, DOD, and industry. He has lectured internationally, founded two high technology research companies (most recently Iktara and Associates, LLC), published three books and over one hundred and seventy papers, and has one patent. He is a Distinguished Alumnus of George Washington University, and was awarded the Outstanding and Superior Performance Award by the National Science Foundation. Dr. Anand is a Fellow of ASME and is listed in Who's Who in Engineering.

Ronald W. Armstrong is Professor Emeritus, Department of Mechanical Engineering, University of Maryland. He was founding director in 1998 of the Center for Energetic Concepts Development. Creation of the CECD followed on from cooperative researches begun in 1980 with navy laboratory colleagues, first, at the Naval Surface Weapons Center, White Oak Laboratory, and then continued with these same and other colleagues at the Naval Surface Warfare Center, Indian Head Division. Two outcomes of the NSWC research collaborations have been: (1) development of the dislocation pile-up avalanche model for mechanically-induced hot spots leading to explosive (energetic) crystal initiations, done with C.S. Coffey and W.L. Elban; and, (2) development of the so-called Z-A dislocation-mechanics-based constitutive equations for hydrocode computations of structural material deformations under extreme loading conditions, done with F.J. Zerilli. Professor Armstrong is Fellow of the American Society for Materials, the Indian Institute of Metals, and the Materials Research Society of India. He has authored or co-authored more than 350 scientific journal and book publications, including more than 50 invited articles on the topics of dislocation mechanics and crystal and polycrystal plasticity and fracturing.

Manfred A. Bohn studied Chemistry and Physics at University of Karlsruhe, Germany, where he got his PhD in Physical Chemistry. He worked for more than 25 years at Fraunhofer ICT, Pfinztal, Germany in the field of stability, compatibility and ageing of energetic materials, which comprise gun propellants, rocket propellants, high explosive charges, all types of energetic components, gas generators, gelled propellants and improvised explosives. Besides experimental work, modelling the data is his interest. Stabilizer consumption, molar mass degradation of polymers, mass loss, chemical decomposition analysed by transition state quantum mechanics, atomistic simulation and modelling belong to these activities. Monitoring of ageing is a newer special topic. Numerous publications and presentations in international conferences and symposia document parts of this work. He is involved in several international collaborations organized in the frame of the European Defence Agency (EDA), and he is a member in the Custodian Nations Group (CNG) of NATO AC/326, SG1.

Adam S. Cumming is recognised as an international authority on energetic materials, representing the UK in several forums. He studied Chemistry at the University of Edinburgh where he gained his PhD, before joining the UK MOD to begin UK work on forensic research on traces of explosives. In 1988 he took over the running of the UK explosives formulation research, to which in 1990 was added gun and rocket propellant work. In 1994, as Technical Manager for Energetics, he was responsible for the content of the UK programme and for leading the UK in international forums. He is still employed by UK MOD as a lead advisor for Energetics research and continues work with other nations. He chairs several Research Groupings involving Europe and the USA, and has received both a Western European Armaments Group award and a NATO AVT Research Panel Scientific Award. In 2007 he was made an Honorary Fellow of the High Energy Materials Society of India. He has served on the advisory boards of several international conferences, including the Czech NTREM where he chairs the scientific committee. He is a member of the editorial board of the Wiley *Propellants, Explosives and Pyrotechnics* journal and is encouraging Indian scientists to publish and to take a more active role internationally. His current interests include leading international studies on the environmental aspects of energetics and on the technology for insensitive munitions.

Wanda Karaś, MSc, graduated from the Department of Chemistry at the Warsaw University (1974). For the next twenty years, she worked as a specialist on plastics and electroplating in the motor industry. Since 1994, she has worked in the Editorial Section at the Institute of Industrial Organic Chemistry and quickly became the Managing Editor of published periodicals: *Pestycydy/Pesticides and Organika − Scientific Papers of the Institute of Industrial Organic Chemistry*. In 2004 Karaś became the Managing Editor of a new quarterly, the *Central European Journal of Energetic Materials* (CEJEM).

Thomas M. Klapötke received his PhD in 1986 (TU Berlin), post-doc in Fredericton, New Brunswick, habilitation in 1990 (TU Berlin). From 1995 until 1997 Klapötke was Ramsay Professor of Chemistry at the University of Glasgow in Scotland. Since 1997 he has held the Chair of Inorganic Chemistry at LMU Munich. In 2009 Klapötke was appointed a Visiting Professor at CECD, University of Maryland. Klapötke is a Fellow of the RSC (C.Sci., C.Chem. F.R.S.C.), a member of the ACS and the Fluorine Division of the ACS, a member of the GDCh, and a Life Member of both the IPS and the National Defense Industrial Association. Most of Klapötke's scientific collaborations are between LMU and ARL in Aberdeen, MD and ARDEC in Picatinny, NJ. Klapötke also collaborates with ERDC in Champaign, IL. He is the executive editor of *Zeitschrift für Anorganische und Allgemeine Chemie* and an editorial board member of *Propellants, Explosives and Pyrotechnics*, *Journal of Energetic Materials*, *Central European Journal of Energetic Materials*, and the *International Journal of Energetic Materials and Chemical Propulsion*. Klapötke has published over 500 papers, 23 book chapters and five books.

Vladimir Y. Klimenko was educated at the Moscow State University. He started his scientific career at the Institute of Chemical Physics in 1972, under the supervision of Dr. Anatoly Dremin. In 1978, Dr. Klimenko opened a new page in shock wave physics, namely, molecular dynamics of shock wave processes, which marked the beginning of detonation study at the molecular level. He has developed new mechanisms of detonation (in particular, the frontal and dislocation mechanisms of explosive decomposition) and numerical models of detonation, which include these mechanisms. From 1988-1992, Dr. Klimenko was the Chair of the Committee on Computer Simulations of

Shock Wave Processes in the Russian Ministry of Science. Since 1990, he has been the Director of the High Pressure Center at the Institute of Chemical Physics. Dr. Klimenko has authored more than 150 publications.

David B. Lempert is an international leader in Energetic Materials and focuses on solid composite propellants. He studied chemistry at the Moscow State University. After that he has been working in the Institute of Problems of Chemical Physics of Russian Academy of Sciences in the department of combustion & explosion (until the middle of 1990s the head of this department was academician George B. Manelis). Since 2001 Lempert has been the head of the laboratory of the thermodynamics of high-temperature processes and vice-head of the department of combustion & explosion. The main topics are: the analysis of potential abilities to increase propellant energy and ballistic effectiveness; study of the thermal stability of different compounds; a search for ways to increase the stability level of individual compounds as well as the level of the compatibility of different compounds in the formulation. In the past decade the laboratory of Dr. Lempert has been investigating processes of filtration combustion too. Since 2005 Dr. Lempert has been Vice Chairman of the Symposium on Combustion & Explosion (2005 and 2008, Russia) and of the conference on filtration combustion (2007 and 2010, Russia). Since 2010 he has been a member of the scientific committee of the international seminar «New Trends in Research of Energetic Materials» (Czech Rep.). Dr Lempert visited many countries (USA, Germany, France, Czech Rep., China, Korea, Belgium, Italy) and many scientific meetings with lectures on solid composite propellants and on filtration combustion.

Andrzej Maranda is Professor at the Military University of Technology in Warsaw, Poland. He is internationally recognized as an expert in the chemistry and technology of explosives. He graduated from the Faculty of Chemistry at Warsaw University of Technology. Prof. Maranda specializes in detonation mechanisms of ANFO explosives, the use of explosive methods in material engineering, and production process safety. He leads research on initiation and detonation progress in non-ideal explosives, the use of explosives obtained by demilitarization of ammunition in the opencast mining, plating and strengthening of metal materials, and obtaining of dense modification of carbon and boron nitride. For many years, Prof. Maranda has been a member of the Scientific Committee of the International Seminar "New Trends in Research of Energetic Materials" in Pardubice, and of the Blasting Techniques organized in Stara Lesna. He is a co-founder and the

Chairman of the scientific quarterly *Central European Journal of Energetic Materials*. He also initiated the International Conference IPO-EX, which had 8 editions, and acts as its chairman.

Tatyana S. Pivina is one of the key leaders of International Energetic Society. As a student she was invited by her mentor, Prof. Sergey Novikov, the founder of the chemistry of Energetic Materials in Russia, to work in his Department at the Zelinsky Institute of Organic Chemistry (ZIOC), Russian Academy of Sciences. She still works for ZIOC. Prof. Pivina is a creator of a unique methodology for Silico Search of Structures for Novel Energetic Compounds with a Promising Set of Physicochemical Characteristics. She is the head of the theoretical group at the Lab of Mathematical Chemistry and Computer Synthesis of ZIOC, and under her leadership some methods and computer programs to estimate the basic characteristics of EMs were elaborated. In her research team a wide arsenal of computational methods are used, including the additive schemes and molecular mechanics, semi-empirical and ab initio quantum chemistry, the method of Atom-Atom Potential Functions, QSPR-methodology (the identification of quantitative structure property relationships), as well as the Artificial Neural Networks approach. Under her supervision about 15 PhD degree works have been defended. She is a member of Scientific Committee of the international seminar «New Trends in Research of Energetic Materials» (Czech Rep.). Prof. Pivina has been working at the different research centers and has presented her lectures on computer modeling of EMs structures and their properties (in Russia, USA, Germany, France, Czech Rep., China, Brazil, New Zealand, etc.).

James M. Short is an international leader in energetics, focusing on combustion. He studied detonation physics at the University of California at Berkeley. After that he was a protege of the eminent detonation physicist, Sigmund J. Jacobs, and explosives chemist, Mortimer J Kamlet. In 1983 Dr. Jacobs selected Dr. Short to be the chairman of the International Detonation Symposium. Dr. Short remained chairman of the Symposium for more than 20 years. In 1980, Dr. Short invited Professor Ding Jing of the Beijing Institute of Technology and three other Chinese Professors to participate in the Seventh International Detonation Symposium. In 1987, Dr. Short was privileged to represent the United States in Beijing and offer three papers at the International Symposium on Pyrotechnics and Explosives. Since 2011 he has served on the Foreign Advisory Board of the International Autumn Seminar on Propellants, Explosives and Pyrotechnics. At this seminar, the 15th in the Czech series on New Trends in Research of Energetic Materials, he joins the Scientific Committee. Now as the Executive Editor of the *Journal of Energetic Materials* (http://www.tandf.co.uk/journals/ titles/ 07370652.asp), he is privileged to publish the work of European energetic scholars, and he also encourages energetics scholars to publish in the *Central European Journal of Energetic Materials*.

Aleksandr S. Smirnov is a well-known expert in the field of experimental and theoretical investigations of Energetic Materials in Russia. He was educated in Mendeleev Institute of Chemical Technology under the guidance of Prof. B. Kondrikov and Prof. A. Fogelzang**.** For more than 10 years he was the head of the Lab. of “Fast acting processes” at the State Scientific Research Institute "Crystal" (Dzerzhinsk-city). Currently he heads the Department of Experimental Physics in the State Scientific Research Institute of Mechanical Engineering after V. Bakhirev (Dzerzhinsk-city). The main topics of his studies are: the experimental investigations of basic characteristics and structures for explosives, including ones with metals and oxidizers, as well as the elaboration of a complex system for calculations more that 25 explosive parameters for EM-s. Smirnov is a permanent participant of Khariton Thematic Scientific Readings (Sarov-city) and the International Conference "Shock Waves in Condensed Matter." Since 2012 he has been a member of the organizing committee of this conference.

Lemi Türker is one of the leading researchers of Turkey in the field of explosives. His interests cover both synthesis, but mostly the theoretical and computational aspects of explosives. He studied nitration kinetics at the Middle East Technical University and then in 1974 joined the Katritzky group at the University of East Anglia for PhD studies. Prof. Türker published about 350 papers in heterocyclic chemistry, chemical topology, computational and mathematical chemistry, dyes and pigments, nanostructures, fuel cells, hydrometallurgy, and catalysis. He is involved in certain Turkish projects on explosive materials. In 2007, he earned the Scopus Award in Turkey.

Svatopluk Zeman, Head of the Institute of Energetic Materials (since 1994) of the Faculty of Chemical Technology at the University of Pardubice, received his M.Sc. from the University of Pardubice in 1966. Due to affairs in the then Czechoslovakia he left the University in 1969, becoming a researcher in the Slovak enterprise CHEMKO Strážske. He defended his PhD thesis in 1990 and his Associate Professor thesis in 1992. In 1993, he returned to the University of Pardubice as Associate Professor. In 1998, he defended D.Sc. thesis and in 2000 was appointed full Professor. He has coauthored about 350 papers cited in *Chemical Abstracts*. His *h*-factor is 18 (ISI). He is a member of editorial boards of the *Chinese Journal of Energetic Materials* and the *Journal of Hazardous Materials*, and vice-chairman of editorial board of the *Central European Journal of Energetic Materials.* He is a co-founder, and since 1999 chairman, of the International Seminars called “New Trends in Research of Energetic Materials,” held annually in April.

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Chapter 1

Teaching of the Chemistry and Technology of Explosives in the Czech Republic

Svatopluk Zeman

A short history and background of teaching the chemistry and technology of explosives in the Czech Republic is presented. Also mentioned is the history of the international seminars held annually at the University of Pardubice on New Trends in Research of Energetic Materials (NTREM).

1.1 History and Background

The year 2010 marked the 90th anniversary of the teaching of the chemistry and technology of explosives in what was previously known as Czechoslovakia. This scientific-pedagogical activity was initiated at the Prague Institute of Chemical-Technological Engineering (*now Institute of Chemical Technology – VŠCHT Prague*) under the guidance of Dr. Cyril Krauz. In the same year, Explosia (a company manufacturing explosives) was established at Pardubice. These two events significantly affected the development of energetic materials in Czechoslovakia, which at that time was a young republic, formed in 1918 after disintegration of the Austro-Hungarian Empire. These developments, together with the high standard of the Czech mechanical engineering industry, resulted in Czechoslovakia becoming a manufacturer and exporter of weapons, ammunition and explosives before the Second World War. The country also possessed relevant scientific research and engineering background.

Teaching was abolished during the Second World War, when the occupying German army closed the universities and colleges between 1939 and 1945. The post-war restoration of scientific pedagogical activities at universities and colleges led to establishing a sub-department called “Technology of Special Production” within the Department of Organic Technology at VŠCHT Prague, headed up by Dr. Ing. Josef Seifer. He was able to use personal contacts to set up the department in the Institute of Chemical Technology (*VŠCHT Pardubice*) in Pardubice in 1950. At present it forms a part of the University of Pardubice, as the Faculty of Chemical Technology. Teaching was supported by Sellier & Bellot in Vlašim (a manufacturer of small arms ammunition). The company loaned laboratories to the first students to enable training and knowledge of manufacturing practice through access to the manufacturing facilities.

In September 1953 the Department of Special Production was established at VŠCHT Pardubice. It was the predecessor to the present Institute of Energetic Materials (IEM), The IEM facility was, and has remained, the only one of its kind in the territory of the former Czechoslovakia. So far, some 360 students have graduated at the MSc level, more than 400 students have graduated in two licensed courses (technology and blasting), and 71 students have graduated at the PhD level. Graduates have included citizens from Hungary, Afghanistan, Yugoslavia and Egypt. At present, overseas students at IEM come from Slovakia, Egypt and China.

The study and scientific activities at IEM represent a multi-disciplinary field:

- Chemical technology - the chemistry and technology of individual explosive substances, and special analytical chemistry of explosives
- Technology of explosives - military & industrial explosives, propellants, primers and initiators, and pyrotechnic products
- Physics of explosion - the theory of explosives and explosion effects, technology and safety of blasting, basics of construction of ammunition and weapons
- Safety engineering - risk and safety analysis of chemical technologies, prevention of accidents and improvement of the safety of chemical plants

In the past, IEM has made a significant contribution to: the development of industrial explosives for a Slovak manufacturer Istrochem Bratislava; the practical problems of safety at work in Czechoslovak factories endangered by explosion hazard and subsurface coal mining; and the problems of development of some special explosives and initiators. In the period following the political transformation in 1989, IEM continued to cooperate on explosive development activities with Slovak explosive manufacturers. Today, IEM is active in the area of development of ecological high explosives and initiators, modern high-performance explosives, the problems of safety engineering in the area of explosions of gaseous and disperse systems, and in the area of risk analysis.

Apart from pedagogical activities at the MSc, PhD and BSc levels, IEM teaches licensed courses for industrial specialists in the areas of explosives theory and technology, and blasting techniques. These pedagogical activities also include participation in European projects concerning the development of education programs for all those working in the field of explosives (EUExnet), and education of blasters within the ESSEEM program. The state of education and research into the theory and technology of explosives in the Czech Republic is described in another paper [1].

1.2 International Seminars NTREM [2]

Significant scientific-pedagogical activities of IEM also include organising international seminars – New Trends in Research of Energetic Materials (NTREM). In May 1998, the Research Institute of Industrial Chemistry (Explosia Co.) organised an internal seminar for its young staff members working in the scientific research area. The organisers also invited IEM’s PhD students to this meeting. The next seminar in this area, held in April 1999, was organised by IEM and attended by a sizeable delegation of scientific research workers and teachers from the Military University of Technology and also from the Institute of Industrial Organic Chemistry, both in Warsaw. In 2000, colleagues from abroad took part in the meeting: from the Institute of Marine Research & Special Technologies in Zagreb and also from the American 3M Company. In 2001 the fourth seminar had the character of an international meeting with English as the lingua franca. This was the birth of the tradition of international NTREM seminars. NTREM has become a part of the teaching provided students at IEM.

The original stimulus for starting the NTREM seminars was teaching young research workers how to present their results in front of a scientific audience. The meetings are 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, applications), and safety engineering. In keeping with the fact that the participants are young people, no fees are required for the Seminar. In view of inflation in the Czech Republic in recent years, starting with the 9th meeting, external participants have not been asked to donate €100.

Help from colleagues from abroad has contributed to the international character of these seminars. From the first Seminar, present were professors from the Military University of Technology in Warsaw, Dr. Stanislaw Cudziło, Dr. Andrzej Maranda and Dr. Waldemar A. Trzciński; the former technical manager of the Institute of Industrial Organic Chemistry in Warsaw, Dr. Bogdan Florczak; and, Dr. Muhamed Sućeska, scientific advisor from the Brodarski Institute – Marine Research & Special Technologies in Zagreb and Associate Professor at the University of Sarajevo.

Starting with the 4th NTREM seminar, the organisation and management activities of the seminars have been assisted by Dr. Adam Cumming from DSTL Fort Halstead in Sevenoaks, UK, and the late Dr. Fred Volk (a great supporter of young scientists) from ICT Pfinztal, Germany. Starting with the 5th seminar, Dr. R. H. Woodward Waesche, former Editor-in-Chief of the *Journal of Propulsion and Power* (now SAIC, Gainesville, USA), became another significant supporter and adviser.

Dr. Adam Cumming is Chairman of the NTREM International Scientific Committee. The committee evaluates the quality of the seminar and of the contributions of the young participants, awards prizes for the best three oral and the best three poster presentations, and makes recommendations for further development of these meetings.

Since the year 2000, the abstracts of papers presented at NTREM have appeared in *Chemical Abstracts*. Table 1.1 shows the number of participants, number of countries represented, and number of papers present at NTREM.

One of the decisive factors in organising these seminars has been the financial assistance of well-wishers. The Seminars have been sponsored by:

- U. S. Army International Technology Center, Atlantic (conference grant)
- U.S. Office of Naval Research Global, Middlesex, UK (conference grant)
- European Office of Aerospace R & D of USAF in London (conference grant)
- Austin Detonator, Vsetin, the Czech Republic
- Explosia, Pardubice, the Czech Republic
- Indet Safety Systems, Vsetin, the Czech Republic (member of Nippon Kayaku group)
- STV Group, Rataje u Kromerize, the Czech Republic
- Faculty of Chemical Technology, Pardubice, the Czech Republic
- OZM Research, Hrochův Týnec, the Czech Republic

Table 1.1: Survey of the seminars attendance.

Seminar		Number of		
No.	year	countries	contributions	participants
3	2000	6	32	88
4	2001	11	41	106
5	2002	19	51	116
6	2003	18	60	129
7	2004	20	87	150
8	2005	22	106	160
9	2006	23	85	189
10	2007	23	108	199
11	2008	24	109	196
12	2009	27	99	195
13	2010	30	98	115*
14	2011	26	117	185

Note: *) This 13th meeting was severely affected by Iceland's volcano eruption (April 16th, 2010) when air traffic was considerably reduced.

The 11th NTREM Seminar was sponsored also by Schlumberger, Reservoir Characterization Group, Clamart, France. The help received from all these institutions is gratefully acknowledged. The organisers appreciate the assistance of each sponsor.

1.3 References

1. S. Zeman, P. Vávra, "Energetic materials - present state and trends in development of explosives" (in Czech). *Chemicke Listy* 104(8): 2010: 791-797.
2. Web sites of Seminars NTREM: http://www.ntrem.com

1.4 Appendix – Lecture Program of the 14th Seminar NTREM (April 2011)

Lecture program of the 14th NTREM – Wednesday, April 13, 2011

08:15 **Meeting of all speakers** of the first Session with Chairman of this Session.

08:40 **Opening of seminar** – speech of Assoc. Prof. Tatiana Molkova, Vice-Rector of University of Pardubice

1. Session

Chairman: Prof. Thomas Klapötke
Ludwig-Maximilians-Universität Műnchen

09:00 Prof. Nina Makhova (invited lecturer)
Zelinsky Institute of Organic Chemistry Russian Academy of Sciences, Moscow, Russia
Synthesis and reactivity of amino and nitrofuroxans.
09:30 Stefan Ek, Nikolaj Latypov
Swedish Defence Research Institute, Tumba, Sweden
Derivatives of 3(5),4-dinitropyrazoles as potential energetic plasticisers.
09:50 Michael Göbel, Konstantin Karaghiosoff, Thomas M. Klapötke, Davin G. Piercey, Jörg Stierstorfer
Ludwig-Maximilian University of Munich, Munich, Germany
Energetic salts and chemistry of the nitrotetrazolate-2N-oxide anion.
10:10 Niko Fischer, Thomas M. Klapötke, Jörg Stierstorfer
Ludwig-Maximilian University of Munich, Munich, Germany
The hydroxylammonium cation in tetrazole based energetic materials.
10:30 – 10:50 Coffee break
10:50 David Millar, David Alllan, Laura Cocker, Adam Cumming, Craig Henderson, Alexandra Mackay, Helen Maynard-Casely, Anna Muszkiewicz, Iain Oswald, Colin Pulham
University of Edinburgh, Edinburgh, United Kingdom
Co-crystallisation of energetic materials: a step towards tailored munitions?
11:10 Selcuk Gumus, Taner Atalar
Yuzuncu Yil University, Department of Chemistry, Van, Turkey
Computational study on all possible diamino-dinitropyrimidines and their mono and dioxide derivatives.
11:30 Andrey Len', Sergey Gerasimov, Mikhail IlyushinPetr Kalmykov
Russian Federal Nuclear Centre, Sarov, Russia
Ignition of light-sensitive compositions with explosive thermochemical sources.
11:50 Petr Kalmykov, Sergey Gerasimov, Mikhail Ilyushin,

Andrey Len' Russian Federal Nuclear Centre, Sarov, Russia
Definition of diversity for ignition of light-sensitive pyrotechnic composition pellets with roentgraph method.

12:10 - 14:00 Lunch break

2. Session

Chairman: Prof. Michel Lefebvre
Royal Military Academy, Belgium

13:40 Meeting of all speakers of the second Session with Chairman of this Session.

14:00 Joseph E. Backofen (invited lecturer)
BRIGS Co., Moneta, Virginia, USA
The two-stage detonation propulsion model: Exploring its intriguing trend-lines and equations.

14:30 Michael P. Messner, Florian Bauer, Peter Moser
University of Leoben, Chair of Mining Engineering, Leoben, Austria
Blasting fumes in underground workings.

14:50 Chris Braithwaite, Jiri Pachman, Jiri Majzlík, David Williamson
Cavendish Laboratory, Cambridge University, U.K.
Improved experimental procedure for the large scale gap-test.

15:10 Michael Hutchinson
AWE Aldermaston, Reading, United Kingdom
Replacing the equations of Fano and Fisher for cased charge blast equivalence.

15:30 Ahmed Elbeih, Svatopluk Zeman, Jiri Pachman, Marcela Jungova, Waldemar Trzciński, Zbynek Akstein
University of Pardubice, Pardubice, Czech Republic
Advanced plastic explosive based on Bicyclo-HMX compared with Composition C4 and Semtex 10.

15:50 – 16:10 Coffee break

16:10 Sara Cerri, Manfred A. Bohn
Fraunhofer Institut fuer Chemische Technologie, ICT, Pfinztal, Germany
Ageing and performance behaviour of rocket propellant formulations with ADN as oxidizer.

16:30 Vinca Prana, Guillaume Fayet, Patricia Rotureau, Carlo Adamo
INERIS (Institut National de l'Environnement Industriel et des Risques), Verneuil-en-Halatte, France

Prediction of impact sensitivity of nitro energetic compounds using QSPR approaches.

Lecture program of the 14th NTREM – Thursday, April 14, 2011

3. Session

Chairman: Dr. Ruth Doherty ,
Dept. of Homeland Security, Washington DC, USA

08:15 Meeting of all speakers of the third Session with Chairman of this Session.

08:40 David Chavez (invited lecturer)
Los Alamos National Laboratory, Los Alamos, NM, USA
Recent efforts in tetrazine chemistry.

09:10 Jian-Guo Zhang, Lei Wei, Tong-Lai Zhang, Yuan-Jie Shu
Beijing Institute of Technology, Beijing, China
Synthesis, Characterization and Properties of 5-Nitraminotetrazole High Nitrogen Salts.

09:30 Robert Hudson, Philip Gill
Cranfield University, Shrivenham, United Kingdom
Multi-person assessment RDX crystals morphology using the RS-RDX round robin method.

09:50 Steven Hunter, Colin R. Pulham, Carole A. Morrison, Peter J. Gould
University of Edinburgh, Edinburgh, United Kingdom
First-principles hydrostatic compression study of Phase I of AP and alpha-, epsilon- and gamma- polymorphs of RDX.

11:10 Sergey I. Gerasimov, Petr N. Kalmykov, Andrey V. Len', Michail A. Ilyushin
Russian Federal Nuclear Centre, Sarov, Russia
Excitation of PETN-charges with safe light-sensitive pyrotecnical compositions by incoherent light pulse sources.

10:30 – 10:50 Coffee break

10:50 Demitrios Stamatis, Edward L. Dreizin
New Jersey Institute of Technology, Newark, New Jersey, NJIT
Thermal initiation of consolidated reactive nanocomposite powders.

11:10 Jim Tucker, Philip Gill, John Hand
Cranfield University, Shrivenham, United Kingdom
Assessment of factors effecting stabiliser extraction from nitrocellulose based propellants.

11:30 Tuuli Grohn, David Williamson, Gordon Morgan
University of Cambridge, Cambridge, United Kingdom
Energetic inks for screen printing.
11:50 Ruth Tunnell, Paul Bunyan, Dave Tod
QinetiQ, Sevenoaks, United Kingdom
The use of accelerating rate Calorimetry to understand the ageing behaviour of complex hybrid propellants.
12:10 – 14:0 Lunch break

4. Session – Poster program – see on Web sites [2]

Chairman: Prof.Stanislaw Cudziło
Military University of Technology, Warsaw

Lecture program of the 14th NTREM – Friday, April 15, 2011

5. Session

Chairman: Dr. Adam Cumming
DSTL Sevenoaks, U.K.

08:15 Meeting of all speakers of the fifth Session with Chairman of this Session.
08:40 Prof. Tatyana Pivina, Dr. David Lempert,
Prof. Alexandr Smirnov, Dr. Dmitriy Khakimov
Russian Academy of Science, Chernogolovka, Russia
Estimation of basic characteristics for some energetic polynitrogen compounds. (invited lecture)
09:10 Valery P. Sinditskii, Manh C. Vu, Ann V. Burzhava,
Alexey B. Sheremetev, Ludmila V. Batog
Mendelejev University of Chemical Technology, Moscow, Russia
Decomposition and combustion of 4,4’-bis[4-aminofurazanyl-3-azoxy]-3,3’-azofurazan and its macrocyclic analog.
09:30 Manfred A. Bohn
Fraunhofer Institut fuer Chemische Technologie, ICT, Pfinztal, Germany
Generic formulation of performance assessment quantities for stability compatibility and ageing of energetic materials.
09:50 Katarzyna Cieślak
Warsaw University of Technology, Warsaw, Poland
Nitrocellulose’s swelling process for liquid nitrate esters.

10:10 Olga Kovalchukova, Svyatoslav Shevelev, Alexander Shakhnes, Konstantin Kobrakov, Andrew Alafinov, Oleg Volyansky, Paul Strashnov
Peoples' Friendship University of Russia, Moscow, Russia
Some physico-chemical properties of products of chemical transformation of 2,4,6-trinitrotoluene.

10:30 – 10:50 Coffee break

10:50 Jose B. Ribeiro, Cristóvão Silva, Ricardo Mendes
University of Coimbra, Coimbra, Portugal
Estimation of the Lee-Tarver reactive flow model parameters for an ammonium nitrate based emulsion explosive.

11:10 Tereza Hudcova, Martin Halecky, Evguenii Kozliak, Jan Paca
Institute of Chemical Technology, Department of Fermentation Chemistry and Bioengineering, Technicka 5, 166 28, Prague, Czech Republic
Continuous aerobic degradation of dinitrotoluenes in packed bed reactors.

11:30 – 12:00 CLOSING REMARKS including AWARDING OF PRIZES

International Scientific Committee of the seminar, chaired by Dr. Adam Cumming (DSTL Fort Halstead) noted that the seminar was again a high level and was very well prepared. It recommended continuing the tradition in these meetings, to limit the scope of contributions to the Proceedings on max 15 pages and a term of the next 15th Seminar ("Disposal and Green Energetic Materials") has established on April 18th – 20th, 2012 again in the University Hall at University of Pardubice. The committee has also undertaken an evaluation of the presentation of young active participants with the following results:

Lecture program:

1. price: Ahmed Elbeih, Jiří Pachmáň, Svatopluk Zeman, Waldemar A. Trzciński, Zbyněk Akštein (*Univ. Pardubice + Wojskowa Akad. Techn., Warszawa + Explosia Pardubice*): Advanced Plastic Explosives Based on bicyclo-HMX Compared with Composition C4 and Semtex 10.
2. price: Sara Ceri, Manfred A. Bohn (*Fraunhofer Inst. für Chemische Technologie, Pfinztal*): Ageing Behaviour of Rocket Propellants Formulations with ADN as Oxidizer.

3. price: David Millar, David Allan, Laura Cocker, Adam Cumming, Craig Henderson, Alexandra Mackay, Helen Maynard-Casely, Anna Muszkiewitz, Iain Oswald, Colin R. Pulman (*University of Edingburg*): Co-crystallisation of Energetic Materials: A Step Towards Tailored Munitions?

Poster program:

1. price: Thomas M. Klapötke, David G. Piercey (*Ludwig-Maxmilian Univ. of Munich*): A Highly Energetic Compounds Containing a Ten-Nitrogen Chain.
2. price: Ahmed Elbeih, Adéla Husárová, Svatopluk Zeman (*Univ. Pardubice*): Low Sensitive HNIW.
3. price: Dimitriy Khakimov, Marina Molchanova, Nina Makhova, Tatina Pivina, Igor Ovchinnikov, Aleksandr Kulikov (*Zelinskii Inst. of Organic Chemistry, RAS, Moscow*): The Puzzle of Diaminofuroxan.

Chapter 2

Central European Research Activities and Collaboration

Adam S. Cumming

The changing face of Europe exposed Western scientists to the work undertaken in Eastern Europe and to the research groups active in the study of Energetics science. In the last two decades there has been an increasing level of activity based on more than just exposure and awareness. It is also based on a mutual appreciation of the scientific quality of the work in both parts of Europe and elsewhere. Assumptions have been challenged on both sides with one result being the development of links between groups whose contacts were once limited.

2.1 Introduction

As contact resumed there have been places where Western scientists have encountered colleagues and discovered the level and quality of research being undertaken. Scientists in the former Warsaw Pact nations found themselves able to talk and openly discuss work for the first time in decades with scientists elsewhere.

The differences in approach made these discussions difficult at first, while later the differences in funding both restricted and accelerated activity: restricted activity because there was no money to support work in those countries, and accelerated activity because Western institutions were seen as sources of financial support.

It was discovered that while the work was comparable and of high quality, the lack of contact on both sides had led to differences in approach. While this sometimes caused disputes, many on both sides of the former divide considered it complementary. Parallel development gave different perspectives on common problems. The restricted resources also encouraged novel approaches and innovative thinking.

Various multinational institutions sought to include the Central European nations in programmes. Central European nations became involved in NATO, first as Partners for Peace and then as full members, giving access to standards and to the research organisations such as the Science Programme and the Research Technology Organisation. They also became involved in the European activities formerly under the Western European Armaments Group (WEAG), and now the European Defence Agency. In each of these there were research activities on Energetic Materials, in which the various nations participated

There are several centres of expertise active in areas from synthesis to disposal, and most of these are linked with others in Western Europe or elsewhere. It should be noted that this discussion does not cover work in the former West Germany, which has always engaged fully in research linked with the United States and others.

Conferences have played a major part in building the new network. Two that have played the largest part are the annual ICT Conference in Karlsruhe, and the New Trends in Research on Energetic Materials (NTREM) held annually at the University of Pardubice and founded by Professor Svatopluk Zeman. The author of this chapter has served as the NTREM Scientific Committee chair since 2003.

NTREM has had a major effect by bringing together young scientists from Central and Eastern Europe and providing one of the most stimulating environments for research anywhere. NTREM will be discussed in greater detail elsewhere in this volume.

2.1.1 Centres of Research – Germany

It is appropriate to briefly consider the German Institutes and activities here for the sake of completeness. They will be covered in detail elsewhere in this book.

Within Germany the major centres for energetics research are still the Frauenhofer Institute fur Chemische Technology and also to a lesser extent the Frauenhofer Ernst Mach Institute, which deals with terminal effects. Assessment is covered by BWB, the Procurement Department in the German Ministry of Defence at Meppen. The Federal Institute handles civil aspects such as fireworks for Materials Research and Testing (BAM) in Berlin.

The ICT has built links across Europe, focusing initially on the Czech Republic, and later more broadly across Europe. Dr. Hiltmar Schubert used the NATO Science Programme to build links to the Czech Republic, Romania, Poland, Russia and elsewhere.

The synthesis of new organic explosives molecules at the Ludwig Maximilian University in Munich under Professor Thomas Klapötke will also be discussed elsewhere. It is worth observing that this group has developed active links with groups in Croatia and the Czech Republic.

2.1.2 Centres of Research – Central Europe

Most of the research institutes in Central and Eastern Europe were government owned and often linked to the Ministry of Industry, which supplied MOD with the needed resources. Often there was a military university where officers were trained in the same way as the United Kingdom does at Shrivenham. The military university most active in research is Poland's Military University of Technology. Cudziło and Trzciński have done significant work on the performance of non-ideal explosives together with other topics (12-15). The Poles have been active in supporting the development of the *Central European Journal of Energetic Materials*. This is also described elsewhere. The Poles were a major initial supporter of NTREM.

Poland also manufactures explosives ingredients and compositions for munitions.

The Czech Republic is the major centre for research activities, with the University of Pardubice leading much of the effort, though supported by Explosia through its Research Institute, VUPCH. They have become very active internationally.

Explosia has carried out work on the novel synthesis of both existing and new molecules, often in partnership with others. The University has looked at explosive characterisation and properties including detonics.

Other groups active to some extent are the Military University at Brno, though they use Pardubice extensively. The former government testing centre in Slavicin, MIWAT was sold to a private company and is now VOP-026 Sternberk and has limited activities including demilitarisation. There are also some disposal research capabilities in Prague at the Institute of Chemical Technology under Jan Paca.

There is also at Synthesia a manufacturing capability.

The Brodarski Institut in Croatia, under Dr. Muhamed Sućeska, has developed a significant capability for the thermal analysis of energetics and its own detonation code, EXPLO5. Links driven by Dr. Sućeska have seen activities develop on the study of munition life in Sarajevo (of importance given the recent history of Bosnia and Hercegovina) with posters exhibited at NTREM.

2.1.3 Centres of Research – Eastern Europe

Both Romania and Bulgaria have research centres. These are linked to the munition industry, which is still closely linked to government.

Within Romania most work is in institutes run by the Ministry of National Defence. The Military Technical Academy is the major source of energetics research, while the MND research agency METRA has applied capabilities. METRA has ranges and laboratories and also operates the Chemical Defence Centre that works with the MTA in certain areas, such as environmental studies. The government owned industry RomArm manufactures explosives and has an R&D arm, RomTechnica.

Bulgaria has a munitions manufacturing capability. However, its research capability is less significant. Both Bulgaria and Romania produced ‘thermobaric’ weapon systems in the last decade.

The Baltic States have limited level activity, with only Lithuania active in areas related to environmental pollution.

2.2 Active Collaboration Areas and Mechanisms

It is useful to consider the role that conferences have played in the development of links and how they have led to the development of both networks and in depth collaboration. In many cases these conference contacts have been the necessary precursors to formal intergovernmental arrangements. Without the awareness and networks that conferences produce it would be difficult to develop formal or in depth processes.

Many countries hold some form of national conference: the UK, France, Romania, and Poland, among others. However, two stand out as the exemplars of the kind described above.

The first and longest running is the ICT conference, held annually in Karlsruhe and run by the Frauenhofer ICT. To date there have been 42 of these. The ICT attracts scientists from across the world, providing a means of discussing detailed and developing work in the Energetic Systems area. It includes scientists from Central Europe. Scientists at ICT, including Dr. Volk, have encouraged such international participation with financial aid. Among those receiving financial aid are Russian participants. Unfortunately, the limited financial aid now available for conference participation has curtailed attendance from Central and Eastern Europe.

However, without ICT many initiatives and collaborations would either not have happened or would have taken much longer to develop. ICT led activities in seeking partners that supported involvement in collaboration activities under NATO. For the author it was the ICT conference that provided introductions to scientists in the Czech Republic and elsewhere.

Other involvements arose from a NATO Science Programme Workshop on Demilitarisation and the Environment, held in Porto, but proposed and supported by Dr. H. Schubert of ICT (1). This workshop led to closer links with Romania.

The second Conference/Seminar activity not merely for Central Europe is New Trends in Research of Energetic Materials, or NTREM. This meeting has now taken place 14 times.

During meetings in Pardubice it had become normal to have a discussion session with Czech scientists on technology developments. At the same time the author was invited to carry out an audit of research activities in the Explosia Institute. This led to contact with the University and with NTREM. The author first took part in the third NTREM Seminar in 2000. Most of the papers were from the Czech Republic or Poland. Very few other nations attended.

The primary importance of the Seminar is in its concentration on recently graduated and postgraduate scientists. NTREM provided a venue where they could present their work, discuss it, and meet others, all in a semi-formal manner and in the presence of invited senior scientists. This is still the format. Its continuation is one of the tasks of the scientific committee. The author joined the scientific committee in 2001 and has chaired it since 2003. One feature of the Seminar is that three papers and three posters are honoured by the scientific committee with the award of certificates and prizes of local gingerbread.

The attendance is normally around 100 to 150 and is now drawn from not just Europe, including Russia, but also the US, China, India and the Middle East. (On many occasions visa problems limit participation.) This range and level of participation is, however, a measure of the steady growth in the importance of this Seminar worldwide.

NTREM has increasingly provided a venue for state of the art discussion and friendly feedback on techniques for presentation. The University of Pardubice and the Department led by Professor Zeman are to be congratulated, first for deciding to hold the Seminar, and second for maintaining it with such high and increasing quality for so many years!

While several research groups use NTREM as a venue for training their post graduate students – for example Germany, UK, Croatia and Poland – it is important that it is not dominated by any one group and that it remains focused on the newer researchers. It is also important that it continues to offer space for the single student from a small group to network and learn. The scientific committee and the organizing committee continue to promote this and to attempt to balance the content, which includes selecting a theme for each year’s conference.

One further important characteristic of NTREM is the quality of the presenters and their openness and enthusiasm. This is particularly true of those from smaller groups. The quality of the science and more particularly of the presentation has steadily increased. There has always been a positive attitude among the participants, and it is to be hoped that this will continue and spread.

The Proceedings for past Seminars are available from the University of Pardubice as noted on the NTREM website, www.ntrem.com.

Other international conferences, such as Europyro and NDIA Insensitive Munitions and Energetic Materials, do take place in Europe but normally are in the West. They rarely involve researchers from Central and Eastern Europe, which is largely due to lack of resources to pay the participation fees. These meetings would benefit from wider participation and discussion, though it is hard to see how this can be obtained so long as cost remains a barrier. The United States Department of Defense offices in London support certain activities including NTREM, but there is a limit to what they can do. Their activity must be primarily for the benefit of the United States forces.

There are other conferences within Eastern Europe that while international in scope are mostly limited in their success.

These are generally organised within the Ministry of National Defence, Armaments Department, and mostly led by either the Military Technical Academy or the Military Equipment and Technologies Research Agency. In addition – and in parallel with the Romanian biannual Military Equipment exhibition, EXPOMIL – a conference, ICOMIL was held until recently, to discuss aspects of defence research including energetics technology. These all had limited international visibility. However, all had sessions covering energetic materials and their applications.

Participation did serve to make others aware of the activities and strengths of the groups in Romania, in the same way that NTREM gave access to Czech, Polish and Croatian scientists and has encouraged involvement in European Defence Agency (EDA) and NATO studies.

Thus, collaboration has been increasing since contact was renewed. There had always been some joint activity, but real collaboration began only once it was possible to discuss details within a joint programme.

ICT in Germany was in the vanguard of these efforts making strong links with the Czech Republic, Russia, and elsewhere. They have produced several papers on life studies of munitions and performance investigation (2).

European governmental activities followed from discussions at NTREM and elsewhere, with involvement of the Czech Republic and Romania in the Western European Armament Group Priority Area (CEPA 14) on Energetic Materials and their applications. Indeed CEPA 14 met in Pardubice just prior to NTREM 2003 (3), and Czech involvement was significant in a nitrocompound synthesis programme under that umbrella (4). This forum has now evolved into a Research and

Technology Area within the European Defence Agency (5), covering Energetics, Missiles and Munitions. The Czech Republic is currently involved in a programme examining the effect of aging on Insensitive Munitions while Romania is active in a programme on Environmentally Responsible Munitions.

Access to NATO through the Partners for Peace initiative allowed structured links with workshops and joint programmes being developed (6). Initially some of these were Collaborative Research Grants, such as a study of contamination on a former test range in the Czech Republic, carried out by the Czechs with Germany and the UK (7). This study involved the author.

Fuller participation in the NATO RTO allowed greater participation, and the use of the support programme to cover the costs of Panel attendance assisted in ensuring dialogue. All energetics and munitions studies fall within AVT (Applied Vehicle Technology), though most of the relevant activities have focused on the environment and life management.

The dialogue has included workshops and meetings throughout Eastern Europe, producing a far greater appreciation of the technical abilities of the laboratories.

To date there has been a major workshop in Sofia under NATO on Demilitarisation. It was part of a joint study that has involved the Czech Republic, Bulgaria and Romania, and the Baltic States in a limited way. This has been reported in an open NATO report (8).

Poland has played a major part in a related NATO Industrial Advisory Group (NIAG) study, and the links forged through these activities have led to other discussions and activities, though these results have not yet been reported.

Other work has developed through such contacts, including work on explosives undertaken in Poland in support of UK interests on the influence of aluminum on blast effects (9, 10).

An overview of collaboration, specifically Defence Energetics Systems collaboration, has been published in Propellants Explosives and Pyrotechnics (11). Unfortunately much of the detailed work is not yet published, but some aspects are covered in the NTREM Proceedings and the ICT Proceedings.

Three journals publish papers from Central and Eastern Europe: *Propellant, Explosives and Pyrotechnics*, published by Wiley; the *Journal of Energetic Materials*, published by Taylor & Francis; and the *Central European Journal of Energetic Materials*, discussed elsewhere, whose existence is largely due to contacts and discussion around NTREM.

Reference should also be made to websites such as www.ntrem.com; www.wtc.wat.edu.pl for the Military Technical Unversity in Poland; www.hrbi.hr for the Brodarski Institute in Croatia; www.acttm.ro for METRA and www.mta.ro for the Military Technical Academy, both in Romania.

No discussion can be complete without consideration of existing academic links. Many are promoted through ERASMUS, “the EU's flagship education and training programme enabling 200,000 students to study and work abroad each year. In addition, it funds co-operation between higher education institutions across Europe. The programme not only supports students, but also professors and business staff who want to teach abroad, as well as helping university staff to receive training.” The website from which this description is taken is http://ec.europa.eu/education/lifelong-learning-programme/doc80_en.htm.

The countries involved are: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Iceland, Hungary, Ireland, Italy, Latvia, Liechtenstein, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovak Republic, Slovenia, Spain, Sweden and Turkey. From the academic year 2011/12 students will also be eligible to work or study in Switzerland and Croatia under the Erasmus programme.

One example of this is the formal link between the Romanian MTA and the Institute of Shock Physics in Imperial College, London. These ERASMUS activities form a counterpart to and complement the MOD links. They rely on Symposia such as NTREM to build the necessary networks in order to make it viable. NTREM with its emphasis on students is ideally placed to develop such networks within Europe.

In conclusion, over the last twenty years there has been a growing level of joint work across Europe, characterised by discussions, papers, conferences and mutual respect. The role of NTREM cannot be overstated as a major catalyst in this growth. NTREM and other activities are supporting future planning, essential with straitened circumstances. Wealthier nations can learn how to do more with less by learning from the Central Europeans.

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Chapter 3

Central European Journal of Energetic Materials – the Newest in Europe

Andrzej Maranda and Wanda Karaś

Central European Journal of Energetic Materials − a forum for the exchange of theoretical and technological knowledge in the field of energetic materials – is aimed at scientists interested in research papers in the area of propellants, explosives and pyrotechnics.

The main target of the journal is the latest results of research on various problems of energetic materials. Topics cover: ignition, combustion and detonation phenomenon, formulation, synthesis and processing, analysis and thermal decomposition, toxicological, environmental and safety aspects of energetic materials production, application, utilization and demilitarization, molecular orbital calculations, detonation properties and ballistics, biotechnology, and hazards testing.

Central European Journal of Energetic Materials is indexed by: BazTech; Chemical Abstracts; Science Citation Index Expanded; Chemistry Citation Index; Materials Science Citation Index; Current Contents/Engineering, Computing and Technology; Scopus and Compendex. ISSN 1733-7178. CASSI abbreviation Cent. Eur. J. Energ. Mater. (popularly CEJEM). URL: http://www.wydawnictwa.ipo.waw.pl.

3.1 The Genesis of *Central European Journal of Energetic Materials*

Studies on synthesis, characteristics and use of explosives have been carried out in Poland since the beginning of the 20th century. The most important research was conducted by professors Tadeusz Urbański, Wacław Cybulski, Juliusz Hackel and Dionizy Smoleński. The first two of them especially received international recognition. A monograph, "Chemistry and Technology of Explosives," by T. Urbański, published in several volumes by Pergamon Press, is still considered as the bible of explosives. Urbański and his contemporaries published their articles about various problems of explosives in the following periodicals: *Zeitschrift für das gesamte Schiess- und Sprengstoffwesen*, *Wiadomości Techniczne Uzbrojenia* (Technical Armament News), *Roczniki Chemii* (Annals of Chemistry) or *Przemysł Chemiczny* (Chemical Industry).

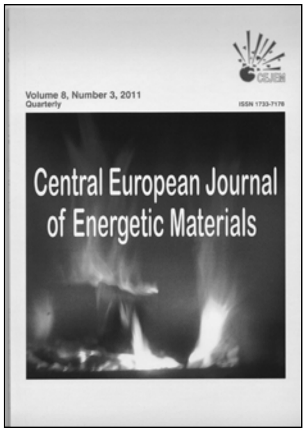

Figure 3.1: ***CEJEM*** **cover.**

After the Second World War, research concerning industrial and military explosives was conducted in Poland on a large scale. The leading research centres were: Military University of Technology in Warsaw, Institute of Industrial Organic Chemistry in Warsaw, Warsaw University of Technology, Military Technical Institute of Armament in Zielonka, and Experimental Mine "Barbara" in Mikołów. Research was also conducted at the Academy of Mining and Smelting Engineering in Cracow, at the Silesian University of Technology in Gliwice, and at the Wrocław University of Technology. Research papers were published mainly in Polish periodicals of an interdisciplinary character and edited in Polish, such as: *Biuletyn Wojskowej Akademii Technicznej* (Bulletin of Military Technical Academy), *Przemysł Chemiczny* (Chemical Industry), *Problemy Techniki Uzbrojenia i Radiolokacji* (Problems of Armament Technology and Radiolocation), *Wiadomości Chemiczne* (Chemical

News), *Przegląd Górniczy* (Mining Review), and *Górnictwo Odkrywkowe* (Opencast Mining), as well as in English, for example: *Journal of Technical Physics* and *Archivum Combustionis*. A small part of research was presented in periodicals edited abroad, for example in *Propellants, Explosives, Pyrotechnics*, *Journal of Energetic Materials*, *Energetic Materials*, *Journal of Hazardous Materials*, *Combustion and Flame* or *Fizika Goreniya i vzryva*. It should be stressed that until 2004 the journal *Propellants, Explosives, Pyrotechnics* was the only specialist periodical concerning energetic materials published in Central Europe. That was the reason why the time between the submission of an article and its publication was relatively long.

Figure 3.2: Founders of a new journal *CEJEM* (from the left side): Prof. Andrzej Maranda, Wanda Karaś – Managing Editor – and Prof. Svatopluk Zeman.

At the turn of the 21st century, interesting initiatives were set up in our region − the seminar "New Trends in Research of Energetic Materials," organized by Prof. Svatopluk Zeman since 1998 at Pardubice (Czech Republic), and the international conference "Explosives: Research − Application – Safety," taking place since 2004 in Ustroń (Poland) and coordinated by Prof. Andrzej Maranda. During these events, researchers presented many papers of high scientific level that were considered worth publishing as soon as possible. That was the reason for establishing a new specialist periodical that could transmit the results of research in the field of energetic materials, for public benefit and market advantage. After consultations with an international committee, the new journal, *Central European Journal of Energetic Materials*, was founded.

It was decided that the new periodical would be edited in Poland, as the number of Polish researchers working on energetic materials was relatively high and the scope of research was broad and diverse. Presently, Prof. Andrzej Maranda is the chairman and Prof. Svatopluk Zeman is the vice chairman of *CEJEM*.

Central European Journal of Energetic Materials has been included recently in the Scopus database, with the following reviewer comment: **“**This is a fine journal that consistently publishes articles of high academic quality, and which shows evidence for tight editorial control”**.**

3.2 Editorial Board

The members of the Editorial Board, almost unchanged since the foundation of the periodical, come from 11 countries, in Europe, Asia and America. The Board is composed of 9 members from Poland, 4 from the Czech Republic as well as from Russia, 3 from the USA, and also 3 from Germany. Belgium, Croatia, Singapore, Sweden and the United Kingdom have one representative each.

The full list of Editorial Board members with their affiliation in alphabetical order is as follows:

Dr. Ronald W. Armstrong, Professor Emeritus of Mechanical Engineering at the University of Maryland, USA; **Prof. Alexander Astachov**, Siberian State Technological University, Krasnoyarsk, Russia; **Dr. Anthony J. Bellamy**, Professor Emeritus of Defence Academy of the United Kingdom at the Cranfield University; **Prof. Jaroslav Buchar**, Mendel University of Agriculture & Foresty, Brno, Czech Republic; **Prof. Stanisław Cudziło**, Military University of Technology, Warsaw, Poland; **Dr. Bogdan Florczak**, Institute of Industrial Organic Chemistry, Warsaw, Poland; **Prof. Zdeněk Friedl**, University of Technology, Brno, Czech Republic; **Prof. Ang How-Ghee**, Nanyang Technological University, Singapore; **Prof. Michael A. Ilyushin**, Saint-Petersburg State Institute of Technology, Russia; **Prof. Thomas M. Klapötke**, Department of Chemistry at Ludwig-Maximilians-Universität, München, Germany; **Prof. Georgii Kozak**, Mendeleev University of Chemical Technology, Moscow, Russia; **Prof. Andrzej Książczak**, Warsaw University of Technology, Poland; **Prof. Nikolaj Latypov**, Swedish Defence Agency (FOI), Tumba; **Prof. Michel Lefebvre**, Royal Military Academy, Brussels, Belgium;

Dr. Carl-Otto Leiber, Rheinbach, Germany; **Prof. František Ludvík**, Military Academy, Brno, Czech Republic; **Prof. Andrzej Maranda**, Military University of Technology, Warsaw, Poland; **Dr. Andrzej Papliński**, Military University of Technology, Warsaw, Poland; **Prof. Peter Politzer**, University of New Orleans, USA; **Prof. Yuanjie Shu**, Institute of Chemical Materials, CAEP, Sichuan, China; **Prof. Valerii P. Sinditskii**, Mendeleev University of Chemical Technology, Moscow, Russia; **Prof. Wincenty Skupiński**, Institute of Industrial Chemistry, Warsaw, Poland; **Dr. Muhamed Sućeska**, Brodarski Instytut, Zagreb, Croatia; **Prof. Ulrich Teipel**, University of Applied Sciences, Nürnberg and Fraunhofer ICT, Germany; **Prof. Waldemar Trzciński**, Military University of Technology, Warsaw, Poland; **Prof. Leszek Wachowski**, Adam Mickiewicz University, Poznań, Poland; **Dr. R. H. Woodward Waesche**, SAIC, Gaineswille, USA; **Dr. Waldemar Witkowski**, Institute of Industrial Organic Chemistry, Warsaw, Poland, and **Prof. Svatopluk Zeman**, University of Pardubice, Czech Republic.

Dr. Fred Volk, Fraunhofer Institut für chemische Technologie, Pfinztal, Germany, regrettably died in 2005.

3.3 Statistics

Until September 2011, in total 160 papers [1-160] were published in *Central European Journal of Energetic Materials.* Figure 3.3 illustrates the share of publications by country.

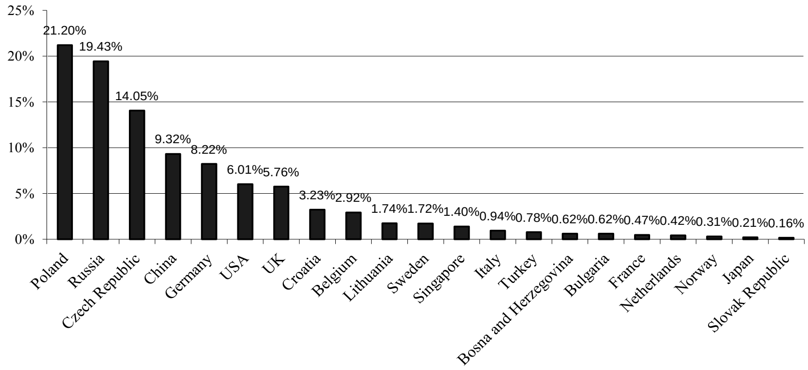

Figure 3.3: Share of world researchers in papers published in *Cent. Eur. J. Energ. Mater.* by country.

This figure shows that in total, almost 55% of publications have come from Poland, Russia, and the Czech Republic. China, Germany, the UK, and USA share between 5% and 10% each, while Croatia and Belgium have about a 3% share. The share of other countries does not exceed 2%.

In Poland, the scientific centers that regularly submit articles to *CEJEM* are: Department of Chemistry and New Technologies and Faculty of Mechatronics at Military University of Technology in Warsaw; Institute of Industrial Organic Chemistry in Warsaw; institutes and faculties at Warsaw University of Technology: Faculty of Chemistry, Division of High Energetic Materials, Institute of Heat Engineering, Institute of Machines Design Fundamentals, Institute of Vehicles; Faculty of Chemistry at Adam Mickiewicz University in Poznań, Central Laboratory of Batteries and Cells, the Poznan Branch of Institute of Non-Ferrous Metals; Industrial Chemistry Research Institute in Warsaw; Institute of Molecular Physics, the Poznan Branch Polish Academy of Sciences, and Institute of Fundamental Technological Research, Polish Academy of Sciences in Warsaw.

The following Russian centers have a considerable share in publications in *CEJEM*: Mendeleev University of Chemical Technology in Moscow; Institute of Problems of Chemical Physics of the Russian Academy of Sciences in Chernogolovka; Zelinsky Institute of Organic Chemistry, the Russian Academy of Sciences in Moscow, and Saint-Petersburg State Institute of Technology.

In the Czech Republic, the Institute of Energetic Materials at the University of Pardubice, as well as Faculty of Chemistry at Brno University of Technology, are important sources of research papers.

As far as China research centers are concerned, most papers were received from: Institute of Chemical Materials, CAEP, Mianyang, Sichuan**;** School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyuan; Department of Chemistry, Nanjing University of Science and Technology, Nanjing.

From Germany, Department of Chemistry and Biochemistry at Ludwig-Maximilians Universität München deserves a particular mention for its generous contribution to *CEJEM*.

It is impossible in such a short note to list all the important research centers that contribute valuable publications to *CEJEM*, but still there should be mentioned: Brodarski Institut – Marine Research & Special Technologies (Croatia); Department of Chemistry, University of New Orleans (USA); Laboratory for Energetic Materials at Royal Military Academy (Belgium); Cranfield University, Defence Academy of the United Kingdom; Department of Energetic Materials, FOI, Swedish Defence Research Agency; and Institute of Biochemistry (Lithuania).

3.4 Subject Area of *CEJEM*

CEJEM is a scientific periodical devoted to issues connected with energetic materials, especially with explosives. Its broad subject area covers mainly: synthesis of initiating and brisant explosives, including materials with reduced sensitivity to mechanical stimuli; explosives based on ammonium nitrate, solid rocket fuels, and pyrotechnic products; sensitivity of explosives to external stimuli; initiating detonation process and modelling high energetic phenomena; estimation of detonation and thermodynamic parameters.

The synthesis of high energetic materials is described in, among others, the papers [14, 27, 49, 53, 66, 70, 75, 79, 90, 131, 140]. S. Ek et al. [27] presented the results of the estimation of numerical thermodynamic and detonation parameters of six energetic plasticizers. They described also methods of synthesis of two plasticizers (2,2-dinitro-1,3-bis(2-azidoacetoxy)propane and 2,2-dinitro-1,3-bis (formyloxy) propane and measured glass transition temperature.

In the paper [49], M.A. Ilyushin described the way of obtaining two energetic perchlorate complexes, in which 1,5-pentamethylenetetrazole (PMT): $Cu(PMT)_4(ClO_4)_3$ and $Co(NH_3)_5(PMT)(ClO_4)_3$ were ligands. Derivatographic analysis proved that the decomposition of complexes took place in several stages. After testing detonation parameters, it was established that the complex can be used to initiate high explosives (HE). In the paper [79], syntheses of derivatives of chloric acid (VII) were also described, even though they were of different type. T.M. Klapötke and J. Stierstorfer obtained chlorates (VII) aminoguanidinium, triaminoguanidinium and azidoformamidimium ($AFClO_4$) and determined their chosen physico-chemical and explosive properties. They noticed, among others things, that salts they had obtained, especially $AFClO_4$, were very sensitive to impact and friction.

N.V. Latypov et al. [53] obtained 1,2-dinitroguanidyne (DNG) and its salts, such as ammonium, lithium, sodium, potassium and hydrazinum, by careful neutralization of its solution in an alcohol with an appropriate base. Referring to the results of their research, they established that DNG is a rather sensitive compound, and its impact and friction sensitivity are very close to those of PETN.

A number of papers concerned IHE (Insensitive High Explosives). A.J. Bellamy and P. Golding [66] analyzed three ways of synthesis of 2,6-diamino-3,5-dinitropyrazine 1-oxide (LLM-105). Two methods of obtaining the starting material 2,6-diaminopyrazine 1-oxide were investigated. According to the authors, the way that starts from the expensive 2,6-dichloropyrazine, *via* 2,6-diaminopyrazine, appears to be the least problematic, although it may be possible to improve the iminodiacetonitrile method. In the paper [84], A.J. Bellamy and P. Golding presented also the results of further research on synthesis of intermediate compounds necessary to obtain LLM-105. During syntheses, they obtained a series of 2,6-dialkoxy-3,5-dinitropyrazines (R = Me, Et, Pr), which were next subject to amination and gave 2,6-diamino-3,5-dinitropyrazine. In the paper [14], vicarious nucleophilic substation reaction was used to prepare other IHE: 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), in the hope of finding a more effective method of its manufacture, and not yet described amine derivates of 1,6-bis(picryloamino)-3,5-dinitropirydyne (PYX).

4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.$0^{5,9}0^{3,11}$]dodecane (TEX) was prepared by reaction of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine with glyoxal in nitric acid [131]. The influences of the acidity of reaction mixture and of the ratios of starting materials on the yield of TEX were examined. The team of N. Fisher, T.M. Klapötke, S. Scheutzow and J. Stierstorfer obtained, as a result of preparatory works, hydrazinum 5-aminotetrazolate – insensitive high explosive containing 83.72% nitrogen, the detonation velocity of which, estimated by means of numerical methods, is 9516 m/s, given density 1.547 g/cm^3 [90].

Papers on synthesis issues are complemented by papers concerned with obtaining the desirable shape of crystals [3, 5, 17]. The paper [5] presents the results of research on recrystallization of nitroguanidine and 3-nitro-1,2,4-triazol-5-one, in the aspect of their application in Plastic Bonded Explosives. U. Teipel [17] presented the technology of recrystallization of FOX-7 grains, HMX and ammonium dinitramide, thanks to which he obtained modified crystal shapes.

Other papers by Chinese researchers present the results of investigation on using caprolactam-based Brønsted acid ionic liquids as catalyst in nitration of toluene and cholorobenzene [70]. They consider also the use of solid catalysts (SO_4^{2-}/TiO_2, SO_4^{2-}/TiO_2-ZrO_2, SO_4^{2-}/WO_3-ZrO_2, SO_4^{2-}/MoO_3-ZrO_2) in regioselective nitration of chlorobenzene [75]. J. Šarlauskas examined other solid state catalysts (MoO_3/SiO_2 and $H_3PO_4/MoO_3/SiO_2$) used in the synthesis of dinitrotoluene (DNT) [140]. Higher yields of DNT were obtained in a shorter time and with a lower excess of nitric acid using $H_3PO_4/MoO_3/SiO_2$. Acidic ionic liquids were also used as catalysts to obtain octogen produced by direct nitrolysis of DPT [149].

Properties of explosives based on ammonium nitrate are examined in many papers [29, 78, 102, 103, 124, 128, 142, 151, 159]. Zhiwen Ye et al. described the method of modifying ammonium nitrate(V) (AN) grains, aimed at obtaining a form that would have a bigger detonation capacity [29]. Grains obtained by evaporative recrystallization had higher specific surface area, detonation velocity, and brisance. In the paper [102], N. Golovina et al. described introducing small additives of organic compounds into AN, mainly by fusion at a temperature close to AN melting point. Using X-ray diffraction, X-ray phase analysis, DTA analysis, UV and IR investigation, they found a new ammonium nitrate phase state, which was stable in temperature range between –50°C and +100 °C.

Several papers discuss the properties of mixtures of ammonium nitrate (V) and powdered aluminum (Al) [78, 103, 128, 142]. In the paper [78], J. Paszula et al. established experimentally and theoretically detonation velocity, heat of explosion, quasi-static pressure and blast wave parameters of the ammonals containing 10, 25 or 40% flaked or powdered aluminum. B. Zygmunt [103] presented the results of measurement of the mass velocity of detonation waves of ammonales and slurry blasting explosives sensitized with flaked aluminum. In the paper [143], B. Czajka et al. established the detonability of chemically pure and water-resistant AN, as well as the detonability of mixtures on its base. Wood flour, aluminum powder, milled foamed polyurethane, trinitrotoluene and paraffin were used as additives. A. Maranda, K. Lipińska and M. Lipiński [128] carried out a research on the influence of adding three propellants, with different content of nitroglicerine, on detonation velocity and parameters of blast wave ammonals. The content of propellants in ammonals (they contained 3, 6 i 10% of aluminum powder having different degree of milling) was between 0-40%. D. Buczkowski and B. Zygmunt [151] examined thermodynamic and detonation parameters of compositions: AN-dolomite, AN-dolomite-aluminium and AN-dolomite-diesel oil. The content of dolomite in explosive compositions came to 50%. They estimated, using numerical methods, the heat of explosion and the volume of Gasek. They determined also experimentally detonation velocity and Guerney's energy, using cylinder tests.

O.B. Litovka et al. [88] determined physicochemical properties of mixtures of AN and urea (UR) 80/20 by means of differential scanning calorimetry (DSC). The team defined the heat of explosion of compositions AN-UR 75/25 with a content of 10% (squares) and 15% (circles) aluminum, as well as detonation velocity and detonability of mixtures of AN/UR 75/25 with 10% aluminum powder when given different density and diameters of charges.

Zhixiang Xu et al. [124], using accelerating rate calorimeter, examined the influence of iron ion on the thermal behavior of ammonium nitrate and emulsion explosives. They established that adding ferric nitrate to AN and an emulsion matrix reduces thermal stability. In the paper [159], O. Němec et al. determined the influence of TNT, collected during demilitarization of ammunition, on detonation velocity and on relative explosive strength. In the experiments, three kinds of TNT were used, for which peak temperature and auto-ignition temperature were determined by means of DTA.

A relatively large number of papers concern solid rocket fuels [51, 55, 56, 81, 95, 98, 119, 122, 134, 135, 137, 138, 145, 152, 158] and, in particular, their stability. M. Miszczak [152] used thin layer chromatography (TLC) in quantitative measurement of the composition of stabilizer (diphenylamine) used to retard chemical decomposition of single-base propellants. Likewise, in the paper [158], new extraction based on chromatographic method, was used for the determination of stabilizers in propellants. The paper [55] describes the use of quantitative infrared microscopy method for the determination of the deterrent diffusion activation energy and spherical propellant. This method permitted characterization of the deterrent diffusion during ageing. S. Matečić Mušanić, M. Sućeska and A. Bakija [56] studied the dynamic mechanical properties of double based rocket propellant, aged for different periods of time at 90 ^{o}C. Dynamic mechanical properties were studied by means of dynamic mechanical analysis, whilst thermal properties were examined using DSC and TGA. In the paper [119], Fiamengo et al. showed that isothermal and non-isotermal thermogravimetry can be used for identifying homogeneous type propellants, as well as for rough quantitative determination of nitroglycerine content in double-base propellants (DBP). Other experimental techniques – non-isothermal DSC and the Ozawa method – were used for studying the kinetics of DBP decomposition [134].

D.B. Lempert et al. [51] described the energetic characteristic of solid composite propellants (SCP) of different type and application – metal free compositions and SCP containing additionally energetic ingredient metals (Al, Be, Mg, B) or metal hydrides (AlH_3, BeH_2, $B_xN_yH_z$). They showed how to optimize SCP destined for missile complexes of different mass characteristics. In the papers [95, 98], B. Florczak presented the results of thermodynamic calculations and investigations of the thermochemical and ballistic properties of aluminized CSP containing FOX-7.

Some papers address pyrotechnic mixtures. B. Czajka et al. presented the physical and chemical characteristics of commercial preparations of iron powders and their solid-state reactivity with $KClO_4$. Iron powders were analyzed in the aspect of possible application as the components of conducting heating mixtures in thermally primary batteries [6]. The paper [11] presents the physicochemical characteristics of the components of the reaction mixture of iron powder and polycrystalline $KClO_4$. In the paper [35], the effect of the kind (Zn, Mo or Ti) and the amount (concentration 0-5 wt%) of metallic powder, used as an activator introduced into the mixture of Fe and $KClO_4$, is studied. The research showed that, as far as future use is concerned, the most promising are powders Ti and Mo. Other research showed that Zr-$BaSO_4$ composition is sensitive to ignition by electric spark energy of 0.82 J, although the activation of Fe-$KClO_4$ mixture depends on the iron powder employed and the composition of its surface oxide layers [143]. Other experiments showed that the modification of iron powder surface carried out by reduction with dihydrogen causes decreasing of the linear rate of burning of mixture Fe-$KClO_4$ but it does not affect its calorific value [97]. D. Meerov et al. [116] examined stoichiometric compositions of Al-MoO_3 prepared by dry mixing and by reactive milling of micro-scale particles. The burning rate of Al-MoO_3 mixtures increased with pressure, reaching the maximum at ~10 atm. Nano-scale MoO_3 powder was also prepared by evaporation with a subsequent condensation onto a cooled plate in an inert-gas flow. The use of nano-sized components could considerably increase the combustion rates of Al-MoO_3 compositions.

Knowledge concerning the level of sensitivity to external stimuli of energetic materials is necessary to handle them, in particular with synthesis of new explosives. That is why these problems are examined in a number of papers [25, 28, 41, 42, 64, 65, 72, 73, 83, 133, 141, 153, 157]. The paper [25] by X. Xu presents molecular geometries, electronic structures, thermolysis mechanisms and theoretical criteria of a series of energetic materials obtained by quantum chemical methods. It was established, among others things, that for energetic materials with similar molecular structures and thermolysis mechanisms, there is normally a parallel relationship between the bond order of trigger bond, the activation energy to break the bond, and the experimental impact sensitivity. S. Zeman et al. determined the electric spark sensitivity (E_{ES}) of nitroamines [41, 42] and polynitro arenes [64, 72]. Research carried out on 16 nitroamines, using two machines (RDAD, ESZ KTTV), showed that E_{ES} values correlate with those of the characteristics of molecular structures that correspond to the primarily leaving nitro group in the nitramine molecule [41]. At the same time, the results of measurements E_{ES} executed for 31 polynitro arenes and their derivates showed that intermolecular interreaction plays a considerable role in this initiation [72]. In the paper [133], thermal stability of PBX with C4 matrix and with Viton A, containing bicyclo-HMX, RDX, HMX and HNIW, was determined, using DTA. Detonation velocity and detonation parameters were also determined using different numeral codes. A.V. Dubovik and D.V. Kokovikhin [141] defined the impact of the sensitivity of binary explosive compositions based on ultradisperse ($d \approx 1$ μm) or nanodisperse ($d \approx 50$ nm), containing inorganic substances of various nature – metals, oxide of metals, and metalloids. J. Szczygielska et al. [153] obtained samples of the ε-CL-20 crystals by precipitation process in a solvent/nonsolvent system, under variable process parameters, and measured their friction sensitivity. A. Elbeich et al. [157] obtained ε-CL-20 by the new method. The product had a small particle size with a smooth surface and regular shape without cracks. The impact sensitivity of the sample was lower than RDX and HMX. In the paper [65], M. Pospíšil and P. Vávra tested the relations between the performance, impact sensitivity, and presence of hydrogen bond interactions in the structure on a set of 30 energetic materials having different structures.

Detonability is an important parameter characterizing explosives that determines their area of use. It depends on primary explosives and stimulants. For that reason, a part of papers concerns the initiation of explosives [8, 20, 22, 34, 37, 39, 106]. The papers [8, 34] present the results of research concerning primary explosives initiated by laser radiation. In the paper [8], the method of synthesis and properties of the coordination complexes of mercury(II) chlorate(VII) with 5-hydrazino-tetrazole as ligand, considered as a potential photosensitive primary explosive, are presented. M.A. Ilyushin and I.V. Tselinskii [34] examined the influence of the structure of the salts azoles on the process of their thermal and laser initiation. R. W. Armstrong [20] examined the role of dislocations in assisting initiation of explosives. The paper [37] concerns the determination of the initiating capability of detonators by underwater explosion tests executed according to the procedure described in European standard EN 13763-15. Experiments were carried out on electric detonators characterized by different mass and type of high explosives. H. Czerski et al. [39] examined by small-scale gap test the detonability of samples of hexogene having different HMX content, specific surface area, angle of repose of powder and theoretical maximum density. In the paper [106], S. Zeman et al. discussed the problem of nitromethane initiation.

Management of explosives collected during demilitarization of ammunition is an important issue in many countries. For that reason, serious research is done on utilization methods that would be technically and economically justified and converge with environmental protection principles [12, 85, 150, 159]. In the paper [85], P. Borkowski et al. discussed the method of washing-out explosives from old artillery ammunition using high-pressure water jet technology. P. Shiskov et al. [150] proposed dissolving single- and double-base propellants (DPB) in acetone and adding afterwards to the solution: n-butyl alcohol, ethylene glycol or polyethylene glycol 400. Porous propellants (0.5-0.7 g/cm^3) with small, regularly distributed voids were obtained by extraction of the rest of solvent and polyethelene glycol 400 from the layer of propellants in water solution after some time of evaporation of acetone. K. Lipińska, M. Lipiński and A. Maranda examined the influence of double-base propellants containing 40% nitroglycerine on detonation characteristics (detonation velocity, blast wave parameters). ANFO and water-in-oil emulsion explosives were investigated, as well as explosive compositions containing 20, 40 or 60% DPB. In the paper [159], O. Němec examined the influence of the grain size and the quality of militarized TNT on detonation parameters of water-in-oil emulsion explosives. Detonation velocity, relative explosive strength (ballistic mortar test), thermal stability and auto-ignition temperature were determined.

The development of computer technology allows numerical modeling of phenomena that take place during high energy transformations, and estimating detonation and thermochemical parameters as well as potential structures and properties of new explosives [2, 4, 16, 19, 46, 47, 77, 93, 109, 125, 146, 160]. S. Grys and W.A. Trzciński [125] elaborated the thermochemical program ZMWN1 that can calculate the parameters of combustion, explosion and detonation of condensed energetic materials. The paper [2] by M. Sućeska and S. Matečić Mušanić, presents numerical modeling of self-ignition explosives. A comparison between calculated times to ignition for some standard explosives with times to ignition determined experimentally were carried out. Researchers from Zelinsky Institute of Organic Chemistry conducted a computer simulation of the decomposition of compounds with nitroguanidine [46] and polifunctional N-nitramines [47], and V.L. Korolev et al. of the decomposition of *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine (TNAD) [77]. In [4], Z.A. Walenta et al. proposed the method of simulation of the detonation phenomenon, based on the Direct Monte-Carlo Simulation. One of the main advantages of this method is that it makes it possible to study detonation in narrow channels and detonation decay under the influence of wall friction and heat exchange. M.A. Bohn et al. [15, 19] presented the results of computational study of mixtures HMX, RDX and CL-20 with Glycidyl Azide Polymer. The paper [16] describes the results of computational investigation of a novel explosive – dinitrofurazanfuroxan (DNTF). It contains estimations of such parameters as: molecular structure, crystal density, heat of formation and detonation, relative specific, impulse, and detonation velocity and pressure. In the paper [146], P. Politzer showed analogical numerical estimations of physicochemical and explosive properties carried out for 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane [146]. The figures were higher than in case of octogen but significantly lower than in the previous paper. I. Zhukov and G.D. Kozak [93] calculated thermochemical (heat of explosion) and explosive characteristics (detonation velocity and pressure) of furoxanes and benzofuroxanes. They noticed that their detonation performances are higher than those of HMX.

3.5 References

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Chapter 4

International Conferences on New Models and Hydrocodes for Shock Wave Processes in Condensed Matter

Ronald W. Armstrong, Vladimir Y. Klimenko, and Davinder K. Anand

A continuing series of international conferences on shock waves began in St. Petersburg, Russia, on October 9-13, 1995. The purpose was to promote the development of accurate, physically-based material models for the next generation of computationally-based hydrocodes. The succeeding (approximately biennial) conferences reflect research achievements in both numerical modeling technology and constitutive equation descriptions of material behaviors under extreme loading conditions. Participation in these conferences by Russian scientists in the previously closed cities of Central Europe enabled technical interactions with researchers throughout the European community and in the United States. The interactions have been beneficial for a number of technical advancements. These include understanding the dislocation defect mechanism for creation of hot spots at the crystal lattice scale and for understanding the role of hot spots in subsequent initiation of detonations [1, 2]. The research continues as demonstrated in Chapter 8 of this book.

4.1 The Early Conferences

The 1995 conference, entitled *New Models and Hydrocodes for Shock Wave Processes in Condensed Matter*, was chaired by founder Vladimir Klimenko, with vice-chairs Yu. I. Mescheryakov (St. Petersburg) and V.G. Morozov (Arzamas-16). Included on the international advisory committee were V.F. Kuropatenko (Chelyabinsk-70), I.G. Cameron (U.K. Atomic Weapons Establishment), and C.S.

Coffey (U.S. Naval Surface Warfare Center, then at the White Oak Laboratory and later at the Indian Head Division).

The main topics covered in the initial conference were:

1. Physical and Numerical Models for Detonation Processes
2. Physical and Numerical Models for Metals, Ceramics and Composites Behavior under Shock Compression
3. Shock Wave Processes at Micro- and Meso-Levels
4. Advances in Numerical Modeling Technology
5. New Hydrocodes
6. Equation of State for Hydrocodes
7. Experiment as Support for Model Development

Some of the 90 oral and poster presentations were published in the Russian Chemical Physics Reports, with English translation of the Russian articles provided by Overseas Publishers Association (OPA), Amsterdam B.V.

4.1.1 International Cooperation

A second conference with the same title was held at St. Catherine College, Oxford, U.K., on September 15-19, 1997. The conference was chaired by I.G. Cameron, Atomic Weapons Establishment (AWE), Aldermaston, U.K. The International Advisory Committee members were from Sandia National Laboratory, Stanford Research Institute, Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), and U.S. Army, and, from the Naval Surface Warfare Center Indian Head Division, C.S. Coffey.

Dr. Coffey was the chair of the July 4-9, 1999, conference hosted by Professor D.K. Anand, Chair, Department of Mechanical Engineering, University of Maryland at College Park, Maryland. That the scope of the conference was broadened was reflected in a new name, *International Workshop on New Models and Predictive Methods for Shock Wave/Dynamic Processes in Energetic Materials and Related Solids*. The conference occurred in the same year that the University of Maryland Center for Energetic Concepts Development (CECD) was founded. R.W. Armstrong was the founding Director. D. K. Anand is the current Director (see http://www.cecd.umd.edu). Figure 4.1 shows the group picture of attendees. There were 50 oral and 31 poster presentations [3].

Figure 4.1: Participants at the "International Workshop on New Models and Predictive Methods for Shock Wave/Dynamic Processes in Energetic Materials and Related Solids," 4-9 July 1999.

An important contribution to the conference at Maryland was the introduction of a panel discussion of *U.S.–Russian Research Co-operations*, chaired by M. Franda, University of Maryland Office of International Affairs. The panel included:

- **W.J. Desmond**, Department of Energy, Program Director for Nuclear Cities Initiative.
- **G.F. Tereshenko**, Vice-Minister, Russian Ministry of Science.
- **A.V. Putilov**, General Director of Department of Industrial Technologies, Ministry of Science.
- **R. Sagdeev**, Director, University of Maryland East-West Space Science Center.
- **C.T. Owens**, Senior Vice-President, Civilian Research and Development Foundation.
- **N.P. Voloshin**, Head of Department, Ministry of Atomic Energy.
- **R.I. Ilkaev**, Director, Russian Federal Nuclear Center, Arzamas – 16.

- **G.N. Rykovanov**, Director, Russian Federal Nuclear Center, Chelyabinsk – 70.

4.1.2 Continuing Conferences

The first three conferences included 90, 134, and 81 oral and poster presentations. The next conferences in the series were:

- May 19-24, 2002, chaired by Y.Yu. Klimenko at Edinburgh, Scotland, with 101 presentations
- May 16-20, 2004, chaired by C.S. Coffey, with CECD support at the University of Maryland, with 91 presentations
- April 9-14, 2006, chaired by R. Dormeval at Dijon, France, with 98 presentations
- May 18-23, 2008, chaired by I. Plaksin at Lisbon, Portugal, with 107 presentations
- May 24-28, 2010, chaired by L. Soulard at Paris, France, with 107 presentations.

4.2 Some Research Results

From the beginning 1995 conference, a balance was sought in presentations describing the advancements in hydrocode computations and the development of improved equations of state or constitutive model equations for material deformations and fracturing under extreme mechanically-induced pressures and loading conditions. Conference sessions have covered subjects such as (1995) *Numerical Schemes for Shock Wave Codes, Models of Detonation Processes, Models of Metals under Shock Compression,* and *Equations of State for Hydrocodes.* Session topics in 2008 included *Numerical Modeling of Detonation Processes*, *Physics of Shock Wave Processes in Inert Materials*, and *Mechanisms of Shock Wave Processes at Micro-Level (Inert Materials).* The last three 2008 topics involved representatives from LLNL; LANL; Commissariate a l'Energie Atomique (CEA); Institute of Chemical Physics, Moscow; and Tomsk State University, Siberia.

An important purpose of the continuing conference series is to bridge the dimensional scales from the macro- to the molecular levels of energetic material behaviors under shock loading conditions. An example of cooperative research activity developed because of the conference sequence is that among Vladimir Klimenko, C.S. Coffey, and Ronald Armstrong. For example see Fig. 4.2. The work appeared in a 2006 paper by Klimenko and I.Y. Kozyreva [1].

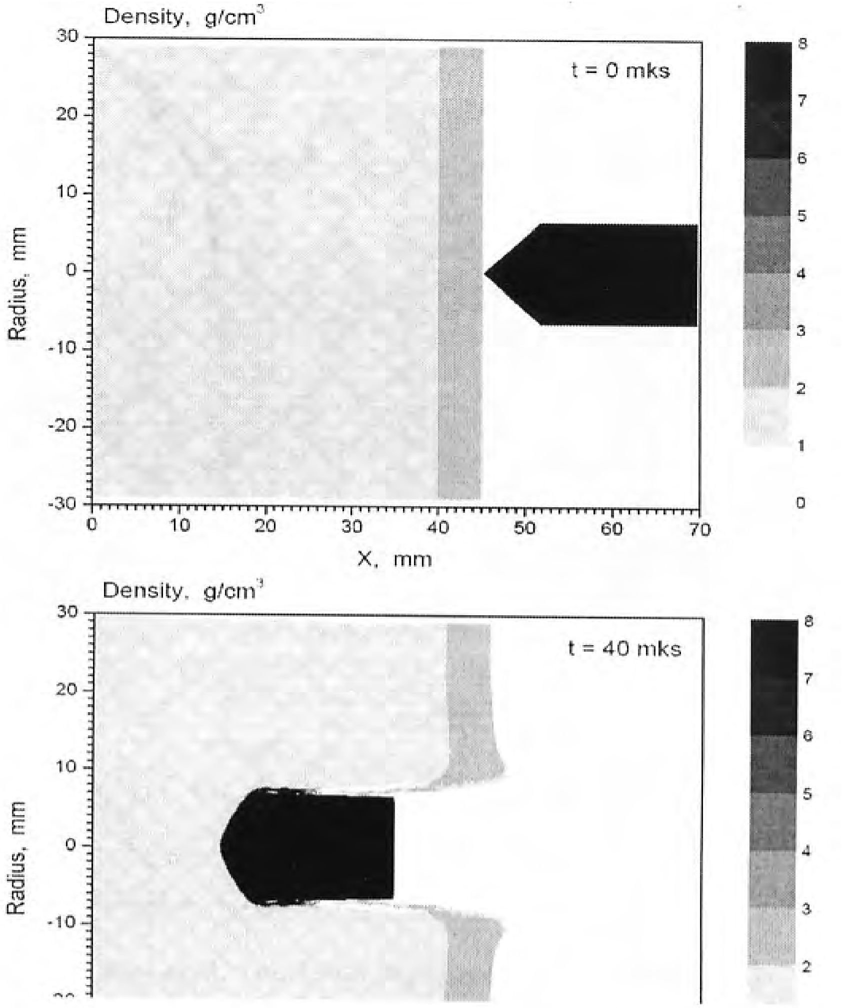

Figure 4.2: Modeled bullet penetration into an aluminum-encased plastically bonded explosive PBX 9404 material [1].

Figure 4.3 shows the proposed counterpart action at the crystal lattice level in the model bullet penetration experiment. Adjacent molecular interactions on an (0-12) plane projection are depicted of shearing consequences in the [100] direction occurring across the horizontal trace of the (021) slip plane. Dislocation movement is thereby proposed to bring adjacent atomic appendages of juxtaposed molecules into critical intermolecular distances on a reaction coordinate basis, as previously described by Armstrong and Elban [4].

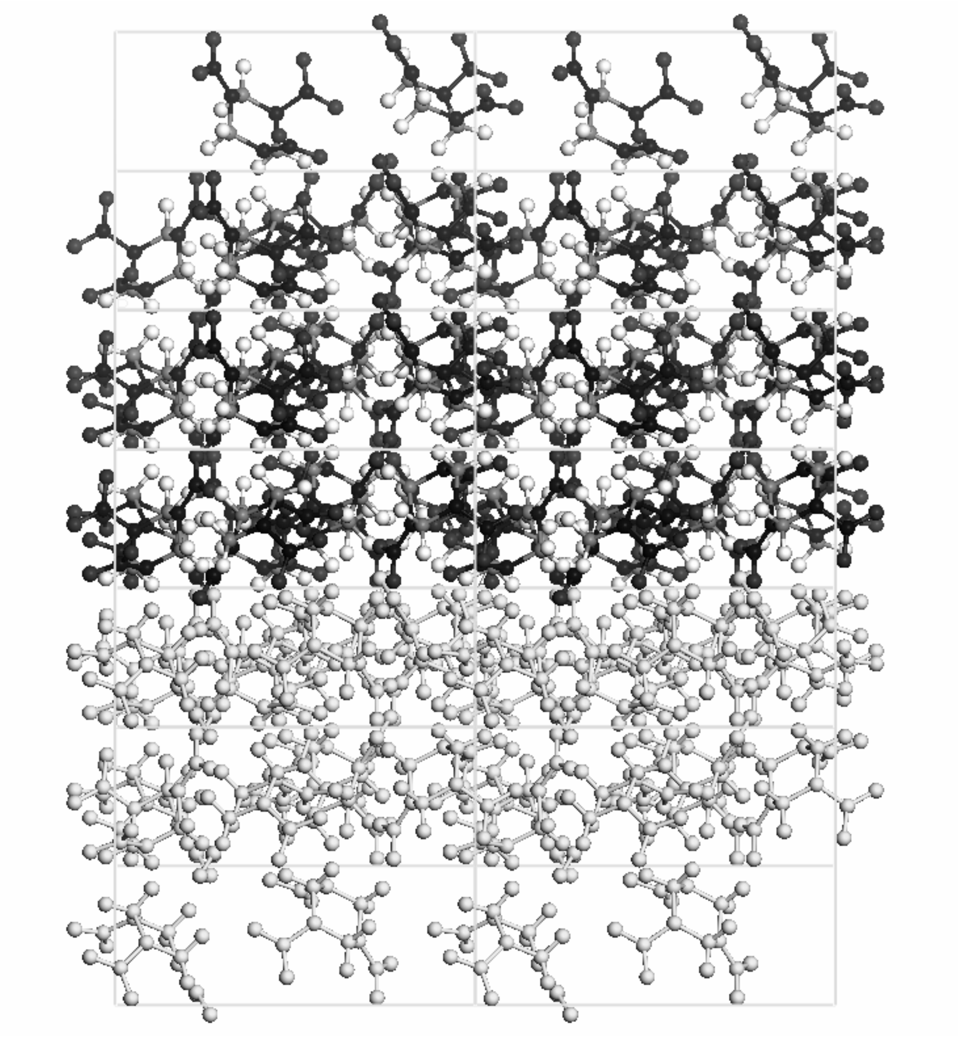

Figure 4.3: Molecular interactions at the molecular lattice level associated with shearing of an RDX crystal on the (021) slip plane in an [100] direction [1, 4].

Connection between the two limiting scales represented by Figs. 4.2 and 4.3 is provided by the model explanation of crystal size influences on the hot spot sensitivity of crystals when subjected to similar shearing actions. See Fig. 9 of Chapter 8 in this book. Such research activity continues in the United States Department of Energy (DOE) national laboratories and in laboratories of the nations in Central Europe.

4.3 References

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Chapter 5

The Synthesis Chemistry of Energetic Materials

Thomas M. Klapötke

The synthesis of *new* energetic compounds in Germany is almost exclusively undertaken at the Ludwig-Maximilian University (LMU) in Munich. Other government research institutions (ICT) and private companies (for example, Diehl BGT Defence, Rheinmetall Defence, Rheinmetall Nitrochemie, DYNA energetics, Bayern Chemie and others) are more involved in formulation, processing and production efforts.

In this chapter we will discuss the synthetic chemistry carried out at LMU in the following areas:

- High explosives (HEDM)
- Oxidizers (HEDO)
- High-nitrogen propellants
- Pyrotechnics
- Primary explosives

5.1 High Explosives (HEDM)

Energetic materials are most commonly used in either high explosives or propellant formulations. Certain parameters are important in determining the effectiveness of new energetic molecules in these formulations. For example, high densities (ρ), oxygen balance (Ω) close to zero, and high detonation/combustion temperatures are desirable for explosives. Desirable for rocket propellant formulations are high specific impulse (I_{sp}), low combustion temperature, high force and pressure, and a high N_2/CO ratio of the reaction gases [Klapötke, 2011].

Using the heat of explosion (Q), the detonation velocity (D) and the detonation pressure (P) as a measure for the performance of a high explosive, one can clearly see from Figure 5.1 that the performance of chemical explosives has improved substantially since the introduction of NG.

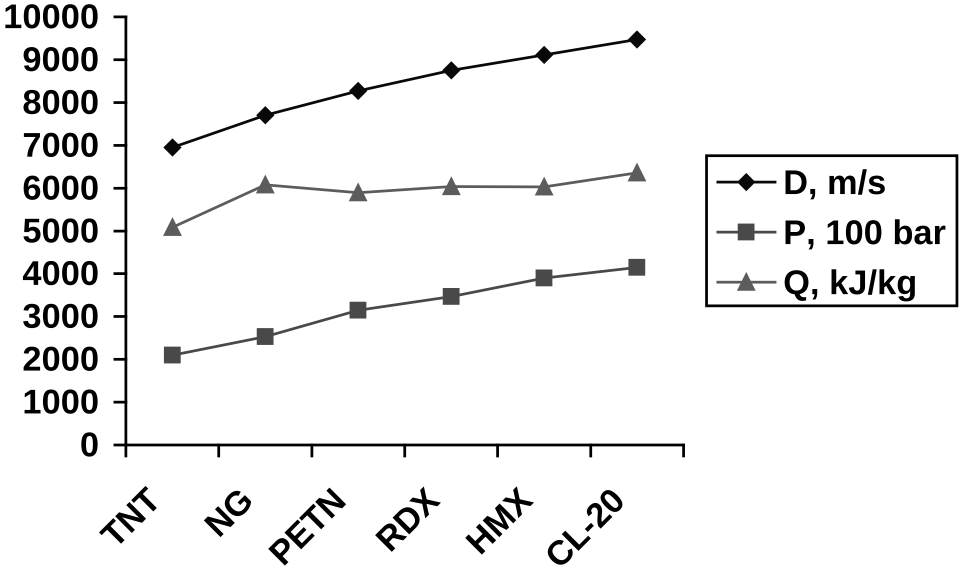

Figure 5.1: Performance of chemical explosives.

Despite many years of research, there are a limited number of possibilities to achieve a substantial increase in the performance in comparison with conventional C-H-N-O explosives. Recent advances in energetics energy output have come in improved processing or inclusion of energetic binders to increase overall formulation energy, but limited success has been achieved in the development of advanced energetics. One reason for this is that conventional nitramine and nitroaromatic explosives such as TNT, RDX, HMX and other similar molecules share the same three problems (Table 5.1):

(i) they are not nitrogen-rich ($N \leq 50\%$)
(ii) their oxygen-balance is not close to zero
(iii) formulations (mixtures of various HEs) are required to achieve a good oxygen balance

Table 5.1: Nitrogen content (N) and oxygen balance (Ω) of conventional HEs.

High explosive	N / %	Ω / %
TNT	18.5	-73.9
PETN	17.7	-10.1
RDX, HMX	37.8	-21.6

Nitrogen rich molecules are desired for use as energetic materials because of the high energy content of N-N bonds. Oxygen balance is defined as the percentage of oxygen that remains after or is needed in the oxidation reaction and can therefore be positive or negative. In this context, oxygen balance (Ω) is defined as the ratio of the oxygen content of a compound to the total oxygen required for the complete oxidation of all carbon, hydrogen and other elements. These elements are oxidized to form CO_2, H_2O, etc. and are used to classify energetic materials as either oxygen deficient or oxygen rich.

Materials with an oxygen balance close to zero are usually, but not always, more effective energetic materials, since all of the oxygen is used up in the reaction. The oxygen balance can be modified through formulation additions to bring the overall oxygen balance of the formulation close to zero.

Researchers have already realized the energy content limit for CHNO based molecules [Göbel, Klapötke, 2009]. Research needs to expand beyond this way of thinking and increase efforts to explore different molecular structures and molecular constitutions in order to realize a substantial increase in performance. Early research has shown that materials with a high nitrogen content offer many advantages in comparison with those with carbon backbones, including the potential for vastly increased energy contents. Research into molecules with high nitrogen content (>50%) has shown the potential for a substantial increase in available energy. The first generation of high-nitrogen compounds, such as hydrazinium azotetrazolate (HZT) and triamino-guanidinium azotetrazolate (TAGZT) (Figure 5.2) [Hammerl et al., 2001], met the criteria for being nitrogen rich and proved to be very desirable ingredients in erosion-reduced gun propellants (Figure 5.9). However, due to the unfavorable oxygen balance, such compounds are not suitable as energetic fillers in high explosive compositions (Table 5.2) [Klapötke, 2007].

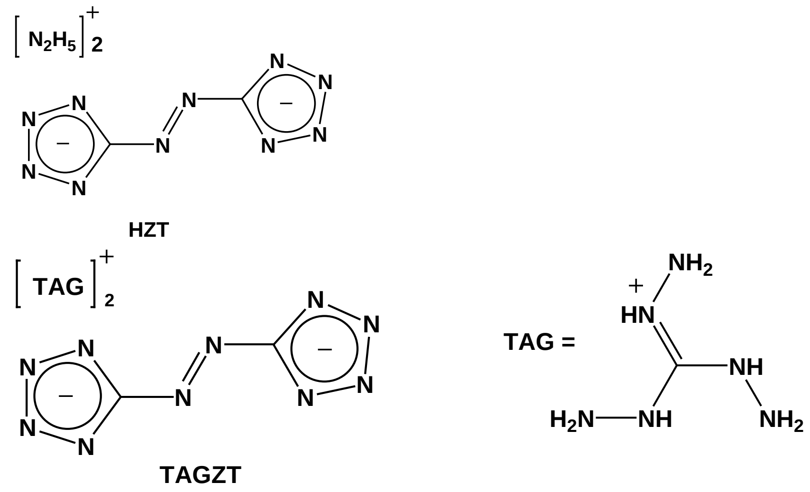

Figure 5.2: Structures of HZT and TAGZT.

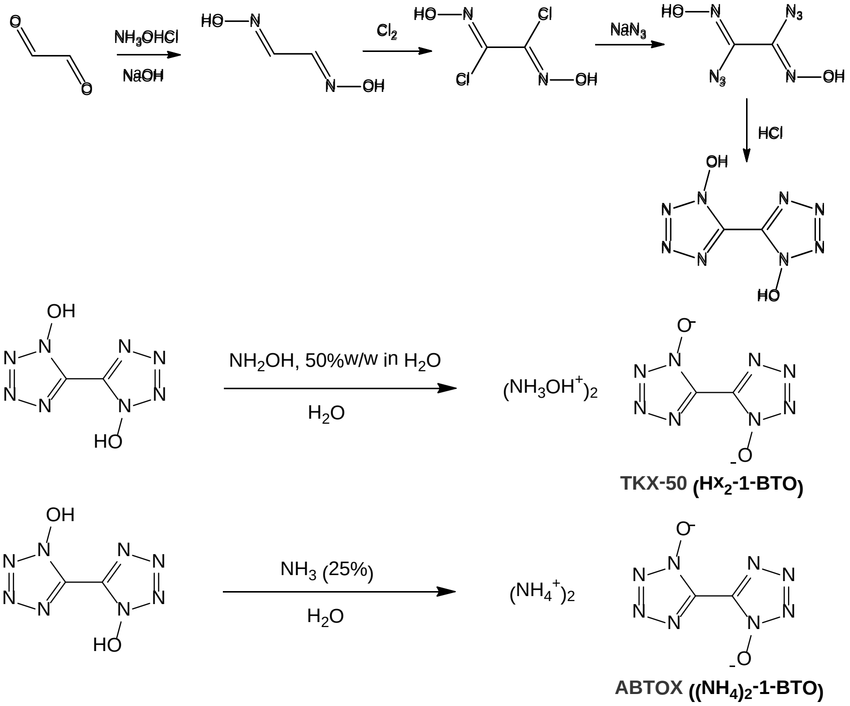

Figure 5.3: Synthesis of 1-BTO from DAGL (top) and synthesis of TKX-50 and ABTOX (bottom).

The second generation of high-nitrogen compounds, which have improved oxygen balances such as TKX-50 and ABTOX (Figure 5.3), combine desirable properties such as a high nitrogen content with a good oxygen balance (Table 5.2) [Klapötke, Stierstorfer, 2011]. These compounds are therefore more suitable for use in high-explosive formulations. Moreover, materials with an oxygen balance close to zero are also suitable as powerful ingredients in solid rocket propellants. An increase in the I_{sp} of only 20 s would be expected to increase the payload or range by ca. 100%. Related to this, Figure 5.4 shows the computed performance parameters for conventional and high-N gun propellants.

The computed and predicted performance values not only exceed those of the first generation of high-nitrogen compounds (e.g. HZT), but also, in the case of TKX-50, the performance values of RDX and HMX (Figure 5.4).

Table 5.2: N content and Oxygen balance (Ω) of high-N compounds.

		N / %	Ω / %
1st generation	HZT	85	-63
	TAGZT	82	-73
2nd generation	TKX-50	59	-27

Future research will lead to even more powerful, high-nitrogen high-oxygen explosives with enhanced and superior detonation characteristics. New energetics will provide vastly increased energy content compared to RDX. They will have up to several times the energetic performance. In addition, these materials will have a high energy density with high activation energy.

With these capabilities, the DoD will be able to develop new applications for energetic materials and vastly improve the performance of munitions. The increased performance of the next generation of energetics will enable DoD to meet the same strategic goals with fewer munitions and less energetic material. The increase in energy output can be harnessed in munitions that require a fraction of the amount of energetics to deliver the same payload or thrust profile. This will allow engineers to put energetics in munitions that have never had them before.

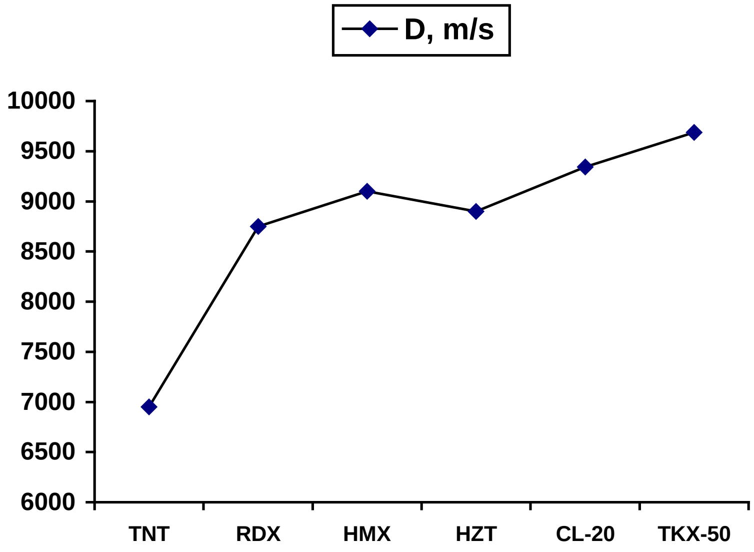

Figure 5.4: Performance of conventional and high-nitrogen explosives (D = VoD).

5.2 Oxidizers (HEDO)

Ammonium perchlorate (AP) has found application in munitions, primarily as an oxidizer for solid rocket and missile propellants. It is also in fireworks and is used as an air-bag inflator in the automotive industry. However, it is also found as a contaminant in agricultural fertilizers. Because of its uses and high solubility, chemical stability, and persistence, AP has become widely distributed in surface and ground water systems. There is little information about the effects of perchlorate on the aquatic life that inhabits these systems. However, it is known that perchlorate is an endocrine disrupting chemical that interferes with normal thyroid function and that, in vertebrates, thyroid dysfunction impacts both growth and development. Because perchlorate competes for iodine binding sites in the thyroid, the addition of iodine to culture water was examined to determine if perchlorate effects can be mitigated. Finally, perchlorate is known to affect normal pigmentation of amphibian embryos.

Examples of high-oxygen explosives have been reported in the literature as research reports and patents. However, often no information is given about the synthetic procedures or the physicochemical characteristics of the compounds obtained. Some of the most promising classes of materials initially considered were polynitroaliphatic compounds containing the dinitromethyl, fluorodinitromethyl and trinitromethyl groups. Among them, the trinitroethyl compounds were found to have the most favorable values for the heats of detonation and oxygen balance. However, the thermal stability of the trinitroethyl containing compounds was reported to be generally limited to 150 °C when solid and 100 °C when molten, which discouraged further investigations into trinitroethyl substituted compounds. We have recently investigated compounds mentioned previously in literature and have also developed and tested novel compounds with the trinitroethyl functionality in order to explore their potential as components in the design of the next generation of energetic materials. One goal is to enhance the thermal stability of compounds containing this functionality.

With the emerging global interest in high-energy, density materials (HEDM), the LMU group is currently developing new energetic materials containing both high oxygen and nitrogen contents. The trinitroethyl group is contributing to a positive oxygen balance value.

While investigating the crystal structures of compounds containing the trinitroethyl functionality, it was found that the trinitroethyl group participated in intermolecular interactions like dipolar nitro group interactions and hydrogen bonding of the acidified methylene-type protons. These interactions mainly govern the molecular packing of these compounds and result in high-crystal-density polymorphs with promising energetic performance parameters. Different new high explosive compounds have been introduced belonging to a new class of energetic materials preferentially containing both high-nitrogen and high-oxygen content. Compounds abbreviated with BTTD and BTAT display superior performance properties compared to RDX. BTAT for example is both less sensitive and displays a better oxygen balance value than RDX. The latter property is responsible for its smokeless combustion and also the formation of less toxic fumes on decomposition. The compounds are water insoluble in contrast to energetic salts. This is a prerequisite to protect the ground and one important environmental advantage amongst the qualification criteria for new HEDM. It has been shown that the thermal stability for solid and liquid compounds carrying the trinitroethyl moiety can be higher than 140 °C. This value applies not only to the decomposition temperatures but is also relevant for the chemical long term stabilities. Our research group has also studied the structures of 2,2,2-trinitroethanol (TNE) [Göbel, Klapötke, 2009], since it is one of the most useful precursors for the preparation of compounds containing the trinitroethyl group as well as that of bis(2,2,2-trinitroethyl) carbonate [Göbel, Klapötke, 2008]. Within this work we extended our investigations from initially looking only at the explosive properties of the compounds synthesised to investigating the suitability of related but different compounds as potential oxidizers and replacements for AP. In particular, the LMU group tries to synthesize oxygen-rich trinitroethyl derivatives that are high-oxygen compounds (oxidizers) but not necessarily high-nitrogen species (explosives).

5.2.1 *Nitroalkylborate Chemistry*

The nitro compounds based on boron esters discussed in this chapter are suitable candidates for high energy density oxidizers and for smoke-free, green colorants in pyrotechnic compositions. Tris(2-nitroethyl) borate and tris(2,2,2-trinitroethyl) borate can be obtained from the reaction of boron oxide with 2-nitroethanol and 2,2,2-trinitroethanol, respectively (Figure 5.5) [Klapötke et al., 2010].

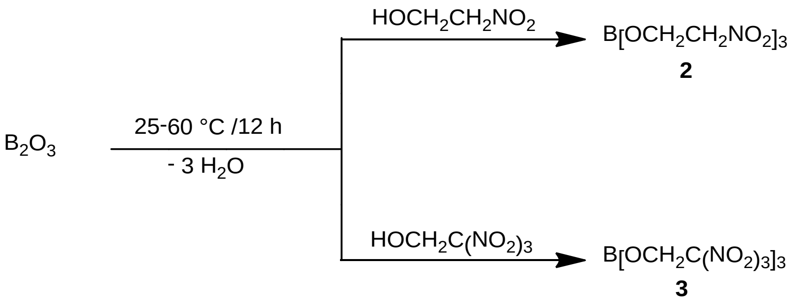

Figure 5.5: Synthesis of tris(2-nitroethyl) borate (2) and tris(2,2,2-trinitroethyl) borate (3).

The oxygen balance of **2** is −59.70 % and of **3** is +13.07 %, and the density of **3** was determined to be 1.982 g cm^{-3}, which is quite high. DSC measurements revealed an exothermic decomposition at 216 °C for **2** and at 161 °C for **3**. In the Bunsen burner flame, **2** and **3** show a green flame colour and smoke-free combustion; however, the burn rate of **3** is faster than that of **2**. The sensitivity data for **3** is given in Table 5.3.

Table 5.3: Sensitivity data for tris(2,2,2-trinitroethyl)borate.

Grain size	< 100 μm
Impact sensitivity	15 J
Friction sensitivity	144 N
Electrostatic sensitivity	0.5 J

The nitroethyl boron compounds tris(2-nitroethyl) borate (**2**) and tris(2,2,2-trinitroethyl) borate (3) have been prepared by reaction of the corresponding nitroalcohol with boron oxide. The preparation is very easy and results in high yields of the corresponding borate compounds. Furthermore, up-scaling is possible with this synthesis method in an easy and safe way. The nitroethyl compounds were fully characterized using multinuclear NMR, IR and Raman spectroscopy as well as mass spectrometry and elemental analysis. Thermal stability was studied using differential scanning calorimetry. Furthermore, the energies of formation were calculated.

5.2.2 Trinitrocarbamate (TNC) Chemistry

2,2,2-Trinitroethyl carbamate (TNC) was synthesized via the reaction of 2,2,2-trinitroethyl chloroformate and an aqueous solution of ammonia. It is used only as a reaction intermediate. The oxygen balance of **TNC** is 0%. The synthesis of TNC uses water as the solvent and the yield of the pure product is about 60 % [Klapötke, Axhammer, 2011].

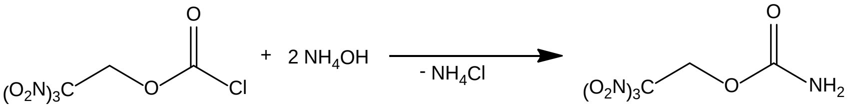

Figure 5.6: Synthesis of 2,2,2-trinitroethyl carbamate (TNC).

TNC was fully characterized by NMR, IR and Raman spectroscopy, as well as with elemental analysis and mass spectrometry and has a density in the solid state of 1.839 g cm^{-3}. TNC shows promise as a new and quite stable potential precursor for high energetic oxidizing materials.

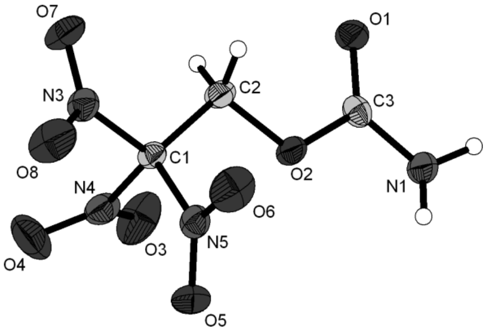

Figure 5.7: Structure of 2,2,2-trinitroethyl carbamate (TNC).

TNC is insensitive towards impact and is stable up to 165 °C. These properties make it a great potential precursor for unknown HEDOs. The compound is soluble in polar organic solvents but poorly soluble in water. Long-term stability and compatibility tests have so far not been completed. The compound is stable towards bases, but acids may cause decomposition.

2,2,2-Trinitroethyl nitrocarbamate (**10**, TNC-NO_2) is a new and quite stable potential high energetic oxidizer. With regards to possible applications, it is very promising. Therefore, the compound has been upscaled to the 10 g scale. The nitration of 2,2,2-trinitroethyl carbamate can be achieved with a mixture of concentrated sulfuric and fuming nitric acids. The compound has been fully characterized using NMR, IR and Raman spectroscopy, as well as elemental analysis, mass spectrometry and single crystal X-ray diffraction.

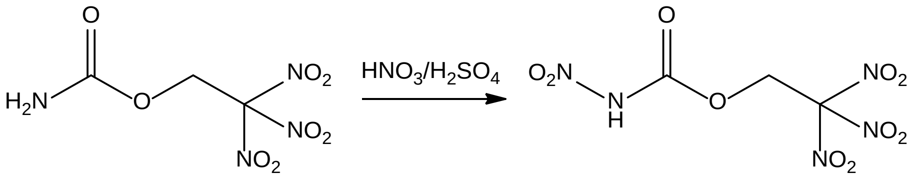

Figure 5.8: Synthesis of 2,2,2-trinitroethyl nitrocarbamate (TNC-NO_2).

The synthesis of **10** was carried out directly in nitro-sulfuric acid. The reaction leads to an almost essentially pure product. **10** crystallizes with a density of 1.725 g cm–3 (Figure 5.9). The sensitivity of **10** towards impact, friction and electrostatic discharge has been determined and found to be comparable with the values reported for RDX. Compound **10** melts at 109 °C (onset) and is stable up to 153 °C (onset). Furthermore, **10** is compatible with fine aluminium powder.

5.3 High-Nitrogen Propellants

For gun propellants we can assume isochoric combustion with the specific energy f_E or force or impetus (f_E = n R T), the combustion temperature Tc (K), the co-volume bE (cm3 g-1) and the pressure p (bar; 3000 – 4000 bar) being the most important parameters. Moreover, a large N_2 / CO ratio is desirable in order to avoid erosion problems [Klapötke 2011]. The loading densities are not as important as for high explosives. Comparing M1 and EX-99 with the newly developed NICO (Low

Erosion Propellant), which is based on TAG_2-BT (TAG2-BT = $(CN_6H_9)_2$-5,5'-bistetrazolate), very similar performance values are observed for M1/NICO, but M1 has a greatly reduced erosion coefficient (N_2/CO) relative to EX-99 and NICO (Figure 5.10).

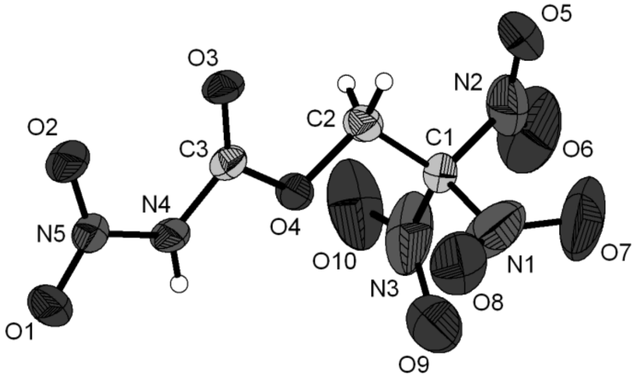

Figure 5.9: Structure of 2,2,2-trinitroethyl nitrocarbamate ($TNC-NO_2$).

5.4 Pyrotechnics

In the area of perchlorate-free red light illuminants, LMU has developed high-N strontium containing salts as colorants (Scheme 4). These were used by the United States Army Armaments Research, Development and Engineering Center to design new high-nitrogen based pyrotechnics. As a result, the full-up prototype testing of perchlorate-free hand-held signal formulations for the US Army's M126A1 red star parachute hand-held signal was recently described. Compared to the perchlorate-containing control, the disclosed formulations were found to be less sensitive toward various ignition stimuli, while offering a superior pyrotechnic performance [Sabatini et al., 2011 & 2012; Crow 2012]. From the military perspective, the new formulations provide further evidence that development of shorter hand-held signals in an environmentally conscious way is a realistic and obtainable goal.

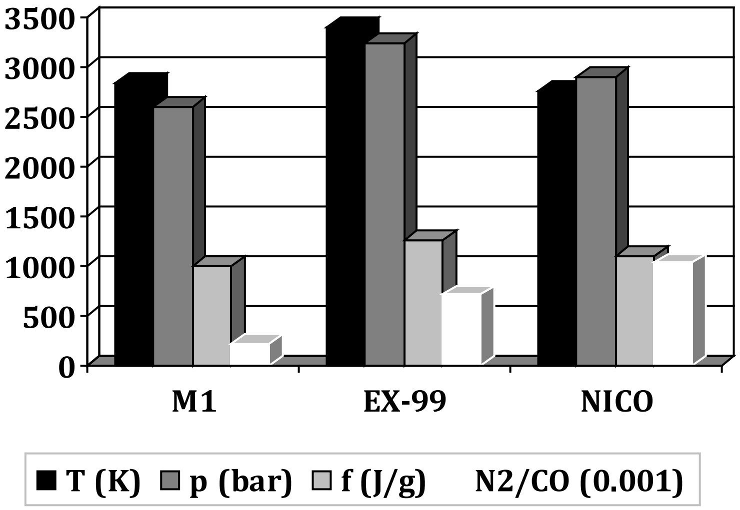

Figure 5.10: Calculated performance of various gun propellants (NICO = TAG$_2$-BT).

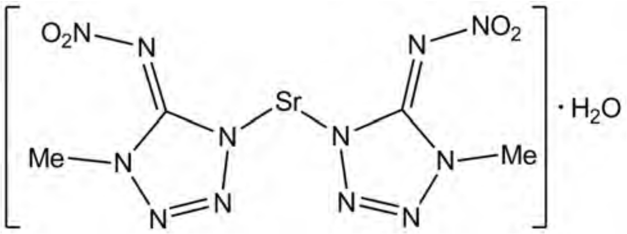

Figure 5.11: Structure of strontium bis-(1-methyl-5-nitriminotetrazolate) monohydrate.

5.5 Primary Explosives

In 2007 the LMU Munich research group reported the compound copper-bis(1-methyl-5-nitriminotetrazolate). This compound may have substantial potential as a lead-free primary explosive.

Another promising and thermally stable (Tab. 5.4) lead-free primary explosive is copper(II) 5-chlorotetrazolate (CuClT, PSEMC & LMU) [Fischer et al., 2011]. The synthesis is achieved in a convenient reaction (Figure 5.12) starting from commercially available aminotetrazole.

CuClT can then be further converted into the synthetically useful compounds sodium chlorotetrazolate and chlorotetrazole (Figure 5.12).

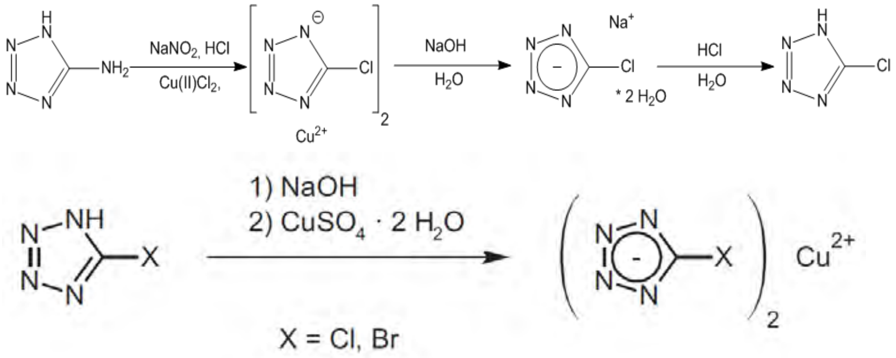

Figure 5.12: Synthesis of copper(II) chlorotetrazolate (CuClT).

Table 5.4: Energetic properties of copper(II) chlorotetrazolate (CuClT).

	CuClT
Formula	$C_2Cl_2CuN_8$
Molecular Mass [g mol^{-1}]	270.53
Impact sensitivity [J]	1
Friction sensitivity [N]	< 5
ESD-test [J]	0.025
N [%]	41.42
$T_{dec.}$ [°C]	289

In the area of metal-free primary explosives, covalently bound azides are often advantageous due to their desirable high sensitivity and usually fast DDT. Although these compounds often do not show the high thermal stability of metal complexes, some may have application as LA replacements in transfer charges. Two of the most promising candidates are triazido triazione (triazine triazide, TTA, ARDEC, see above) and diazidoglyoxime (DAGL, LMU). The latter can be prepared according to Figure 5.13 (Table 5.5).

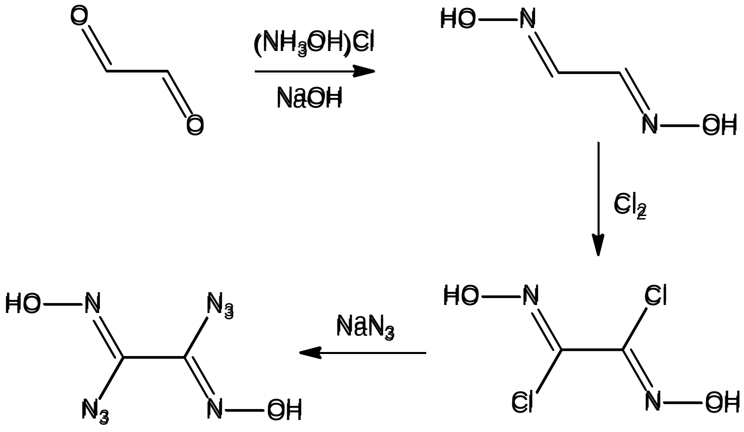

Figure 5.13: Synthesis of diazidoglyoxime (DAGL).

Table 5.5: Energetic properties of TTA and DAGL in comparison with LA.

	DAGL	LA
Formula	$C_2H_2N_8O_2$	N_6Pb
Molecular mass (g mol^{-1})	170.1	291.3
Impact sensitivity (J)	1.5	2.5 – 4
Friction sensitivity (N)	< 5	0.1 – 1
ESD (J)	0.007	0.005
$T_{dec.}$ (°C)	170	315

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Chapter 6

The Total Energy and Density of Certain Explosives: A Curious Relation

Lemi Türker

An interesting linear relationship has been found between the E/M ratios and densities of a large group of explosives having C-NO_2 and N-NO_2 bonds. In this relation E values are the total energies calculated at the level of UB3LYP/6-31G(d), and M stands for the molecular weight of each explosive considered. Thus, some factors effective on densities of explosives at the molecular level have been found.

6.1 Introduction

Density is an important characteristic of explosives. By changing the loading density (which is the ratio between the weight of an explosive cartridge and its volume [1]), performance of an ammunition can be changed. The loading density is of course related to the theoretical maximum density (TMD) of the charging explosive [2].

Raising the density by pressing or casting improves brisance and detonation velocity [1]. Low density explosives in contrast produce a milder thrust effect. Loading density is a very important parameter, both in propellant powders and brisant explosives. On the other hand, molecular density is as important as loading density. Density has been termed “the primary physical parameter in detonation performance” [3]. An increase in the solid-state density is hence desirable in terms of the amount of material that can be packed into a volume limited warhead or propulsion configuration. Due to that, a great deal of effort accumulates on novel energetic materials having high density.

In the literature there exists some surprisingly accurate methods of estimating the theoretical maximum density (TMD). For instance, Eremenko found that TMD could be estimated within the range of 2-3% error by a simple linear relationship between the density and the hydrogen content of substituted organic molecules [4,5], $\rho(\mathrm{TMD}) = a_i - k_i H$, where $\rho(\mathrm{TMD})$ is the theoretical maximum density, a_i and k_i are certain constants, and H is the percent by weight hydrogen in the explosive molecule. However, the method depends on H being greater than zero and less than around 6% ($0 < H < 6\%$) [2]. Moreover, a_{ir} and k_{id} vary from one group of explosives (such as liquid aliphatics) to another (e.g. solid, noncyclic aliphatic compounds having one nitro group), thus its applicability is highly limited. Keshavarz suggested an empirical method for the prediction of densities of various types of explosives based on their elemental compositions [6].

The theoretical maximum density has many applications in various calculations, for e.g. in Rothstein's method of detonation velocity [7, 8], Kamlet and Jacobs calculation of detonation velocity and pressure [9, 10], etc. Some methods have been published in the literature [11-19] for the prediction of densities of explosive materials. Also, some complex quantum chemical approaches can be cited for the calculation of densities of energetic compounds [16-21].

Molecular Orbital (MO) methods have long been used to estimate crystal density. For the purpose of getting results accurate enough, one often performs calculations at high levels of the theory, such as QCISD(T) (quadratic integration including configuration single and double substitutions with a triples contribution to the energy) and MP2 (second order Möller-Plasset) methods with electron correlation correction. Unfortunately, both sets of methods are computationally expensive, and even impossible for large systems. On the other hand, the Density Functional Theory (DFT) method, particularly the B3LYP hybrid functional with various basis sets, can produce reliable geometries and energies while requiring less computer time and resources. Thus DFT provides an efficient tool for molecular density calculations.

In density calculations the existence of a vibrationally stable minimum on the potential energy surface has to be considered. In addition to that constraint, the lowest energy conformer should be taken into examination. The vibrational analysis confirms that there are no imaginary frequencies. That means all the optimized geometries stand for truly local energy minima on the potential energy surface.

The molecular density is calculated by calculating the molecular volume by means of molecular orbital techniques (over properly geometry optimized structures) and then applying a Monte-Carlo approach. An almost standard method involves the calculation of molecular volume by the statistical average of 100 single-point molar volume calculations. The molar volume is defined as inside a contour of

0.001 electron/Bohr^3 density. Türker et al considered various novel potential explosives and calculated their densities prior to application of Kamlet–Jacobs equations to estimate their detonation velocities and pressures [22-24].

On the other hand, connections between the molecular structures of organic compounds and their physicochemical properties are an interesting field of chemistry. The structure-property or structure-activity studies involve sets of compounds for which the property of interest are analyzed by representing their molecular structures with calculated molecular numerical descriptors and then developing certain regression models that relate the descriptors to the property/activity [25]. Topological indices of various types are used in such studies [25-31]. The topological indices are certain numbers associated with constitutional formulas by mathematical operations on the graphs representing structures [25, 26].

Some properties of molecules root from the gross topology of the structures, which include the number of bonds (edges of the molecular graph), the number of atoms (vertices of the molecular graph), etc. Other properties of molecules are interrelated to their fine topology [27-29]. These descriptors are obtained by means of elaborate mathematical/quantum chemical approaches. In some cases angles play the role of topological descriptors [29-31]. The angle of detonation velocity defined in the literature is such a descriptor of topological type [32-34]. It is a function of a topological component: the total energy. By the help of descriptors of fine topology, some hidden functional relationships between structures and properties/activities of molecules become evident [27-29].

In two recently developed methods by Türker, based on quantum chemical calculations, detonation velocity has been shown to be a linear function of E/M ratio, where E and M are the total energy and molecular weight of the explosive material, respectively [32-34]. Also, Türker recently developed a trigonometric model (circular model) for detonation velocity, which interrelates the detonation velocity (D) with the total energy (E) (D=f(E), at the level of UB3LYP/6-31G(d)) [35]. Based on that model, densities of certain explosives have been found to be related to tanΦ, where Φ is the azimuth angle in the model. As an extension of that work, here a theory is developed and a model is suggested indicating the relationship between the densities of some nitro explosives (C-NO_2 and N-NO_2 compounds) and their total energies obtained based on DFT calculations (UB3LYP/6-31G(d)) .

6.2 Theory

Consider a hypothetical shell consisting of an explosive charge in a case having a very negligible mass. In front of it there exists a bullet. Both parts have the same mass M (see Figure 6.1). Assume that kinetic energy produced in the explosion of that explosive is transferred to the bullet. Furthermore, assume that M is also equal to the molecular weight of the explosive used in the explosion. Additionally, suppose that the explosive under consideration is self oxygen balanced. Then, the total kinetic energy of the gases produced in the explosion is expressed as

Figure 6.1: A hypothetical shell having bullet and explosive charge, each of which has mass M.

$$E_k = \frac{1}{2}\sum m_i v_i^2 \tag{1}$$

which is transferred to the bullet of mass M. Then,

$$E_k = \frac{1}{2}MU^2 \tag{2}$$

In eqs. 1 and 2, m_i, v_i and U are the mass of gas i, the velocity of gas i, and the velocity of the bullet, respectively. Now assume that a certain fraction of the total energy (E) of the explosive used is converted to the kinetic energy, E_k, ($E_k = kE$, where k is a proportionality constant) of the bullet. Then, eq.1 becomes

$$kE = \frac{1}{2}\sum m_i v_i^2 \tag{3}$$

Whereas eq.2 gets the form of

$$kE = \frac{1}{2}MU^2 \tag{4}$$

The mass of charge of the shell used to push the bullet is,

$$M = Vd \tag{5}$$

where V and d are the volume and density of the explosive, respectively. Note that mass of the charge is equal to mass of the bullet. Insert eq.5 into 4 to obtain,

$$kE = \frac{1}{2}VdU^2 \tag{6}$$

Solving for d,

$$d = \frac{2k}{VU^2}E \tag{7}$$

Let $l=1/d$, then,

$$V=lM \tag{8}$$

Inserting eq.8 into 7,

$$d = \frac{2k}{lU^2}\frac{E}{M} \tag{9}$$

Below, it will be shown that a d vs E/M graph is almost linear for certain sets of explosives for which E values were obtained by means of UB3LYP/6-31G(d) type DFT calculations.

6.3 Computational Method

In the present study, after achieving the initial geometry optimizations by using MM2 method, the semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [36,37] at the restricted level [38,39] were performed. Then Slater-type orbitals (STO), Restricted Hartree-Fock (RHF) and finally Density Functional Theory (DFT-UB3LYP) [40,41] type quantum chemical calculations have been consecutively performed for the geometry optimizations with 6-31G(d) basis set to obtain energetically the most favorable structures of the presently considered species. In DFT calculations the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [41,42]. The correlation term of B3LYP consists of Vosko, Wilk, Nusair

(VWN3) local correlation functional [43] and Lee, Yang, Parr (LYP) correlation functional [44] .

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N$-6 vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred during the geometry optimization process. Geometry optimizations and the vibrational analysis computations were performed by using the Spartan 06 package program [45].

6.4 Results and Discussion

The present research considers various nitro explosives including not only C-NO_2 linkage(s) having compounds but also several nitramine type compounds that contain N-NO_2 linkage(s). Note that some of these structures are acyclic and some are cyclic compounds. Table 6.1 is the list of those explosives as well as some of their calculated properties and molecular weights.

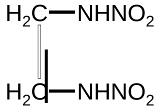
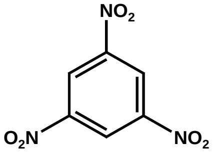
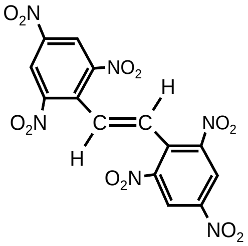
According to formula 9, density of an explosive material is a function of E/M and it should be linear as long as k/lU^2 term is constant (or nearly so). Actually, in eq.9, by definition, $l = 1/d$, thus k/U^2 term has to contribute in such a way to cancel the fluctuations due to variation of densities from one compound to another.

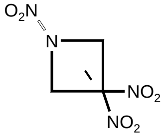
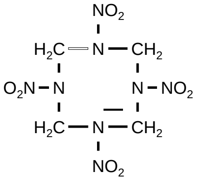
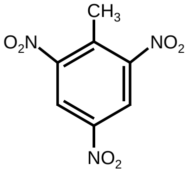
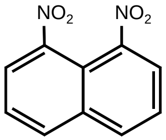
Various explosives have been considered to test if eq.9 is valid. For that purpose, a linear regression equation of type,

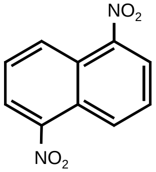
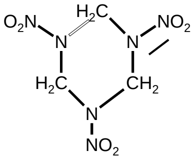
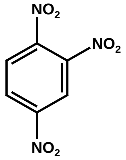
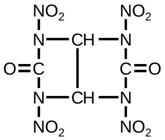
$$Y=AX+B \tag{10}$$

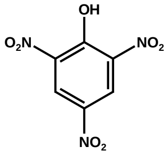
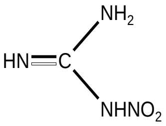
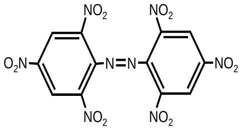
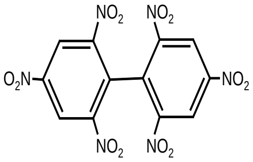
has been used as a model where Y and X stand for d and E/M, respectively. A and B are regression coefficients. Figure 6.2 shows the scatter of d vs E/M data and the best-fit line for the data group. The data points lie along a line, although R^2 value (goodness of fit [46, 47] is low for this set of explosives (the population number, N=30). Since density in eq.9 (derived based on some physical principles) is a linear function of E/M ratio, then compounds on the line in Figure 6.2 are in accord with

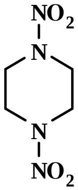
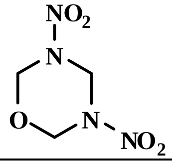
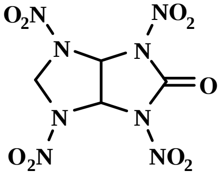
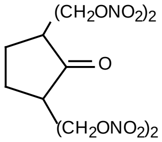
Table 6.1: Some data for the compounds considered (Ω: Oxygen balance, M: Molecular weight).

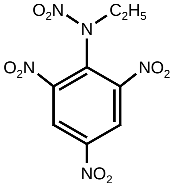
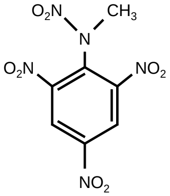
No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
1	**$(CH_3)_2NNO_2$**	DMNA	90	-88.8	-339.56	-3.76946	1.36
2	 $\begin{array}{l} H_2C-NHNO_2 \\ \vert \\ H_2C-NHNO_2 \end{array}$	EDNA	150	-31.98	-599.37	-3.99331	1.75
3		TNB	213	-56.31	-845.63	-3.96813	1.76
4		HANS	450	-67.52	-1767.42	-3.92557	1.74

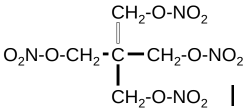
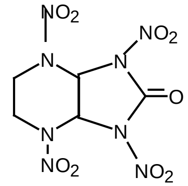
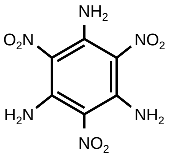
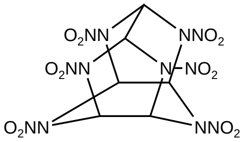
No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
5		TNAZ	192	-16.66	-786.60	-4.09688	1.84
6		HMX	296	-21.61	-1196.35	-4.04174	1.91
7		TNT	227	-73.96	-884.91	-3.89601	1.65
8		1,8-DNN	218	-139.34	-794.72	-3.64269	1.57

No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
9		1.5-DNN	218	-139.34	-794.73	-3.64273	1.61
10		RDX	222	-21.61	-897.26	-4.04173	1.81
11		1,2,4-TNB	213	-56.31	-845.62	-3.96804	1.73
12		SORGUYL	322	4.97	-1343.19	-4.17011	1.98

No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
13		PICRIC ACID	229	-45.39	-920.84	-4.01939	1.76
14		NITRO GUANIDIN	104	-30.75	-409.76	-3.93745	1.77
15		HNAB	452	-49.53	-1799.48	-3.97929	1.79
16		HNDP	424	-52.8	-1690.05	-3.98413	1.74

No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
17			176	-72.73	-676.76	-3.84520	1.63
18			178	-35.95	-712.67	-4.00375	1.82
19			308	-5.19	-1269.16	-4.12064	1.91
20	$(O_2N)_3CC(NO_2)_3$		300	-19.87	-1306.59	-4.35454	1.99
21			384	-57.48	-1546.26	-4.02451	1.62

No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
22		ETHYL TETRYL	301	-61.09	-1183.99	-3.93128	1.63
23		TETRYL	287	-47.36	-1144.70	-4.12332	1.73
24	**$O_2NC(CH_2ONO_2)_3$**		286	0.000	-1201.81	-4.20053	1.64
25	**$CH_3C(CH_2ONO_2)_3$**		255	-34.51	-1036.61	-4.06293	1.47
26	**$HOCH_2C(CH2ONO_2$**		257	-9.34	-1072.53	-4.17148	1.54

No	Compound	Common Name	M (g)	Ω	Corrected total energy (au)	E/M (au/g)	Density (g/cm^3)
27		PETN	316	-10.12	-1635.21	-4.18043	1.80
28			322	-19.87	-1308.46	-4.06166	1.96
29		TATB	258	-55.78	-1011.67	-3.91893	1.93
30		HNIW	438	-10.95	-1196.35	-4.08895	2.04

the theory. When the data points far off the line in Figure 6.2 are removed a subset (N=20) are constituted as shown in Figure 6.3 (which stands for compounds conforming to the theory best), for which R^2 value of the fit is 0.85.

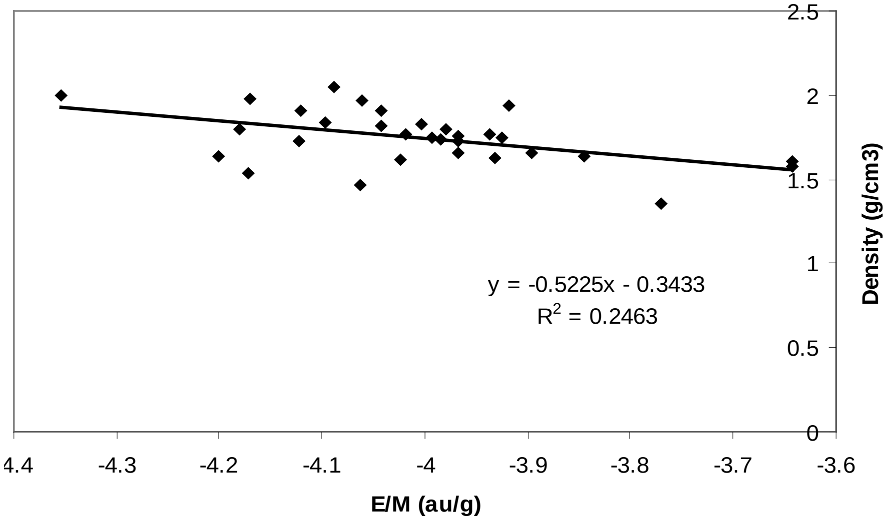


Figure 6.2: The graph of density vs. E/M for various explosives (see Table 6.1 for the structures).

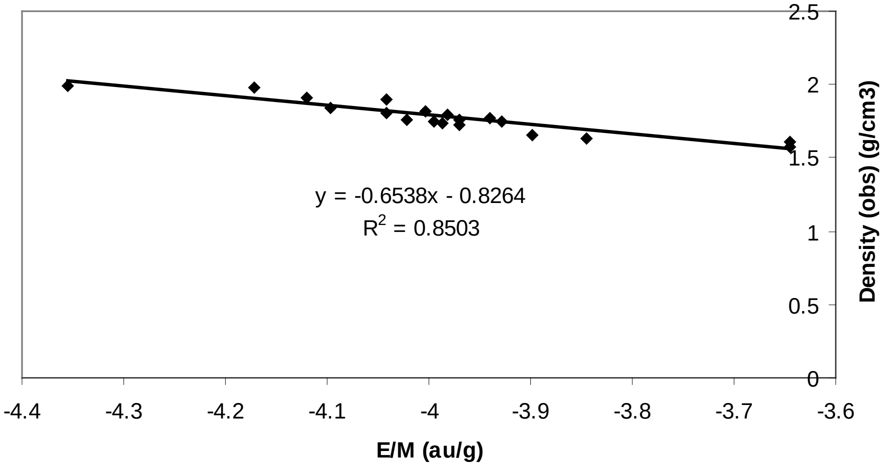


Figure 6.3: The graph of density vs. E/M for some selected explosives (see Tables 6.1 and 6.2 for the extra information).

Compounds used for Figure 6.3 include cyclic and acyclic nitramines, nitro aromatics, etc. Examining the structures involved in Figures 6.2 and 6.3, it is hard to conclude any further structural generalizations that indicate which type of compounds conform to the linear equation of type eq.10, although densities of so many compounds are a linear function of their E/M values. It is also worth mentioning that in deriving equations, it has been assumed at the beginning that the explosive considered is oxygen balanced (for the purpose material balance of the system). However, the results indicate that even oxygen insufficient explosives fall on the straight line, whereas some having better oxygen balance values are off the line. Then, obviously for those compounds on the line, $2k/lU^2$ term does not fluctuate much. It could be an overall effect of each contributor, but also it could be either due to i) normally large value of U as compared to other terms (so the whole term becomes rather insensitive to changes in other multipliers) or ii) comparable values of each term (k, l , U) for the multipliers from compound to compound. Actually, factor "k" in eq. 7, which reflects the fraction of total energy converted to the kinetic energy, should be structure dependent. Then, the velocity U has to be different for each propellant/ explosive.

The regression equation for the compounds 2-20 and 23 (those data points which are not far off the line in Figure 6.2) in Table 6.1 is represented by eq.11.

$$d= -0.6538\ (E/M)-0.8264 \tag{11}$$

that has the R^2 value of 0.85 (σ values for the coefficients are 0.06653 and 0.26513, respectively). The observed and calculated densities (eq.11) as well as percent errors in densities are shown in Table 6.2. The percent errors are within 5% utmost in absolute value and in most of the cases are much less than that. Note that the densities used (excerpted from the literature) are experimental. They might have some errors. On the other hand, density of a compound is highly affected by its crystal packing, whereas the total energies calculated in the present study are for single molecules in the gas phase.

On the other hand, inserting d = M/V in the left hand side of eq.9 one obtains,

$$\frac{M}{V} = \frac{2k}{lU^2}\frac{E}{M} \tag{12}$$

By rearranging eq.12,

$$\frac{2k}{lU^2} = \frac{M^2}{EV} \qquad (13)$$

Then, for propellants having comparable M^2/EV ratios, the $2k/lU^2$ term in eq.9 can be taken as constant. Then, the densities of those propellants/explosives can be predicted by using eq.11. Since, molar volume, V, can be approximated by some additive methods [48-50] the M^2/EV ratios for a series of propellants/explosives can be calculated to check whether eq.13 gives an approximately constant value for the coefficient of E/M ratio in eq.9. If so, eq.11 can be applicable.

According to the present model, k (see eq.13) reflects the fraction of total energy convertible to kinetic energy. Obviously, it should be an implicit function of molecular topology, including chemical bonding and energetic, etc. Inspection of Table 6.2 reveals that gross topology of the molecules are a very important deterministic factor on the densities of the isomeric compounds, and the predictive power of eq.11 is affected accordingly. For instance, 1,3,5- and 2,4,6-TNB or 1,5- and 1,8-DNN are isomeric compounds, but the percent errors (in absolute value) of densities of isomers are different. On the other hand, HNS and HNNB are not isomeric compounds but are isoconjugate of each other, and their gross topologies are similar. They are characterized with low percent errors and comparable densities.

The group or volume additivity methods are the simplest, earliest and most widely used for the density prediction purpose. Basically, these methods are based on summing up volume contributions of atoms or functional groups to get the molar volume. However, these methods have the drawback that they cannot readily account for either the isomerization and conformational changes of molecules or crystal packing efficiency. Namely, the same density value is produced for various isomers or conformations of a particular compound. Also, the crystal density variations due to crystal polymorphism are neglected. In the present treatment density has been shown to be a function of E/M ratio for some nitro compounds including a large spectrum of structures. The E/M ratio is equal to tanØ in the frame work of circular model of detonation velocity developed by Türker. Figure 6.4 shows that relationship. Note that in Figure 6.4, a masses, M_1 and M_2, for two different explosives lie on the ordinate axis. Q_1, Q_2 and $Ø_1$, $Ø_2$ are the angle of detonation velocities and angle of densities, respectively. As shown above for the explosives of present concern, density (d) is a linear function of the E/M ratio.

Note that in the present study, the total energies are obtained by means of precise computational techniques. Thus, E values differ for isomeric compounds and even for conformers. In that sense, the present approach is superior to some empirical or group additive methods. The deviations from linearity arise from the fact that E values have been obtained for isolated molecules in vacuum, whereas density values have been excerpted from the literature for solid materials. In the crystalline form the situation is of course different from the gas phase (vacuum conditions). In theory, different crystalline forms of an explosive material are expressed by different values of Q (the angle of detonation velocity) and Ø (angle of density) [35]. If E values of explosives in solid state are calculated, as a conjecture, E/M ratios should regress with densities in a much better way.

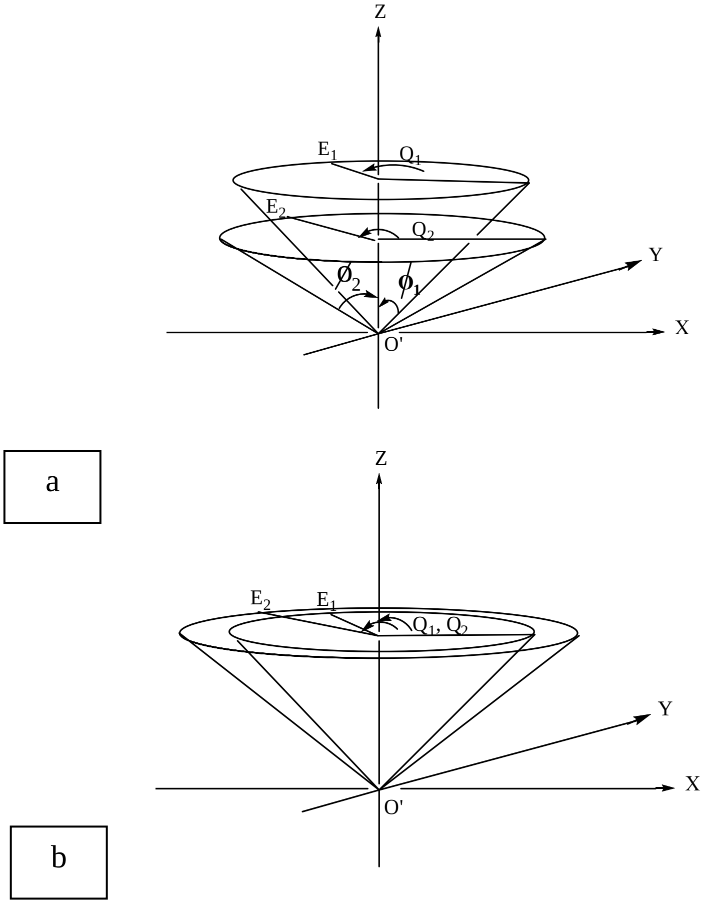


Figure 6.4: The most general form of the model, a) two different explosives, b) two isomeric explosives.

Table 6.2: The observed and calculated (eq.11) densities (g/cm^3) for some of the compounds considered (see Table 6.1 for the structures).

Compound no	d_{obs}	d_{calc}	% error
2	1.75	1.78	1.96
3	1.76	1.76	0.42
4	1.74	1.74	-0.32
5	1.84	1.85	0.61
6	1.91	1.81	-4.63
7	1.65	1.72	3.98
8	1.57	1.55	-1.41
9	1.61	1.55	-3.55
10	1.81	1.81	-0.48
11	1.73	1.76	2.16
12	1.98	1.90	-4.02
13	1.76	1.80	2.38
14	1.77	1.74	-1.27
15	1.79	1.77	-0.85
16	1.74	1.78	2.17
17	1.63	1.68	3.36
18	1.82	1.79	-1.66
19	1.91	1.87	-2.25
20	1.99	2.02	1.61
23	1.73	1.77	2.86

As seen in Table 6.3, the angle of densities (Ø) varies in rather a small range. The average value is -1.32582 rad and skewness is 0.760205. However, densities are dictated by such small changes. For example, the isomeric compounds 8 and 9 (or 3 and 11) have almost the same Ø values. Then, the difference between the densities for those structures is mainly due to the total energy (E) differences of such isomers. Note that the angle of detonation velocity (Q=f(arccos (D/E)) where D: detonation velocity [32-35]) and angle of density (Ø) are independent from each other.

Table 6.3: The E/M ratios and angle of densities (see Table 6.1 for the structures).

No	E/M (au/g)	Ø (rad)
1	-3.76946	-1.31148
2	-3.99331	-1.32542
3	-3.96813	-1.32393
4	-3.92557	-1.32136
5	-4.09688	-1.33139
6	-4.04174	-1.32825
7	-3.89601	-1.31955
8	-3.64269	-1.30287
9	-3.64273	-1.30288
10	-4.04173	-1.32825
11	-3.96804	-1.32392
12	-4.17011	-1.33544
13	-4.01938	-1.32695
14	-3.93745	-1.32208
15	-3.97929	-1.32459
16	-3.98412	-1.32488
17	-3.84520	-1.31637
18	-4.00375	-1.32604
19	-4.12064	-1.33272
20	-4.35454	-1.34507
21	-4.02451	-1.32725
22	-3.93128	-1.32171
23	-4.12332	-1.33287
24	-4.20053	-1.33708
25	-4.06293	-1.32947
26	-4.17148	-1.33551
27	-4.18043	-1.3360
28	-4.06166	-1.32939
29	-3.91893	-1.32096
30	-4.08895	-1.33094

6.5 Conclusion

The present study has shown that densities of so many explosives conform to a linear relation, which is a function of E/M ratios. Thus, some light has been put on the factors effective on densities of explosives at the molecular level. The mathematical model and the regression equation obtained can be tested for a much larger group of explosives for the purpose of amelioration. Also, many advanced basis sets can be used for better geometry optimizations. Even in the present form it might be used to guess the densities of nonexistent explosives in explosive design procedures. Note that density of an explosive is important for the calculation of detonation velocity of it. The presently considered surprising relationship between the densities of those explosives and their E/M ratios might be arising from fact that an E value is geometry dependent, thus it should be an implicit function of volume.

6.6 References

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Chapter 7

Characterizations of Energetic Polynitrogen Compounds

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Energetic Materials are widely used for different applications due to their detonation ability. However, detonation, which is the main explosive property, is to be avoided for the aims of rocketry. The effectiveness of explosives depends on the energy concentration, which is dependent upon their density and energy content. HMX is a standard to which other high-energy compounds are compared. The search for high-density and high-energy compounds led to the synthesis of CL-20 at the Naval Air Warfare Center in China Lake, California. At the same time, synthesis chemists came to understand that an increase in the number of NO_2-groups does not always ensure an increase in density (e.g., octanitrocubane).

Recent research has considered the synthesis of polynitric substances as a way to create new high energy compounds. There are many promising prognoses for their density and the enthalpy of formation. Compounds that are built with the N-atoms only ("polynitrics") were estimated to be twice as powerful as HMX. But polynitrics are not an isolated area of chemical compounds. Therefore, during our work forecasting the properties for "polynitrics," we considered all polynitrics, not just those known to be energetic. Our forecasts are made on the basis of the relationships between chemical content and structure, on the one hand, and the energetic parameters (found out by analyzing a huge number of compounds that were studied earlier), on the other hand.

7.1 History

Up to the end of the 1960's, the main way to search for promising structures was laboratory synthesis. There were not many rules to guide the selection of target molecules. Perhaps, the only requirement was to search for compounds with high oxygen balance and high heat of explosion. It was known these compounds would have the high detonation velocity, a characteristic of effective explosives.

In the 1950's a goal was to obtain explosives with the detonation velocity exceeding 25000 m/s. In the 1970's the goal was to exceed 10000 m/s. This empirical approach is understandable given the absence of methods to model the basic characteristics of EM-s at that time.

Synthesis results in the 1970's and 1980s enabled scientists to formulate some simple models that were useful to guide synthesis chemists toward specific classes of compounds. For example, Eremenko et al. [1-3] assumed the existence a density limit for C,H,N,O compounds. This limit was determined with structure and physicochemical property relationships. About the same time, F. Walker [4-6] hypothesized that limited the value of detonation velocity of C,H,N,O compounds to the range of 10,000 to 12,000 m/s. Walker's idea was that detonation velocity is determined by compound structure and the nature of the detonation process.

Investigations of energetic characteristics (e.g., thermo chemical properties) of explosives were considerably expanded. Fundamental studies of thermo chemical properties for organic compounds were done at the Institute of Chemical Physics of the Russian Academy of Sciences by Yu. Lebedev, V. Pepekin, Yu. Matyushin, E. Miroshnichenko, and more [7-9]. These investigations found dependence of the enthalpies of formation, evaporation, sublimation, and more on the structure of compounds. Based on these studies, computational methods were developed to estimate thermo chemical and impulse characteristics of compounds and density. These methods provided guidance to synthesis chemists in search of more powerful Energetic Materials. Still, these computational methods did not allow estimation of other characteristics of compounds, such as relationships between explosives properties, structure, and safety characteristics.

It is known there are different ways to calculate physical-chemical parameters of EM-s. There are additive schemas, molecular mechanics, quantum chemistry, computer simulation, statistics models, and more. An example of a procedure for the basic characteristics evaluation is the Quantitative Structure-Property Relationship (QSPR) approach. The main principles of all these approaches have been presented in some papers and monographs [10-29]. Each approach has advantages and disadvantages.

Consider polynitrogen compounds as explosives. In the literature there are data overestimating the performance of these compounds and their physical-chemical parameters. The effectiveness polynitrogen compounds in propellants is overestimated too. For example, based on calculated performance, the synthesis of tetraazatetranitrocubane, hexaazadinitrocubane and other polynitrogen compounds has been proposed [30-34]. However, the performance calculations have proved to be overestimations, not in harmony with previous investigations of physical-chemical parameters for Energetic Materials.

The goal of the present study is the development of principles for reliable, science based forecasts of the performance of EM-s. Our goal is to find the limits for physical-chemical parameters of EM-s and provide statistical models for their determination.

7.2 Methodology

One of our main principles for the forecasting performances of EM-s is the statement that ***energetic compounds do not represent some isolated class of chemical substances***. They are related with the aggregate of chemical substances sharing a lot of similarities with other chemical substances in the same class. Therefore the investigation of the similarities is not limited to energetic compounds. The basic set for designing computational schemas is to make them as large as possible, but not so large as to be of no practical utility. The necessary requirements of statistical models (we are considering namely these models for forecasting of physical-chemical performances for EM-s) are the assurance of randomization, orthogonality, and richness of the initial data file.

It is impossible to provide any adjusted step in chemical content variation, because changing the content of any element requires changing the content for all elements. The process of elements content change is related to the rules of modeling incoming functional groups and the basis molecule frame. All regions of chemical substances' existence are built on clear rules, and the performance’s change inside this region cannot be casual. Therefore, a regressive equation, describing any performance, is reliable only for the region in which the values were investigated. The possibility to extrapolate the regularities outside the range in which the values were investigated has to be controlled with special procedures that determine the regularities outside of the known region. The requirement of using the largest file of experimental data enables the aspiration to provide high calculation accuracy.

The procedure to detect regularities among a number of factors, for examples chemical structure and chemical content, uses regression analysis. A single step regression analysis is used to discover the relative importance of factors such as chemical structure and chemical content. The most important factors (the valuable factors) are included in the subsequent analysis; the least important are excluded from the analysis. Along with screening of experimental data, a traditional statistic procedure has been carried out too. As a rule, this procedure was conducted through a few of iterations with the output of new regularities and with the evaluation of accuracy by statistical methods after each step. The amount of deselected results was usually not higher than 10-20% of the initial file.

As an example of the formulated basic principles, we are considering the density **ρ** as it is a very important parameter of Energetic Materials. Fig.1 illustrates the interconnection of the density with the specific summary content for moles of chemical elements (**B**) in the structure of compounds. The value **B** (so called «gross-sum») is the sum of all atoms in gross-formula, referred to the molecule mass.

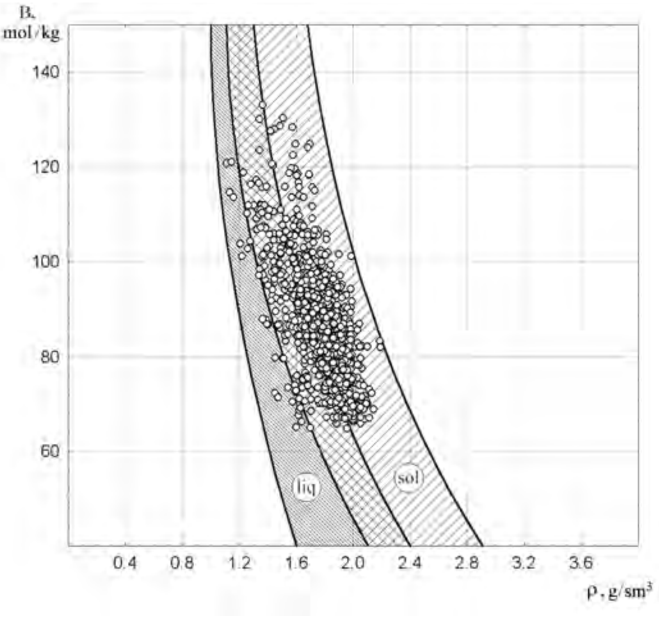


Figure 7.1: Dependence of ρ upon B for 900 ($C_aH_bN_cO_d$) chemical substances (the domain of energetic compounds is situated among points «○»).

In Figure 7.1, the area shaded with positive sloping lines is the domain of solid compounds. The area shaded in gray corresponds with liquids. The area between these two shadings is the area of existence of both solid and liquid compounds. Outside these regions, energetic compounds cannot exist in these two aggregative states (limited values of physical-chemical performances will be demonstrated below). We should note that the gross-sum (**B**) of «polynitrics» (N_x) is equal to 71.4 mol/kg. Thus according to Fig.1 the maximal density for polynitrics is not higher than 2.3 g/cm^3.

7.3 Calculational Tools for Prediction of EMs Parameters

Based on the stated principles, we have elaborated the statistical models for evaluation of basic physical-chemical performances for compounds from different chemical classes, which may be used as high energy materials.

We have studied experimental data of 250 individual energetic compounds considering the following characteristics: heat of explosion (55 compounds), detonation velocity (138 ones), C-J pressure (90 ones), shock sensitivity by large scale gap-test (25 ones), metal acceleration performance (74 ones), as well as some other parameters.

The set of experimental compounds under consideration had the following range in elements content (gram-atoms/kg):

$C \in [0; 44.1]$; $H \in [0; 49.1]$; $N \in [7.0; 39.3]$; $O \in [0; 40.8]$.

For estimation the correlations between EM-s parameters, on one hand, and the element content and the molecular structure, on the other hand, we developed new methods for the main EM-s parameters calculations. The regression analysis procedure was used. Average (%) and root-mean-square errors were the following: 0.077 and 1.256, respectively, for the detonation velocity; 0.59 and 6.84 for the C-J pressure; 0.11 and 1.88 for the metal acceleration performance; and 0.28 and 3.45 for the heat of explosion. The value of the relative deviation of calculations was almost constant for all the area of variation.

Metal acceleration is a way to estimate the effectiveness of an explosive and compositions containing it. Metal acceleration is determined by measuring the rate of expansion of a cylinder accelerated by a detonating explosive, or by measuring the velocity of a plate thrown by a detonating explosive. Cylinder expansion may be used for derivation of an equation for the state of detonation products [35].

In our study the metal acceleration performance in comparison with HMX (η) has been estimated from the velocity of a butt end bar thrown by explosion products:

$$\eta = 1.23\cdot\rho^{0.871}\cdot Q_{cal}^{0.432}\cdot N_g^{0.230} \qquad (1)$$

The critical pressure of detonation initiation (P_{cr}) is also a valuable parameter for explosives effectiveness evaluation. The method of its measurement is the Gap-test [36, 37] (the transfer of an initiating variable impulse through an inert barrier). P_{cr} correlates with characteristics describing the material stability to shock, to penetrative actions, and parameters of combustion to explosion transfer.

We calculated P_{cr} as the shock sensitivity of a compound in a large scale gap test (eq.2):

$$P_{cr} = (\rho\cdot B)^{2.732}\, Q_{max}^{-1.534}\cdot\alpha^{-1.105} - 5 \qquad (2)$$

For many decades detonation velocity (D) has been considered to be the most informative detonation parameter. D is a simple parameter to measure accurately and repeatedly. In our investigation the detonation velocity (D) has been estimated with:

$$D = 0.481\cdot\rho^{0.607}\cdot c^{0.089}\cdot\alpha^{0.066}\cdot Q_{cal}^{0.221}\cdot N_g^{0.19} \qquad (3)$$

C-J-detonation pressure ($P_{C\text{-}J}$) is also considered for explosives effectiveness evaluation. However, in our opinion, this value determines just a shattering effect of the explosion. We suggested estimation the C-J-detonation pressure ($P_{C\text{-}J}$) with:

$$P_{C\text{-}J} = 2.139\cdot 10^{-2}\cdot\rho^{2.100}\cdot c^{0.102}\cdot\alpha^{0.147}\cdot Q_{max}^{0.519}\cdot N_m^{0.554} \qquad (4)$$

Calorimetric heat of explosion (Q_{cal}) is the main energetic parameter of explosion and widely used for preliminary evaluation of energetic abilities of explosives as well as for the calculation of different kinds of explosion and detonation parameters. The Q_{cal} numerical value is equal to the maximum efficiency work of explosion. The method for this parameter estimation [40-42] is based on measuring the temperature growth (due to the heat release at the explosion) of the calorimetric liquid in a calorimetric chamber. Calorimetric heat of explosion for compounds containing C,H,N,O-elements is estimated with:

$$Q_{cal} = Q_{pvm}\cdot 4.261\cdot\rho^{0.291}\cdot c^{0.049}\cdot d^{0.072}\cdot(\Delta H_f^0 + 1000)^{-0.261}\cdot a^{-0.107}\cdot b^{-0.012} + \Delta H_f^0 \qquad (5)$$

Calorimetric heat of explosion for compounds containing C,H,N,O,F- elements is estimated with:

$$Q_{cal} = Q_{pvm} \cdot 0.59 \cdot \rho^{0.075} \cdot (\Delta H_f^0 + 1000)^{0.018} \cdot a^{-0.063} \cdot c^{0.132} \cdot e^{0.027} + \Delta H_f^0 \tag{6}$$

The number of moles of gaseous products (N_g) is determined in the same experiment as the heat of explosion by gas pressure measurement after the explosion [40-42]. Together with the heat of explosion, the value N_g is used for calculations of detonation parameters and explosion action. The number of moles (N_g) of gaseous combustion products is calculated with:

$$N_g = 0.777 \cdot \rho^{-0.153} \cdot B^{0.715} \cdot (\Delta H_f^0 + 1000)^{0.1} \cdot Q_{max}^{0.238} \tag{7}$$

where ρ is the density of explosive; Q_{max} – maximal heat of explosion; B – gross-sum of gram-atoms for all chemical elements containing in 1 kg of the explosive under consideration,·α - the coefficient of oxidizer excess; Q_{cal} – calorimetric heat of explosion; N_m - amount of moles of gaseous combustion (explosion) products corresponding to Q_{max}; a,b,c,d,e – amount of moles of chemical elements in 1 kg of $C_aH_bN_cO_dF_e$-explosive; Q_{pvm} – maximal energy of combustion products; ΔH_f^0 – the enthalpy of formation.

We compared the accuracy of the main physical and chemical parameters calculated using our method to others [41, 43-45]. Using the dispersive analysis we determined that our technique (equations 1-7) is of higher accuracy than the others.

The advantage of our methods for evaluation of properties for individual and composite explosives (equations 1-7, as well as others, described in [39]) is not only their high accuracy but also the small number of parameters used in the calculations. We should note that all calculated methods examined by us are based on using the similar set of sampling parameters for composition and structure. Therefore, to estimate the adequacy of calculation results, one can use the experimental data of one or two detonation parameters but not the whole set of characteristics calculated with the equations 1-7. For example, the detonation velocity is one of the most accurately determined characteristics for a detonation process, and thus it may be used for the evaluation of appropriateness for explosives parameters prognosis as a whole. To verify the comparative accuracy of our complex schema for explosives properties calculations in Table 7.1, the experimental and calculated data of detonation velocity are presented.

Table 7.1: Comparison of calculated and experimental values for detonation velocity of explosives with C,H,N,O-atoms.

	Explosive	ρ, g/cm^3	D, km/s		Error	
			Exp.	Calc.	Abs.	%
1	NQ	0.510	3.49	3.51	0.02	0.46
2		1.590	7.38	7.36	-0.02	-0.25
3		1.740	7.72	7.81	0.09	1.14
4	TATB	1.800	7.57	7.57	0.00	0.01
5		1.847	7.66	7.70	0.04	0.52
6		1.895	7.86	7.83	-0.03	-0.39
7	TNT	0.732	4.20	4.12	-0.08	-1.94
8		1.450	6.40	6.43	0.03	0.51
9		1.645	6.96	6.98	0.02	0.35
10	NTO	1.770	7.79	7.72	-0.07	-0.85
11		1.810	7.96	7.84	-0.12	-1.54
12	HMX	0.850	5.45	5.33	-0.12	-2.12
13		1.680	8.34	8.32	-0.02	-0.24
14		1.899	9.11	9.01	-0.10	-1.07
15	PETN	0.500	3.60	3.61	0.01	0.20
16		1.600	7.77	7.70	-0.07	-0.85
17		1.770	8.22	8.23	0.01	0.10
18	CL-20	1.710	8.47	8.30	-0.17	-2.02
19		2.000	9.40	9.44	0.04	0.42
20	Glycol dinitrate	1.480	7.49	7.56	0.07	0.88
21	NM	1.138	6.29	6.19	-0.10	-1.59
23	TNM/NM 18.6/81.4	1.197	6.57	6.51	-0.06	-0.95
25	TNAZ	1.840	8.73	8.78	0.05	0.63
26	Comp.B	1.713	8.03	8.07	0.04	0.47
27	Pentolit-50/50	1.650	7.47	7.42	-0.04	-0.58
29	Octol-23/77	1.825	8.60	8.55	-0.05	-0.55
30	HMX / BTNENA 30/70	1.880	9.10	9.09	-0.01	-0.08
31	HMX / TNAZ 60/40	1.851	8.98	8.87	-0.11	-1.26

The accuracy of the calculations made with equation (3) has been compared with the accuracy of experimental data [44-49]. All of them, in any event, connect the detonation velocity with the explosive structure and chemical content. The detonation velocity was calculated according to each method. Then the deviation between the calculated and the experimental data was determined. Then using a procedure known as dispersion analysis, the selected dispersions were found, as well as the corresponding Fisher criterion (F-criterion). The F-criterion was compared with tabulated values [50]. The values of errors, dispersions, and F-criterion for each of above-mentioned methods are presented in Table 7.2. It is evident that our method is more accurate in comparison to all others.

Apparently, the reason the others are less accurate is that they are based on smaller data files corresponding to a smaller range of explosive characteristics and structures. Having data on high-nitrogen, high-enthalpy, and high-density substances allowed us to expand the data files on which our equations are based far beyond the data files of the others.

Table 7.2: The accuracy of detonation velocity calculations using different methods*).

No	Method	Error, km/s		Dispersion, (s^2)	F
		Mean error average	Standard deviation, (s)		
1	Avakyan [46]	0.262	0.622	$3.87 \cdot 10^{-2}$	56.19
2	Pepekin [48]	$2.2 \cdot 10^{-2}$	0.225	$5.07 \cdot 10^{-2}$	7.37
3	Kamlet [44]	$1.0 \cdot 10^{-2}$	0.294	$8.64 \cdot 10^{-2}$	12.56
4	Aizenshtadt [47]	$1.4 \cdot 10^{-2}$	0.258	$6.66 \cdot 10^{-2}$	9.68
5	Calculations with equation (3)	$3.7 \cdot 10^{-4}$	0.083	$6.88 \cdot 10^{-3}$	-

*)Table value of F-criterion for 400 compounds with probability of 0,95:1,78 [50].

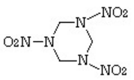
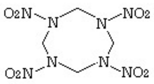
The estimation of 250 individual energetic compounds has been carried out using published methods [39, 51] for predicting explosive properties. In the substances set under consideration there were organic compounds from different chemical classes with the following range of element content (mol/kg): $C \in [0; 45.8]$, $H \in [0; 60.0]$, $N \in [7.0; 49.9]$, O∈[0; 43.0] (for the full-nitrogen compounds (N_x), naturally, N = 71.4 mol/kg). Such a wide range of element content covers practically all regions of any covalent EM-s substances existence. Thus, based on such a wide set of substances and using rather precise calculation methods we may affirm that our complex system for predicting explosives properties should be quite effective.

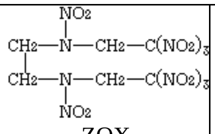
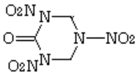
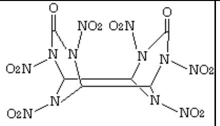
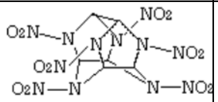
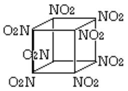
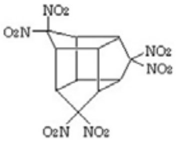
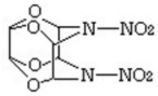
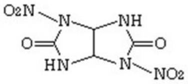
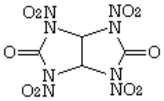
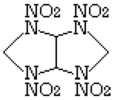
7.4 Analysis of the Possible Capacity for Energetic Materials Parameters

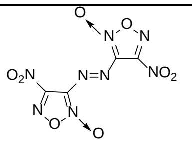
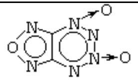
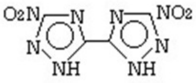
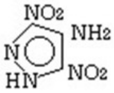
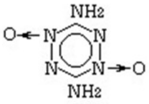
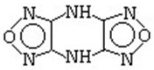
7.4.1 Powerful Explosives

In 1970s and 1980s investigators anticipated that explosive characteristics, providing exploitation and technology safety, must be close to RDX parameters. After synthesis of powerful explosives such as CL-20 and TNAZ, the level of the safety performances was appreciably decreased (up to PETN level). The increase of performance may be accomplished either with the balancing of oxidizer and combustible fragments in the substance under consideration or with the introduction of high-enthalpy structures. Table 7.3 represents the main parameters, determining the increase of the explosive energy. If in column D there are two values, the first one is the *experimental* detonation velocity D, and the second one is the *real density of the charge* (i.e. 8600_{1730}); if in column D there is only one value, it means the *calculated* detonation velocity for monocrystal density.

Table 7.3: The main parameters of some powerful explosives.

No	Compound	α	$\rho_{0,}$ g/cm^3	ΔH_f^0	Q_{cal}	D, m/s	P_{CJ}, GPa	η, %	P_{cr}, GPa
				kJ/kg					
1	 RDX	0.67	1.816	276	5564	8600_{173}	32.7	96.7	2.05
2	 HMX	0.67	1.907	251	5523	9100_{190}	36.1	100	2.4

3	 ZOX	1.00	1.875	14	6426	9100_{187}	35.9	$102^{1)}$	1.5
4	 K-6	0.88	1.930	-182	5543	$9170^{1)}$	36.0	$99^{1)}$	2.0
5	 HHTDD-1	1.00	2.071	-33	$5774^{1)}$	$9800^{1)}$	$42.5^{1)}$	$105.7^{1)}$	$1.2^{1)}$
6	 CL-20	0.80	2.040	837	$5857^{1)}$	9460_{1930}	$42.8^{1)}$	$105.9^{1)}$	$1.6^{1)}$
7	 ONC	1.00	1.982	937	$7271^{1)}$	$9350^{1)}$	$39.0^{1)}$	$108.2^{1)}$	$0.9^{\ 1)}$
8	 HNPU	0.46	1.840	366	$5309^{1)}$	$8010^{1)}$	$26.4^{1)}$	$95.1^{1)}$	$2.9^{1)}$
9	 TEX	0.53	1.990	-2063	$3598^{1)}$	$7950^{1)}$	$28,1^{1)}$	$83.4^{1)}$	$8.3^{1)}$
10	 DINGU	0.60	1.982	-1347	$3958^{1)}$	$8260^{1)}$	$27.9^{1)}$	$84.7^{1)}$	$5.2^{1)}$
11	 Sorguyl	1.03	2.030	155	5440	9260_{203}	$39.7^{1)}$	102	$1.3^{1)}$
12	 BC-HMX	0.73	1.890	701	$5831^{1)}$	$9060^{1)}$	$35.7^{1)}$	$101.2^{1)}$	$1.6^{1)}$

13	 ANF	1.00	2.000	2320	7280[2]	9700[2]	40.6[2]	110.3[2]	0.2[2]
14	 FDTO	0.75	1.852	4184	7530[1]	9600[1]	40.3[2]	106[1]	0.3[1]
15	 DNPP	0.44	1.870	1373	4770[1]	8320[1]	27.7[1]	90.5[1]	3.0[1]
16	 DNBT	0.44	1.820	1405	4396[1]	8160[1]	26.0[1]	85.5[1]	3.1[1]
17	 LLM-116	0.53	1.930	0	4419[1]	8450[1]	30.0[1]	90.7[1]	4.1[1]
18	 LAX-112	0.33	1.860	1395	4151[1]	8340[1]	28.4[1]	88.6[1]	9.6[1]
19	 PDF	0.22	1.932	2353	4320[1]	8340[1]	25.5[1]	92.1[1]	10.5[1]

[1] – the calculated value (calculation of the detonation velocity and the metal acceleration performance in comparison with HMX (η) has been carried out for the density value indicated in the column ρ_0);

[2] – calculation accordingly the data [7,8 and some others].

Let us consider the main ways to increase energy for some nitramines (see, for example, K-6 (keto-RDX) [52]) and ZOX (1,1,1,3,6,8,8,8,-octanitro-3,6-diaza-octane [53], No 5, Table 7.3). The heat of explosion for ZOX is higher than HMX by 1000 kJ/kg. That difference almost compensates for the density decrease of 0.03 g/cm^3. The metal acceleration performance of ZOX is 2% higher than for HMX. It is an important example of the interrelation between density and energetic capacity. In molecule HHTDD-1 (2,4,6,8,10,12-hexanitrazatricyclo (7.3.0.0) dodecan-5,11-dione [54], No 5, Table 7.2), the hydrogen content is lower than in K-6. The number of cycles is higher and that may be the reason for increased density (up to 2.07

g/cm^3). Correspondingly, even in the case of slightly increasing the explosion heat value, the metal acceleration performance for HHTDD-1 is 105.7% of HMX. Parameters of CL-20 [55,56] also illustrate the influence of the number of strained cycles and decrease of hydrogen content on the performance.

A long-term search for ways to synthesize octanitrocubane (ONC) had rather ambitious perspectives. However, the compound synthesized had a monocrystal density 0.2 g/cm^3 lower than the expected value. So the beam of hope for ONC disappeared. CL-20 is a compound of a new generation with unique properties. But its comparison to other representatives of nitramines shows that CL-20 does not have the highest parameters in this class of compounds.

Investigations for improving the technology process of obtaining CL-20, as well investigations of neat CL-20 and formulations basing on CL-20, have been carried out. As a result of wide international cooperation, the production technology of CL-20 and the properties of CL-20 formulations are well understood. In some papers [14] it was shown (using «Drop height» and «Friction test») that the sensitivity level of CL-20 is close to PETN. So far all attempts to improve the quality of CL-20 crystals and to decrease its sensitivity (as was done with I-RDX) failed.

ONC and HNPU (4,4,8,8,11,11-hexanitropentacycloundecane) [57], No 7, Table 7.2) demonstrate that neither the number of nitro groups nor number of internal cycles increase the density or explosion effectiveness. On the other hand, high density does not guarantee high effectiveness (e.g., TEX (diazatetracyclo-(5.5.0.05,9 03,11)dodecane) [58] and DINGU (dinitroglycoluril) [59] (No. 9 and No. 10 in Table 7.2)). It is wrong to consider density and energetic capacity separately. We have to consider the influence of change of chemical content on all explosive parameters. Contrary to the above example (influence of density on the effectiveness), Sorguyl (No 11, Table 7.2 [60]) overpowers in both α value and density. But accompanied by reductions in formation enthalpy and heat of explosion, the advantage of Sorguyl over BC-HMX in the metal acceleration performance is rather negligible.

In the 1970s and 1980s, furazan and furoxan derivatives were considered as promising explosives. The introduction of diazene groups increased the energy capacity of ANF (4,4'-dinitro-azofuroxan) [62] and increased the metal acceleration. But the safety properties of ANF are unacceptable (see, e.g., the values of shock sensitivity (P_{cr})). The compound FDTO (furazanotetrazinedioxide) [63] has an extremely high enthalpy of formation (among all synthesized explosives), as well as the worst safety properties (e.g. shock sensitivity values). Resuming the analysis of furoxan derivative parameters, we have to notice that structural peculiarities of these substances are the reason for the relatively low mechanical strength of the crystals.

Besides, we should notice that the example of substances No 14-19 [64-68] in Table 7.1 is evidence of the fact that the enthalpy of formation is not the main factor determining the metal acceleration performance.

7.4.2 Oxidizers

Explosive oxidizers are considered here as a separate group for their future prospects. An α value of more than 1.0 is not advisable for the power of an individual explosive.

But the emphasis in listing oxidizers is generally based on the requirement of $\alpha \geq 1$. An advantage is gained for explosives with «excess» oxygen in mixtures, and this points the way in a search for perspective compounds.

Table 7.4 lists the calculated parameters for some oxidizers that are of the highest interest because of their properties. Ammonium perchlorate (AP), the most widely used compound in solid composite propellants and explosive compositions, is included for comparison.

Ammonium dinitramide (ADN) [69,70] has an α value equal to 2, that is lower than the value α of AP (2.67), but the main advantage of ADN in comparison with AP comes from the higher value of the enthalpy of formation; and that is why ADN has been chosen as a better oxidizer in many formulations for solid composite propellants.

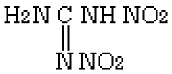
Alternatively, the lower density of ADN weighs against its successful use in explosive compositions, where the «cost» of density is rather more important than in rocket propellants.

Table 7.4 lists equal values of P_{cr} for DNQ (dinitroguanidine [71]) and GNF (guanidine nitroformate [72]) at 1.2 GPa, much higher than for BTNENA (bis(2,2,2-trinitroethyl) nitramine [73]).

The detonation parameters for bis(2-difluoramino-2,2-dinitroethyl) nitramine (B(DFADNE)NA) have been published previously [74]. Table 7.4 shows that the molecular structure of B(DFADNE)NA leads to a reasonable density and power for the compound.

Sometimes our calculations give lower values for the listed properties than have been reported by other researchers. But we stand by the very high energetic properties that are reported here. We note that these substances are extremely dangerous. Increase of the enthalpy of formation and molecular crystal density (that is the main way to raise performance) to such upper limiting values provides additional proof that the thermal stability of the substances should fall drastically. Notice should be taken that rather high variations in estimated performances are often due to difficulties encountered with the value of the explosion heat in the throwing process, and due to the neglect of this consideration using metal acceleration performances in many calculating algorithms.

Table 7.4: The main parameters of some oxidizers.

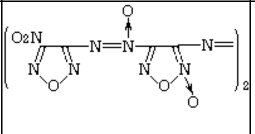
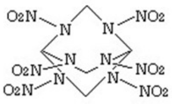
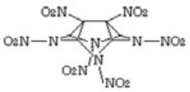
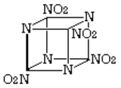
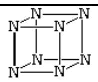
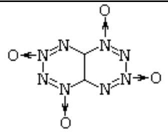
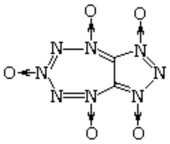
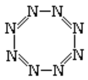
No	Oxidizer	α	$\rho_{0,}$ g/cm^3	ΔH_f^0	Q_{cal}	D, m/s	P_{cr}, GPa
				kJ/kg			
1	NH_4ClO_4 AP	2.67	1.950	-2125	2008	4390	3.4
2	$(NO_2)_2\bar{N}\ NH_4^+$ ADN	2.00	1.840	-1209	3096	6480	2.5
3	 $H_2N\,\underset{\underset{N\,NO_2}{\|}}{C}\,NH\,NO_2$ DNQ	1.14	1.906	0	4979	9200	1.2$^{1)}$
4	$H_2N-NH_2\cdot CH(NO_2)_3$ GNF	1.33	1.910	-393	5146	9200	1.2$^{1)}$
5	$O_2N\,N[CH_2C(NO_2)_3]_2$ BTNENA (HOX)	1.4	1.960	-63	5397	8750	6
6	$O_2N\,N[CH_2C(NO_2)_2NF_2]_2$ B(DFADNE)NA	1.25	2.045	-100	6234	9100	0.3

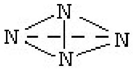
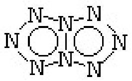
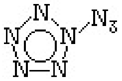
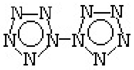
Analysis of much experimental data on the explosion heat and the metal acceleration performance test [75-77 and others] showed that the missile velocity correlates most strongly with the calorimetric heat of explosion, and such consideration allows for the estimation of performance with an accuracy close to the experimental accuracy.

7.4.3 Hypothetical Structures

Table 7.5 provides calculated parameters of some hypothetical structures. It also shows (No 2-3) an increase of density for 2,4,6,8,9,11-hexa(nitroaza)tricycloundecane (HNTU) and 1,3,5,7,9,10-hexanitro-1,5,9,10-tetraazapenta-cyclodecane (HNTPD). Molecules containing oxidizer and fuel in the optimal ratio (e.g. OANT (octaazanaph talinetetraoxide)) also offer a preferable way to increase explosives effectiveness in comparison with polynitrics No 8-12 (Table 7.5).

Table 7.5: Calculation data for hypothetical structures of power explosives.

No	Compound	α	ρ_0, g/cm^3	ΔH_f^0	Q_{cal}	D, m/s	P_{CJ}, GPa	η, %	P_{cr}, GPa
				kJ/kg					
1	 BNAFFO	0.75	1.99	3260	7320	9700	43	110 (122)	0.9
2	 HNTU	0.86	2.01	1200	6513	9750	44	111.3 (124)	1.2
3	 HNTPD	0.86	2.02	736	6137	9390	40	106.4 (113.2)	1.0
4	 TNTAC	1.00	2.04	1810	7030	9860	45	110 (121)	0.6
5	 OAC	-	2.28	5615	5615	10970	59.7	112.9 (127.5)	0.1
6	 OANT	1.00	2.22	3350	7030	10700	55	120 (144)	0.5
7	 GATO	1.25	2.26	3170	6700	10800	53	119 (141)	0.4
8	 OATE	-	1.81	6200	6200	9950	42	99 (98)	0.4

9	 TATE	-	1.513	6800	6800	9060	26.9	89.8 (80.8)	0.1
10	 PP	-	1.94	6443	6443	10290	43.3	105.4 (111.1)	0.4
11	 PA	-	1.77	6109	6109	9640	34.8	95.7 (91.6)	0.2
12	 BP	-	1.93	5569	5569	9920	39.7	98.5 (97)	0.6

* in the column for «η», the value in parentheses is obtained from the square of the velocity of butt-end-bar throwing as this parameter is used by several researchers.

7.5 Effectiveness of Compounds as Components for Solid Composite Propellants

Energetic compounds from Tables 7.3-7.5 were investigated as potential components of solid composite propellants (SCP), mainly as oxidizers. Definitely, it is difficult to call compounds of formula N_x or compounds with an α value lower than 0.5 as «oxidizers», but in principle, if the enthalpy of formation is very high, such compounds may serve as rather energetic components of compositions and can have rather high specific impulse (I_{sp}) [77]. In that case the main problem is the question of the enthalpy of formation value that may compensate for partial or even full absence of oxygen in a compound.

The ballistic effectiveness of an SCP depends not only on its I_{sp} value but also on many other parameters (density, combustion temperature T_c, combustion lowering, sensitivity to mechanical influence, thermal stability, chemical compatibility, etc.). In this work we are comparing compounds under consideration according to the maximum value of I_{sp} that they may provide. Since an SCP must contain at least 18 volume percent of a binder (for guarantee of the necessary properties of propellant mass before solidification and satisfactory physico-mechanical properties of solidified propellants), we are considering the I_{sp}, d, T_c parameters only for compositions containing that optimal percentage of binder.

Two different types of binders have been considered – the standard hydrocarbon binder (HCB, $C_{73,17}H_{120,9,}$ $\Delta H°_f$ = -381 kJ/kg, ρ=0.91 g/sm^3) and the active binder (AB, $C_{18,96}H_{34,64}N_{19,16}O_{29,32,}$ $\Delta H°_f$ = -757 kJ/kg, ρ =1.49 g/sm^3 – that is polyvinylmethyltetrazole plasticized with a mixture of nitroglycerine and 2,4-dinitrodiazapentane).

Tables 7.6–7.8 present data for compositions with the value of I_{sp} higher than 245 s (compositions basing on SHCB with the definite oxidizer are included in tables only if their I_{sp} values are higher than the I_{sp} values of compositions basing on AB with the same requirement for binder volume percentage).

In many SCPs one introduces aluminum (we may introduce it up to 20-22% but at higher content other undesirable consequences may appear even if I_{sp} still rises). However, the effectiveness of aluminum introduction decreases rather quickly with an enthalpy of oxidizer (so, total enthalpy too) increase [78]. Besides, aluminum introduction may be effective only if the oxidizer has a high α value. Therefore, for many compounds from Tables 7.6 and 7.8, aluminum introduction into the composition (even with active binder) is not effective, so these compositions are not included in the tables. Oxidizers from Table 7.6 have rather high α values and $\Delta H°_f < 0$. Aluminum introduction into compositions basing on such oxidizers is rather effective in case of both binders (AB as well as HCB).

All I_{sp} and T_c data have been calculated (at the chamber pressure Pc= 40 atm, the ambient pressure Pa=1 atm) using standard code TERRA [79] for high-temperature chemical equilibrium calculation..

First, let us consider compositions with real oxidizers (Table 7.6). Only for No. 3 (DNQ) compositions with AB have higher I_{sp} value than with SHCB. The explanation is evident - DNQ has the lowest α and the highest $\Delta H°_f$ value among all other compounds of Table 7.6. Compound No. 6 is the only one with active fluorine (NF_2- group), and therefore it shows the higher I_{sp}, but as fluorine presence transfers this oxidizer into another compounds category (other safety level, other pollution level), we will not discuss much energetic abilities of this oxidizer. Among oxidizer with no fluorine HNF, is the best (I_{sp}= ~265).

Considering compounds from Table 7.7, we can notice that compounds with α<0.54 (No 8- 9, 15-19, and No 10) and having α=0.6, but with rather low ΔH_f^0 (that does not compensate oxygen deficit), have a low effectiveness. Other ones show an I_{sp} from 245 to 275 s. Only one among them (No. 7) with α = 1 contains less nitrogen than Nos. 3 and 13, and shows an I_{sp} with HCB higher than for AB. The highest I_{sp} values (266–276 s, which differ considerably from all others compounds from Table 7.7) are for oxidizers with maximal ΔH_f^0 values, hereby No. 14 having α = 0.75 only has an extremely high ΔH_f^0 (4184 kJ/kg) and increases I_{sp} drastically in comparison with No 13 (ΔH_f^0 = 4184 kJ/kg, α=1). We should note that an Al addition influences slightly the I_{sp} in this case.

Table 7.6: Compositions from oxidizer with Al and a binder.

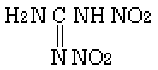
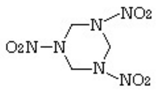
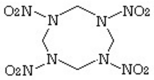
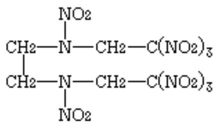
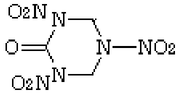
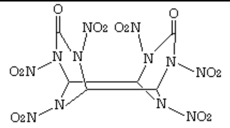
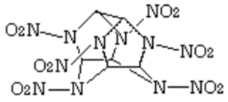
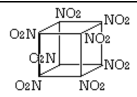
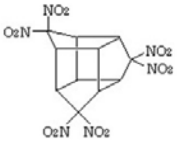
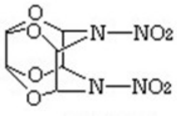
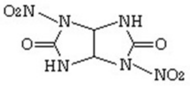
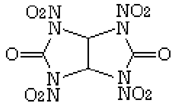
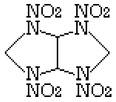
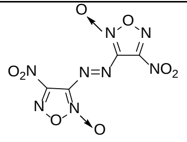
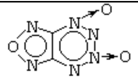
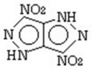
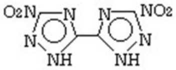
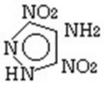
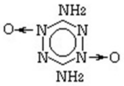
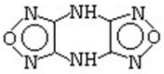
	Compound	α	ρ,	ΔH_f^0,	Binder	Al,%	d,	I_{sp} ,	T, ^{0}K
1	NH_4ClO_4, AP	2.67	1.95	-2125	AB	20	1.97	242.9	3880
					HCB	20	1.87	253.2	3720
2	$(NO_2)_2\bar{N}\ NH_4^+$ ADN $H_4\ N_4O_4$	2.00	1.84	-1209	AB	20	1.90	254.6	3875
					HCB	20	1.79	261.4	3630
3	 $H_2N\,\underset{\underset{N\,NO_2}{\Vert}}{C}\,NH\,NO_2$ DNQ, $C_1H_3N_5O_4$	1.14	1.91	0	AB	18	1.93	256.1	3924
					HCB	14	1.8	254.6	3370
4	$H_2N-NH_2\cdot CH(NO_2)_3$ HNF $C_1H_5N_5O_6$	1.33	1.91	-393	AB	16	1.95	260.1	4000
					HCB	20	1.83	265.7	3667
5	$O_2N\,N[CH_2C(NO_2)_3]_2$ BTNENA $C_4H_4N_8O_{14}$	1.4	1.96	-63	AB	20	1.98	252.5	4224
					HCB	16	1.85	262.1	3920
6	$O_2N\,N[CH_2C(NO_2)_2NF_2]_2$ B(DFADNE)NA $C_4H_4N_8O_{10}F_4$	1.25	2.05	-100	AB	8	1.98	263.1	3815
					HCB	0	1.84	270.2	3663

Table 7.7: Compositions of the oxidizers with a binder.

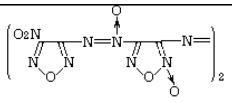
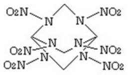
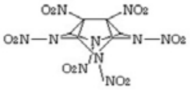
No	Compound	α	ρ_{0}, g/cm^3	ΔH_f^0 kJ/kg	Binder	d, g/cm^3	I_{sp}, s	T, ^{0}K
1	 RDX $C_3H_6N_6O_6$	0.67	1.816	276	AB	1.76	251	3190
2	 HMX $C_4H_8N_8O_8$	0.67	1.907	251	AB	1.84	251.2	3200
3	 ZOX $C_6H_8N_{10}O_{16}$	1.00	1.875	14	AB	1.8	256.5	3420
					HCB	1.7	252	3200
4	 K-6 $C_3H_4N_6O_7$	0.88	1.930	-182	AB	1.85	248.8	3300
5	 HHTDD-1 $C_6H_4N_{12}O_{14}$	1.00	2.071	-33	AB	1.95	245	3350
6	 CL-20 $C_6H_6N_{12}O_{12}$	0.80	2.040	837	AB	1.94	255.5	3450
7	 ONC $C_8N_8O_{16}$	1.00	1.982	937	AB	1.88	253	3660
					HCB	1.78	259	3660

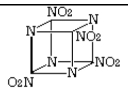
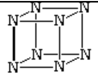
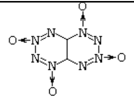
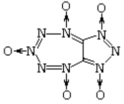
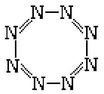
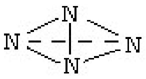
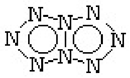
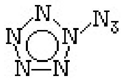
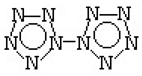
8	 HNPU $C_{11}H_8N_6O_{12}$	0.46	1.840	366	AB	--	lower 235	--
9	 TEX $C_6H_6N_4O_8$	0.53	1.990	-2063	AB	--	lower 210	--
10	 DINGU $C_4H_4N_6O_6$	0.60	1.982	-1347	AB	--	lower 210	--
11	 Sorguyl $C_4H_2N_8O_{10}$	1.03	2.030	155	AB	1.93	245	3380
12	 BC-HMX $C_4H_6N_8O_8$	0.73	1.890	701	AB	1.82	256	3370
13	 ANF $C_4N_8O_8$	1.00	2.000	2320	AB	1.91	266	3790
					HCB	1.81	266	3750
14	 FDTO $C_2N_6O_3$	0.75	1.852	4184	AB	1.79	275	4020
15	 DNPP $C_4H_2N_6O_4$	0.44	1.870	1373	AB	--	lower 230	--

16	 DNBT $C_4H_2N_8O_4$	0.44	1.820	1405	AB	--	lower 220	--
17	 LLM-116 $C_3H_3N_5O_4$	0.53	1.930	0	AB	--	lower 220	--
18	 LAX-112 $C_2H_4N_6O_2$	0.33	1.860	1395	AB	--	lower 215	--
19	 PDF $C_4H_2N_6O_2$	0.22	1.932	2353	AB	--	lower 215	--

Half of the compounds from Table 7.8 (hypothetical substances) represent substances containing N-atoms only. Their ΔH_f^0 values (5615-6800 kJ/kg) are considerably higher than all of the others.

Table 7.8: Compositions of oxidizers and a binder (Al is not needed).

No	Compound	α	$\rho_{0,}$ g/cm^3	ΔH_f^0, kJ/kg	Binder	d, g/cm^3	I_{sp}, s	T, ^{0}K
1	 BNAFFO $C_4N_8O_6$	0.75	1.990	3260	AB	1.89	269.6	3900
2	 HNTU $C_5H_8N_{12}O_{12}$	0.86	2.010	1200	AB	1.91	264.5	3500
3	 HNTPD $C_6H_4N_{10}O_{12}$	0.86	2.020	736	AB	1.92	255	3500

4	 TNTAC $C_4N_8O_8$	1.00	2.040	1810	AB	1.93	255.5	3670
					HCB	1.82	257.5	3600
5	 OAC N_8	-	2.280	5615	AB	2.10	262	3850
6	 OANT $C_2N_8O_4$	1.00	2.220	3350	AB	2.07	263.6	3750
					HCB	1.97	264	3710
7	 GATO $C_2N_7O_5$	1.25	2.260	3170	AB	2.1	262.4	4070
					HCB	1.99	273.8	3800
8	 OATE N_8	-	1.810	6200	AB	1.75	272	4060
9	 TATE N_4	-	1.513	6800	AB	1.5	280	4100
10	 PP N_8	-	1.940	6443	AB	1.85	275.6	4130
11	 PA N_8	-	1.770	6109	AB	1.72	270	4000
12	 BP N_8	-	1.930	5569	AB	1.85	262	3850

The ultrahigh ΔH_f^0 values supply the reason for the high I_{sp} values. All pairings of these compounds (N_x) with HCB have considerably lower I_{sp} values than pairings with AB (at the accessible binder volume percentage).

Figure 7.2 demonstrates that I_{sp} values of the binary systems (N_x+AB) depend practically linearly on the ΔH_f^0 value of N_x. It is possible to use the data in Figure 7.2 for preliminary evaluation of energetic abilities for any other compounds with the formula N_x: I_{sp}= 177.3 + 0.0152 $\cdot\Delta H°_f$, where $\Delta H°_f$ - the enthalpy of formation of N_x (kJ/kg). In this $\Delta H°_f$ -range the value of I_{sp} increases about 1.5 s for each 100 kJ/kg increase of $\Delta H°_f$.

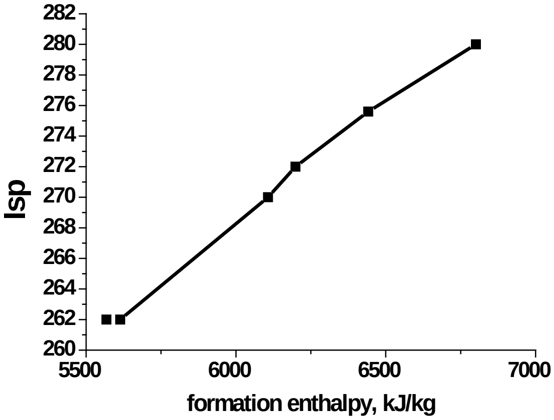


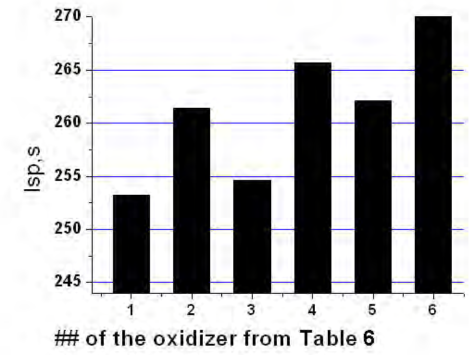
Figure 7.2: Optimal I_{sp}-value for binary system N_x+AB as a function of the enthalpy of formation of N_x.

Thus, if we propose the possibility that compounds with formula N_x for $\Delta H°_f$ >6800 kJ/kg exist, the achievement of an I_{sp} value with 280 s may become real.

As for other compounds from Table 7.8, we can note that compound No. 7 with the highest value α (1.25) shows the maximum I_{sp} with HCB, not with AB (273.8 against 262.4 s). Compounds Nos. 4 and 6 with α = 1 show almost the same I_{sp} values, both with AB and HCB (257.5 against 255.5 for No. 4 and 264 against 263.6 s for No. 6).

Compounds Nos. 1-3 with α < 0.86 in a binary mixture with HCB are less favorable than mixtures with AB. Compound No. 1 looks rather accessible, and in the binary mixture with AB it promises a value of I_{sp} = 270 s - today it is practically an unreachable value for SCPs of compounds based on C,H,N,O-atoms only, and even with aluminum (except aluminum hydride that allows the achievement of an I_{sp} up to 277 s or so).

Figures 7.3-7.5 show the differences in effectiveness of all these compounds as components of SCPs in the best binary systems of oxidizer + binder (either HCB or AB).



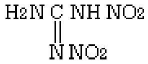
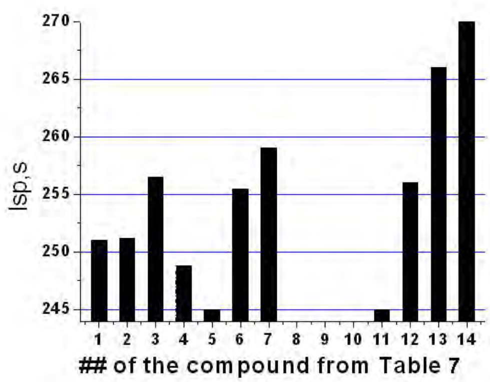
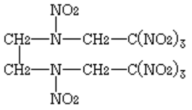
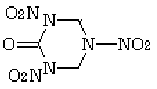
1. AP.
2. ADN.
3. 
$H_2N\,\underset{\underset{NNO_2}{\|}}{C}\,NHNO_2$
4. $H_2N{-}NH_2\cdot CH(NO_2)_3$
5. $O_2NN[CH_2C(NO_2)_3]_2$
6. $O_2NN[CH_2C(NO_2)_2NF_2]_2$

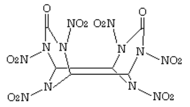
Figure 7.3: The highest I_{sp} values of compositions: oxidizer (Table 7.6) + Al (not higher than 20%) + binder (not higher than 18 vol.%).



1. **RDX.** 2. **HMX.**

3. 

4. 

5. 

6. CL-20

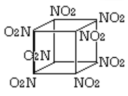
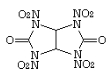
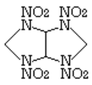
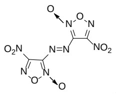
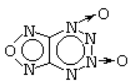
7.  11.  12.  13.  14. 

Figure 7.4: The highest I_{sp} values of compositions: oxidizer (Table 7.7) + binder (not higher than 18 vol.%).

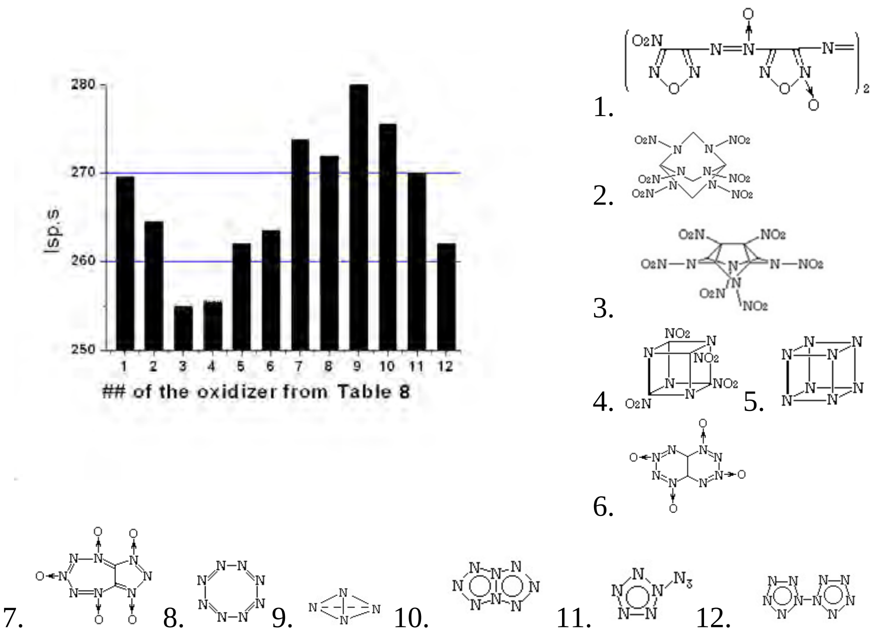


Figure 7.5: The highest I_{sp} values for several compositions: oxidizer (Table 7.8) + binder (not higher than 18 vol.%).

7.6 Results and Discussion

In order to assess the quality and effectiveness of the obtained equations for evaluation of the basic performances for EMs, and for the limits of their existence, we can consider the isolines of the metal acceleration performance (η) in Figure 7.6. As we noted above, this parameter (η) determines the effectiveness of EMs.

It follows from Figure 7. 2 that an increase of energetic capacity of a compound is accompanied with an increase of its sensitivity to external influences. The interdependence between the sensitivity and energetic capacity determines the borders for the region of the Ems' existence. Decrease of the energetic capacity below a critical value makes the compound incapable of detonation. In Figure 7.6 such compounds are limited by the (heavy line) bisector of the coordinate angle. If a compound accumulates extra-energy, it becomes extra-sensitive and extra-unstable as a chemical substance. The region of an Ems' existence is limited by the Y-axis, beginning from a null value for the critical pressure for initiation.

It follows from the analysis of the foregoing parameter estimations and presented equations for the EMs & explosives that a relative increase of sensitivity (eq.2), related to the energy capacity (Q_{max}), is considerably greater than the relative increase in the detonation parameters (eq.3,4) and the detonation effectiveness (eq.1).

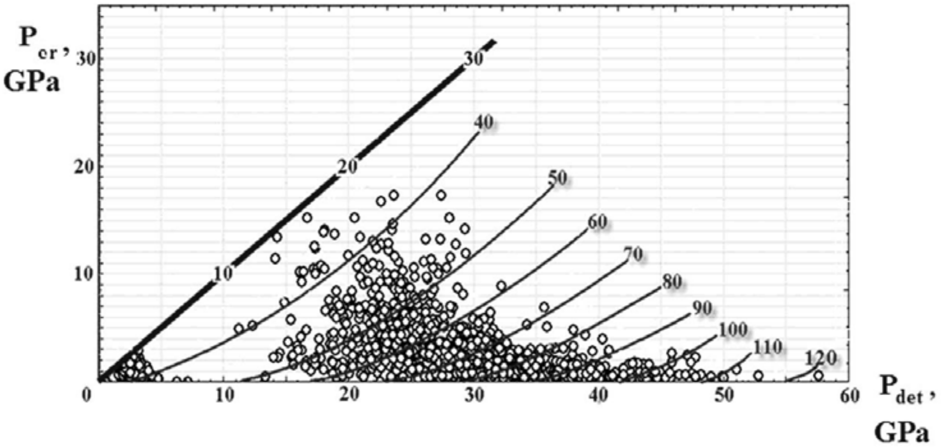


Figure 7.6: The metal acceleration performance isolines on axes: X-coordinate – the detonation pressure (P_{det}) and Y-coordinate – the shock sensitivity (P_{cr}).

From analysis of the region for existence of the EMs, it is possible to determine the following extreme parameters:

- monocrystal density ≤ 2.2 g/cm^3,
- enthalpy of formation ≤ 6000 kJ/kg or so,
- heat of explosion ≤ 7800 kJ/kg,
- detonation pressure ≤ 50÷60 GPa,
- acceleration ability (m-40) ≤ 120% (in comparison with HMX),

However, at such limits, the explosives would have unacceptable safety properties associated with shock sensitivity (1.5÷5 kbar).

The estimated properties for polynitrogen compounds with their different structures indicates that the most promising ones should have a density 2,0 g/cm^3, an enthalpy of formation ~6800 kJ/kg (that equals the heat of explosive transformation), a pressure of detonation 50 GPa, and an impulse of throwing action above 115 % (in comparison with HMX). The estimation of basic characteristics for compounds used as components of solid rocket propellants has shown that the best values of specific impulse are reached for mixtures of polynitrogen high enthalpy compounds. Unfortunately, the sensitivity of substances exhibiting the extreme parameters is reasoned to be unacceptably high.

7.7 References

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4. Walker F.E., Wasley R.I., "Critical Energies for Shock Initiation of Heterogeneous Explosives." *Explosivstoffe*. 1, 1969: 9-13.
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Chapter 8

Study of the Initiation Reactivity of Energetic Materials

Svatopluk Zeman

This chapter reviews the most important results from the studies of initiation reactivity of energetic materials (EMs) published by the authors from the University of Pardubice, Czech Republic, mostly since 1990. The studies include impact, shock (detonation), friction, electric spark and thermal reactivity (sensitivity). The findings are that primary fission processes of EM molecules in low-temperature thermal decomposition are the same processes observed during initiation by mechanical stimuli, including shock and electric spark. The primary chemical fragmentation of these materials during detonation is the same as that during shock compression. That is to say that the detonation transformation is preceded by an induction period. Experimental observation of reaction centers and reactions during the induction period in polynitro arenes and nitramines are done through Nuclear Magnetic Resonance observation of chemical shifts of atoms and calculated net charges, Q_{NO2}, or the electron charge, q^N, on their nitrogen atoms. Concerning specifying the reaction center, it is pointed out that the Density Functional Theory calculations of isolated molecules are useful for only the simplest EM molecules. Interpretation of the specific behavior of nitromethane under influence of small admixtures of amines or water is also mentioned.

8.1 Introduction

Sensitivity of energetic materials (EMs) is primarily due to the chemical character of these materials; in this connection it is possible to use the term '**initiation reactivity'** of EMs [1]. Studies of shock and impact sensitivities, and during the past 22 years the preferred tools for this, have involved quantum mechanics and quantum chemistry [1] (and references therein). Using chemistry to address these problems has been sporadic and rather tentative. Zeman has applied a physical organic chemistry approach for 32 years [1 - 3]. This paper presents results, mostly published after 1990, obtained by authors from the Institute of Energetic Materials.

8.2 Approach to the Problem

Relationships have been found between the output of non-isothermal differential thermal analysis (DTA, i.e. low-temperature non-auto catalyzed thermolysis) and the detonation characteristics of polynitro arenes [2, 3], nitramines, nitrosamines and nitrate esters [3]. The choice of the evaluation methodology for DTA recording was based on the fact that a higher brisance of an individual explosive usually has a steeper decomposition DTA exothermal curve [2, 3]. A more detailed analysis of these results for polynitro arenes shows that their classification is given by (a) steric conditions and (b) electron configuration in the ground state of the reaction center of the molecule [1-3]. The term reaction center means the group of atoms and/or functional groups in the molecule whose primary chemical changes initiate decomposition of the molecule.

8.2.1 Methods of Classification of the Reaction Center in a Molecule

Both the electron configuration and steric conditions in the reaction center of the molecule can be characterized by the:

- NMR chemical shifts of key atoms of the molecule's reaction center (semi-empirical determination of the nitro groups that are the first to react in the initiation) [1, 3-16]
- direct correlation of reaction characteristics with electron charges at the nitrogen atoms of these first-reacting nitro groups [1, 3, 13, 14, 17-22] or with net charges of these nitro groups [1, 13, 14, 22 - 24]
- direct correlation of reaction characteristics with the bond dissociation energies (BDE) of the weakest bonds [23, 25 - 27]
- DFT-B3LYP calculation of the more probable pathway of initiation [1, 28, 29]

The above approach was first demonstrated on a group of secondary nitramines [1, 3, 4, 6, 10, 16], because these compounds have simple molecular structures, and the mechanism of their primary fission is well known (see references in Refs. 1, 10). On the basis of these findings, the approach was extended to the application of ^{13}C [1, 4, 11] and ^{15}N NMR

[1, 5 – 10, 13 – 15, 23] chemical shifts in polynitro arenes. Although it is known that NMR studies in solution neglect important crystal-lattice effects that are vital in the determination of explosive properties [1], several recent papers [1, 4 – 11, 13 – 16, 23] have shown that this fact has no fundamental significance for studies of the chemical micro-mechanism of initiation of energetic materials.

The calculation of electronic charges, q^N, at nitrogen atoms and net charges, Q_{NO2}, of nitro groups of the individual EMs investigated was carried out by means of the Mulliken population analysis of electron densities obtained *ab initio* by the DFT B3LYP method, under total geometry optimization (i. e. for an isolated molecule at 0 K). However, the important crystal-lattice effects are not under consideration in this solution. As it turns out, DFT calculations for isolated molecules give acceptable results only for relatively simple molecules (nitramines, etc.) [13, 14, 30, 31].

8.2.2 Comparison of Different Sensitivity Data

It is a generally accepted idea that nitro groups represent the primary cause of initiation of polynitro compounds [1, 3, 4] (and references therein). Therefore, it is natural that relationships exist between the characteristics of low-temperature thermal decomposition [1, 3, 5, 10, 19, 20, 29, 32-36] and sensitivities to impact [1, 7, 36] or electric spark [37, 38], detonation characteristics [1–3, 10, 33, 35, 39] and friction sensitivity of polynitro compounds [40]. Relationships [43] between detonation characteristics and sensitivities to impact [36, 41] and friction [42] can be found as well as between both the mentioned sensitivities [43], etc. It has been stated [1, 3, 4, 7, 10, 23, 24, 33, 39, 40, 42, 43] that the primary fragmentation processes of molecules of energetic materials in low-temperature thermal decomposition should be identical with those in the impact, electric spark, shock and friction initiations. Comparisons of this kind are an important part of the initiation reactivity study.

Polarography can be considered as a special case of sensitivity measurement. The electrochemical reduction of the polynitro arenes in an aqueous medium can give values of half-wave potentials, $E_{1/2}$, which give a logical linear dependency on the squares of detonation velocities of the polynitro arenes [44].

8.2.3 Selection of the Required Characteristics of EMs

The thermal decomposition characteristic used included the Arrhenius parameters obtained by means of the Russian manometric method (RMS, see Refs [1, 3, 5, 32, 39] and quotations therein) or by means of methods that give comparable results (especially differential scanning calorimetry) [38] (and quotations therein). The data obtained by the RMS method are known to correspond to the non-auto catalyzed stage of thermal decomposition of the given material (i.e. to molecular structure – Refs. [32, 39] and quotations therein), and also to the absolute values of the corresponding Arrhenius parameters. Another source of these characteristics was the simple non-isothermic differential thermal analysis (DTA). The output was evaluated by means of the Kissinger method [1, 3, 19, 21, 22, 34 - 36] (and references therein). The reactivity was expressed as the E_aR^{-1} slopes of the Kissinger relationship (E_a is activation energy and R is the gas constant). In several cases output from the Czechoslovak isothermal vacuum stability test STABIL was used [33, 36].

In the case of electric spark sensitivity, the data were obtained with an instrument [23, 45] whose design and construction were achieved with a contribution from the Institute of Energetic Materials. These data are spark energies, E_{ES}, for a 50 % probability of initiation.

The impact sensitivity data considered were the drop energies, E_d, obtained by conversion of drop height values, $h_{50\%}$. Attention was given both to the impact sensitivity as "the first reaction" (detection with respect to the first decomposition) [1, 4, 8, 10, 46], and impact sensitivity detected by sound (see [1, 4, 26, 41, 43, 46, 47] and references therein). The friction sensitivity was determined by means of a BAM friction test apparatus; this was used by applying standard test conditions (see in [15, 40, 42, 43]).

The studies of shock sensitivity were based on the detonation velocities, D, calculated by the Kamlet & Jacobs method (see citations in Refs. 4, 6, 9, and 16), and in some cases they also were determined experimentally [16, 34]. The heat of explosion, Q_{real}, was calculated by means of the semi-empirical relationships of Pepekin et al. (see citations in Refs. [4, 6, 9, 39]). Both these quantities characterize the shock wave due to chemical transformation of EMs, i.e. the detonation wave.

The previously mentioned method using polarographic half-wave potentials, $E_{1/2}$, was employed for 24 polynitro arenes measured in an aqueous medium buffered at pH 7, at a concentration of $0.5 \cdot 10^{-4}$ M [44]. The strong dependence of $E_{1/2}$ on the conditions and manner of making the polarographic measurements, along with the very limited solubility of the polynitro compounds studied in an aqueous solution, considerably restrict the use of polarography in studying the chemical micro-mechanism of initiation of organic energetic materials [44].

The ^{13}C and ^{15}N NMR chemical shifts were obtained using experimental measurements [4, 5, 6, 9, 11, 14, 16].

Basic Mechanisms of Thermal Decomposition of Polynitro and Polynitroso Compounds

The basic problem of defining the kinetics and mechanism of the thermal decomposition of energetic materials lies in the strong dependence of the kinetic parameters on temperature, pressure, and the nature of the materials in contact with the decomposed sample [39]. Hence, obtaining consistent or coherent results from thermal analyses of energetic materials using different methods and/or different types of apparatus of different origin is very rare [5, 39]. So far the most reliable results are the theoretical and practical findings obtained by Russian scientists on the basis of their manometric method (this uses a special kind of vacuum stability test). The mechanisms of unimolecular fragmentation in low-temperature thermal decomposition of organic polynitro and polynitroso compounds, specified mostly by the Russian authors, can be divided into the following classes [4, 32]:

- *homolysis of C–NO_2, N–NO_2, O–NO_2 and N–NO bonds*. The homolytic fission of the first bond, particularly that connecting a sterically hindered nitro group, is characteristic for the decomposition of polynitro paraffins and unsubstituted polynitro arenes [4, 11 – 14, 22]. Homolytic splitting of the N–NO_2 bond is typical of secondary nitramines [3, 4, 6, 10, 31], that of the O–NO_2 bond is typical of nitric esters [4], and that of the N–NO bond typical of nitrosamines [4, 35].
- *homolysis via a five-, six- or seven-member transition state or aci-form (in the last case homolysis of N–OH bonds).* The six-member transition state (or aci-form) is connected with the presence of a hydrogen atom at the γ–position with respect to the nitro group [1, 4, 48, 49] in derivatives of polynitro arenes, i.e. with polynitro compounds exhibiting the so-called trinitrotoluene mechanism of thermal decomposition [48 - 50] (see Schemes 8.1, 8.2, 8.3, 8.5). A five-member transition state might have significance in a group of polychlorinated derivatives of 1,3,5-trinitrobenzene whose thermal decomposition represents an analogy with the decomposition of its polymethyl derivatives [51] (and quotations therein). The primary step of the thermal decomposition of chloro-derivatives could perhaps be connected with the chemical interaction between the chlorine atom and oxygen of the *ortho*-standing nitro group (which is also indicated by the negative values of the respective activation entropy $\Delta S^{\ddagger}$ - see quotations in Ref. [4]). An analogous interaction of this oxygen atom with the sulfur atom in the dipicrylsulfide (DIPS) molecule could also start the decomposition of this

substance (again the respective $\Delta S^{\ddagger}$ value is negative - see quotations in Ref. [4]), even though the primary homolysis of the C–S bond was originally presumed in this case [4] (and references therein). A seven-member transition state can be present, for example, in the first step of thermal decomposition of 1,5-dinitronaphthalene (it should begin by an interaction between the oxygen atom of the nitro group and the hydrogen atom at the *peri*-position [8] – see Scheme 8.5).

- *homolytic fragmentation without a primary participation of a nitro group*. In the case of hexanitroazobenzene it was assumed that its thermal decomposition was started by primary fission of the bond between the carbon atom and the azo-bridge (see [4] and quotations therein). Similarly, dipicrylsulfone and the already mentioned DIPS should be liable to C–S bond homolysis (see in [4] and references therein and also Scheme 8.4). However, the $\Delta S^{\ddagger}$ value of the corresponding decomposition is negative in all cases (see in [4] and references therein), i.e. the reaction should proceed through a cyclic transition state.

Heats of Fusion and Crystallographic Data of the Polynitro Compounds Studied

The characteristics of their solid state, above all the heats of fusion, $\Delta H_{m,tr}$, and crystallographic information, are very important data for a study of initiation reactivity of individual energetic materials.

The $\Delta H_{m,tr}$ value is taken as a sum of the heats of all polymorph transitions and the heat of melting (it is characteristic for a given compound). Before the 1990s such data for EMs were relatively rare in the literature. Therefore this problem was solved experimentally (by means of DSC [52, 53]) and using predictions [25, 52 - 54]. Thus, the $\Delta H_{m,tr}$ values were obtained also for EMs that are decomposed during melting or in the solid state, such as: 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) [52], *cis*-1,3,4,6-tetranitrooctahydro-imidazo[4,5-d]imidazole (BCHMX) [25], *trans*-1,4,5,8-tetranitrodecahydro-pyrazino[2,3-*b*]-pyrazine (TNAD) [52], 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL20) [54], 4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraazaisowurtzitane (Aurora 5, TNIW-5) [25], 4,6,10,12-tetranitro-2,8-dioxa-4,6,10,12-tetraaza-isowurtzitane (Aurora 6, TNIW-6) [25], 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX) [54], quite a number of polynitro arenes [53] and nitramines that have not yet been synthesized [52], i.e. 1-nitro-1-azaethylene (Digen), 1,3-dinitro-1,3-diazetidine (Tetrogen) and 1,3,5,7,9-pentanitro-1,3,5,7,9-pentazecane (Decagen).

Published crystallographic data have been taken into consideration analyzing relationships of non-isothermal DTA data and detonation characteristics of polynitro arenes [2]. Our data, obtained on the basis of an X-ray crystallographic study [12 - 14, 16], were used for a more detailed description of the initiation reactivity of 2,2’,4,4’,6,6’-hexanitro-1,1’-biphenyl (HNBP), 2,2’’,4,4’,4’’,6,6’,6’’-octanitro-1,1’:3’,1’’-terphenyl (ONT), 2,2’,2’’,2’’’,4,4’,4’’,4’’’,6,6’,6’’,6’’’-dodecanitro-1,1’,:3’,1’’:3’’,1’’’-quaterphenyl (DODECA) and BCHMX. A very important finding from these studies, which needs further investigation, is that non-binding inter-atomic distances between oxygen atoms inside all of the nitro groups in these polynitroaromatic molecules are shorter than those corresponding to the intermolecular contact radii for oxygen in carbonyl or nitro groups. This distance is especially short inside the most reactive nitro groups. The same phenomenon was found in the case of the most reactive nitro group in the molecule of *cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-*d*]imidazole [16] (BCHMX). These facts, and also the short intermolecular distances of nitro groups in the crystal lattice of polynitro compounds, led Vávra to conduct research on free spaces in crystals of EMs and of their influence on the sensitivity of the energetic compounds described [30, 31].

8.3 Initiation by Heat

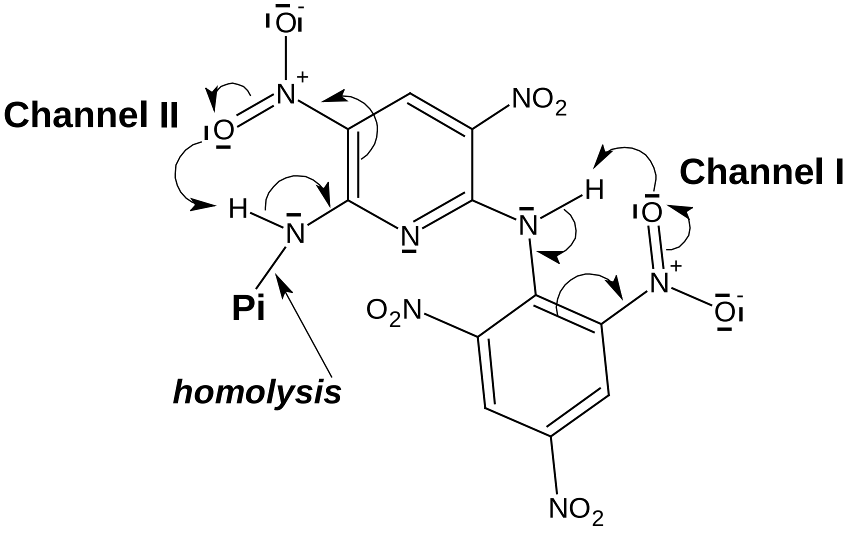
Initiation by heat, especially low-temperature decomposition below 600 K, has been the most frequently studied topic (see Refs [32, 39] and references therein). Molecular-dynamic simulations of thermal decomposition of individual energetic materials, including RDX, at extremely high temperatures [55] have been done. The high temperature initiation mechanism is entirely different from the low-temperature mechanism. In the case of the RDX uni-molecular decomposition, elimination of the NO_2 group by homolysis of one N–N bond is observed for all reaction conditions, whereas triazinane ring fission (depolymerization to 1-nitro-1-azaethylene) is the predominant reaction at higher temperatures in the gas phase thermal decomposition of this nitramine (see Ref. [1] and quotations therein).

So far we focused our attention on the use of results of low-temperature decomposition of polynitro compounds [1–5, 7, 10, 18–22, 32–36, 39, 48-51]. The use of ^{15}N NMR chemical shifts, δ_N, of the nitrogen atoms in nitro groups to the analysis and prediction of kinetic data of the thermal decomposition of nitramines is the topic of several papers [2–5, 10]. For molecules containing non-isochronous nitrogen atoms (the linear and non-symmetrical cyclic nitramines), the findings show different values and, hence, different reactivity of the nitro groups in these molecules [1–5, 10]. It has been shown that, in the case of HMX, the effect of the liquid phase on its thermolysis should be absent even if the thermolysis is realized at temperatures above 553 K (see discussion in Ref. [5] – HMX has "ungenuine" melting). Analogous dependencies for polynitro arenes are presented in Ref. [1, 9]: here a verification of the reaction centers in molecules of eighteen polynitro arene and azaarene derivatives has been carried out using relationships of activation energies from the Russian Manometric Method (RMM) and the δ_N values of nitro groups, the groups being primarily responsive to initiation [1, 9]. These relationships sharply differentiated those polynitro arenes with the primary fission of the C-NO_2, from those with primary fission of the N-OH bond (aci-form) [1, 9]. The carbon atoms, which are bearers of the primary reactive nitro groups during initiation of "genuine" polynitro arenes, might also be specified on the basis of relationship of the ^{13}C NMR shifts and the thermostability thresholds of these compounds [11]. These thresholds are calculated from Arrhenius parameters, obtained using the RMM [11].

On the basis of the relationship between the square of the Mulliken electron charges, q^N, at the nitrogen atoms of the first-reacting nitro groups, and the DTA onsets, T_D, of exothermic decomposition of polynitro arenes (modified Einstein–Nernst relationship – see quotations in Ref. 20), these substances can be divided into several logical subsets [1, 20]: One subset with the dominant stabilizing effect of a crystal lattice, one subset in which the effects of the mechanism of primary homolysis dominates, and one subset characterized by a combination of both above-mentioned effects. An addition of a solvent (TNB) to substances will suppress this stabilizing effect - the stability of tripicryl-s-triazine (TPT) decreases here so markedly that it does not correlate with any of the classes. The existence of these relationships might be connected with the electrostatic interaction of "instantaneous point dipoles" at the reaction center of the polynitro arenes [1, 20].

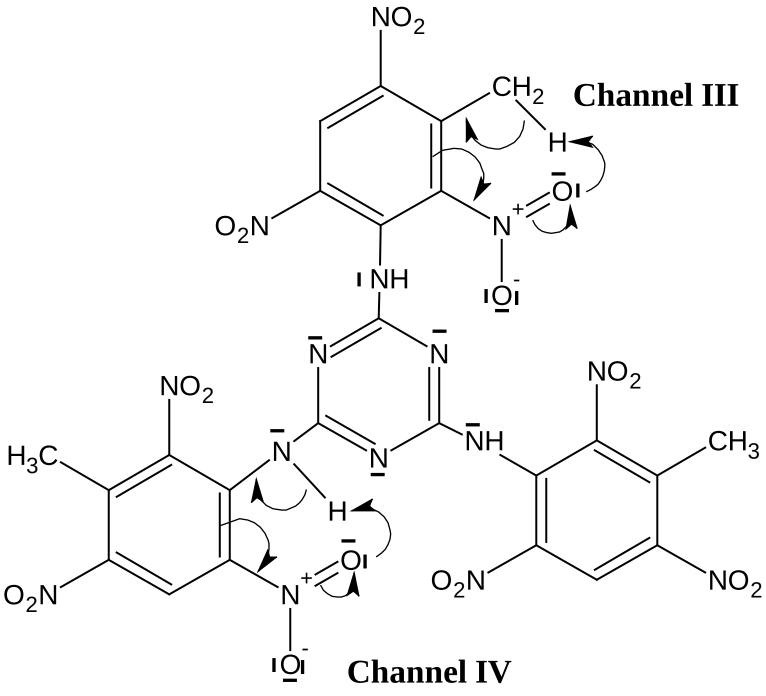
Another relationship is described in Refs. [1, 3, 19] between the slopes of the Kissinger relationship, E_aR^{-1}, and the Mulliken electronic charges, q^N, at the nitrogen atoms of the primary reactive nitro groups for nitramines. The discussion of this relationship confirmed the differences between linear and cyclic nitramines [1, 3, 19] from the standpoint of the initiation energy transfer to the reaction center. The quantum chemical calculation revealed the nitrogen atoms in the nitro groups to be different from the point of view of their potential participation in the primary initiation splitting processes [1, 19]. A similar approach applied to highly thermally stable polynitro arenes resulted in the relationships between $E_aR^{-1}$and q^N values described in paper [1, 22]. In addition, in this particular case one can clearly see very close molecular-structure dependence and, at the same time, the effect of the state of aggregation (liquid versus solid) [1, 22].

From the results in papers [1, 4, 28, 50] it follows that a molecule of energetic material can contain more than one potential initiation reaction center. As examples, we can cite N,N'-*bis*(2,4,6-trinitrophenyl)3,5-dinitropyridine-2,6-diamine (PYX) and *N,N´,N″*-tris(3-methyl-2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine (TMPM) [1, 28] – see Schemes 8.1 and 8.2.



Scheme 8.1: Presumed reaction mechanisms (centers) of primary fission of the N,N'-*bis*(2,4,6-trinitrophenyl)3,5-dinitropyridine-2,6-diamine (PYX) molecule in initiation processes.

In Scheme 8.1, Pi- is 2,4,6-trinitrophenyl whose breakaway (a secondary process) as a radical and subsequent reaction with other fragments of the PYX molecule gives dipicrylamine (DPA). It was found that both reaction centers in the PYX molecule probably participate in the first fission caused by initiation stimuli, although primary participation of the picryl nitro group in position 2 (together with amino bridge) in this process seems to be more probable (Channel I) [1, 28, 50].



Scheme 8.2: Presumed reaction mechanisms (centers) of primary fission of the 2,4,6-*tris*(3-methyl-2,4,6-trinitrophenylamino)-1,3,5-triazine (TMPM) molecule in initiation processes - primary participation of the nitro group in position 2 together with the methyl group in position 3 during initiation processes (Channel III) in this molecule should be a unique reaction center [1, 28].

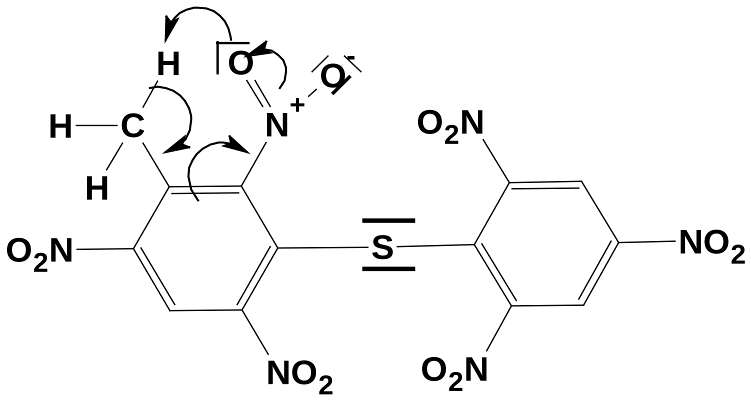
Relationships between electronic charges of the reaction centers (obtained by DFT calculations) and slopes of the Kissinger relationship, E_aR^{-1}, have been found for four nitramines and two nitrosamines contaminated by an admixture of 2 % by wt. of ammonium nitrate [21]; the mixtures mentioned have an increased thermal reactivity due to acydolitic attack of the aza-nitrogen atom of the substances studied by the nitric acid resulting from dissociation of ammonium nitrate [21].

8.4 Impact Sensitivity (Reactivity)

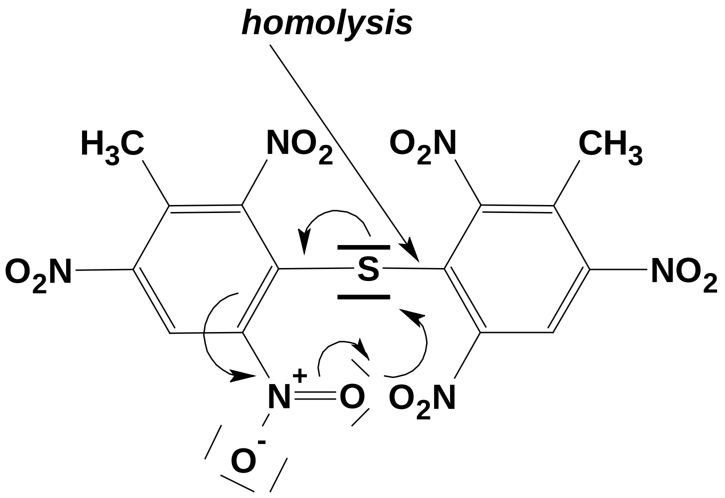
8.4.1 Impact Sensitivity as "The First Reaction"

The problem of the title impact sensitivity (i.e. without acoustic effect) has been experimentally studied [1, 4, 7, 10]. Linear relationships were found between the ^{15}N NMR chemical shifts, δ_A, of aza (amino) nitrogen atoms carrying the most reactive nitramino groups and the drop energies, E_{dr}, of "the first reaction" [1, 4, 7, 10]. These relationships show that the impact reactivity of linear polynitramines (more than two nitramino groups in a molecule) is connected with primary homolysis of the "inner" N–NO_2 bonds in their molecules. This finding is in agreement with the mechanism formulated for this process on the basis of molecular dynamics (see quotations in Refs. 1 and 4). It must be stated that the aza (amino) nitrogen chemical shifts, δ_A, in the nitramino groups are expected to be influenced by the nitrogen hybridization, the size and conformation of molecule, and the extent to which the lone nitrogen pair is involved in π-bonding with the NO_2 group. As the conformation and size of the molecule play a dominant role in the intermolecular interactions in the corresponding crystal, the interactions should have a significant influence on the impact sensitivity.

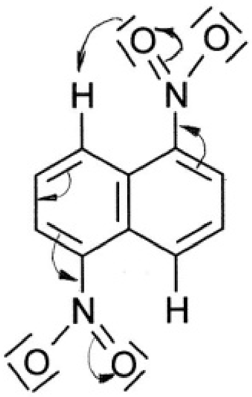
This hypothesis is supported by a semi logarithmic relationship between the E_{dr} values and heats of fusion, $\Delta H_{m,tr}$, of nitramines [1, 4, 7, 10]. As the heat is related to the work needed for formation of defects in the crystal lattice, the relationships found seem to agree with the ideas about the decisive role played by dislocations and plastic deformations of the crystal in the initiation of energetic materials. Likewise, for nitramines, a relationship exists between E_{dr} values and ^{13}C NMR chemical shifts, δ_C, of the most reactive nitro group "bearers" (i.e. carbon atoms in the reaction centers of the molecule) in polynitro arenes [1, 8]. As papers [1, 8] have shown, the relationship between the E_{dr} and δ_C values of polynitro arenes has again the same form as that valid for nitramines. The more complex molecular structure of these arene derivatives (particularly the mesomeric and steric effects) and the two presumed basic mechanisms of primary splitting, as compared with nitramines, result in a more varied assortment of shapes of this relationship. These relationships were used for predicting a likely primary mechanism of splitting of 3,3´-dimethyl-2,2´,4,4´,6,6´-hexanitrobiphenylsulfide (DMDIPS), which possesses two potential reaction centers in its molecule (Schemes 8.3 and 8.4); in this kind of initiation the more likely is the primary splitting in the sense of Scheme 8.4 [1, 4, 8](see also references therein).



Scheme 8.3: Theoretical, less probable mechanism of electron shifts at the beginning of the low-temperature thermal decomposition of DMDIPS with participation of the nitro group at the 2-position in the reaction center (typical "trinitrotoluene mechanism") [1, 4, 8].



Scheme 8.4: Presumed mechanism of a more probable electron shift at the beginning of the low-temperature thermal decomposition of DMDIPS with participation of the nitro group at 6-position in the reaction center [1, 4, 8].



Scheme 8.5: Presumed electron shift at the beginning of low-temperature thermolysis of 1,5-DNN [8].

On the basis of these relationships, an electron shift at the beginning of 1,5-dinitronaphthalene (1,5-DNN – see Scheme 8.5) decomposition was assumed, which means that the thermal decomposition of this compound should begin by the interaction of the oxygen atom of the nitro group with the hydrogen atom at the *peri*-position [8], as opposed to the presumed homolysis of the C–NO_2 bond.

The relationships between impact sensitivity in the sense of "the first reaction" of polynitro arenes and their heats of fusion on the one hand, and the ^{13}C NMR chemical shifts at the reaction centers of their molecules on the other hand, are of the same type as those found for nitramines [1, 8].

8.4.2 Impact Sensitivity Detected by Sound

The relationship between the impact sensitivity (E_{dr}) detected by sound and the ^{15}N NMR chemical shifts of nitramines is mathematically different from that in the case of "the first reaction" [1, 12, 14, 16]. Thisjh difference is also evident in the relationship (logarithmic) between the sensitivity and the $\Delta H_{m,tr}$ values [1, 47]. These differences could be interpreted by the different mechanisms of transfer of drop energy to the reaction center of the molecule in the case of "the first reaction" as compared with the impact sensitivity detected by sound [1, 46, 47].

Figure 8.1 represents a typical semi logarithmic relationship between the E_{dr} and δ_A values for nitramines; a part of this Fig. is taken from [16] supplemented by the δ_A values [16, 6] and drop energies, E_{dr} [26]. This Fig., for example, highlights the difference between impact sensitivities of “commonplace” (technical grade) and those for pure ε–HNIW (see [56]).

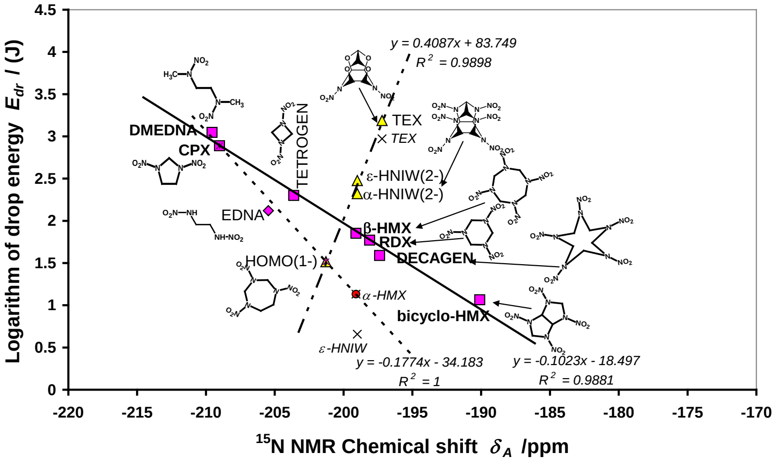


Figure 8.1: Relationship between impact sensitivity, E_{dr},, detected by sound, and ^{15}N NMR chemical shifts, δ_A, of aza-atoms which are bearers of primary reactive nitro groups (in brackets the numbering of positions in the molecules).

The same shape relationship has been shown to exist between the impact sensitivity, detected by sound, and ^{13}C NMR chemical shifts of “the bearers” of the most reactive nitro groups in the polynitroaromatic molecules [1, 4]. According to this relationship, there are the nitro groups in the 2-position of 1,3-diamino-2,4,6-trinitrobenzene (DATB), 1,3-dimethyl-2,4,6-trinitrobenzene (TNX), trinitroresorcine (TNR) and 3,3’-dimethyl-2,2’,4,4’,6,6’-hexanitrobiphenyl (BITNT) [1]. These groups are also the most sterically crowded [1]. As is demonstrated in Scheme 8.1, two potential reaction centers in the PYX molecule exist [1, 4, 50], which is also verified by these kinds of relationship [1, 4]. As the X-ray study of HNBP showed [12], and the relationship of its E_{dr} value (in a set of these values for other six polynitro arenes) and ^{15}N NMR shifts of the nitrogen atoms in the primary reactive nitro groups also indicates, there are two reaction centers in the molecule of this “genuine” polynitro arene

(i. e. C—NO_2 homolysis in positions 2 and 4 of the HNBP molecule) [14].

There appear to be some logical relationships between impact sensitivity and net charges (obtained by DFT calculation) of the primary reactive nitro group [1, 12, 22]: here linear condensed polynitro (poly)arenes are sharply differentiated from their spatially condensed analogues (i.e. NTFA, TPT and TACOT-Z). However, if the DFT calculations are carried out on the real molecular structure that was described by X-ray crystallography, entirely different primary reactive nitro groups will be found [13, 14]; this means that the DFT calculations for isolated molecules logically cannot give good results (certain exceptions might be found for relatively simple molecules - see in 2.1 and also in [13, 14, 30, 31]). However, not taking account of the intermolecular forces effects in the UB3LYP calculations of the weakest N—N bond dissociation energies, *BDE*, leads to ambiguous relationships between the E_{dr} and *BDE* values of nitramines [26]. Nevertheless, these relationships enabled forecasting the E_d values for three new nitramines [26].

8.4.3 Classification of Polynitro Compounds on the Basis of their Impact Sensitivities

The mechanism of drop energy transfer to the reaction center of the molecule in the case of the impact sensitivity as “the first reaction” should differ from that in the case of impact sensitivity detected by sound. Comparison of the drop energy values, E_{dr}, of the two types of impact sensitivity leads to the relationships shown in Ref. [46], according to which the polynitro compounds fall into three classes. Each of these classes includes compounds having a characteristic range of values for thermolysis rate constants – these constants correspond to the temperatures at which their exothermic decomposition starts. The given temperatures result from Differential Thermal Analysis of the compounds. This finding corresponds with the known relationships between impact sensitivities and the characteristics of thermal decomposition of polynitro compounds [1, 8]. This means that there exists a relationship between vibrational excitation by impact and thermal activation of energetic material molecules [46].

8.5 Initiation by Shock

For the purposes of this study, we are discussing a shock wave generated by detonation (i.e. a shock front), because there is a relationship between detonation pressure and two other characteristics (i.e. *D* and *Q*). It is these two characteristics that were used as representative of shock using a rough approximation [1, 4, 6]. By means of an approach analogous to that used in the case of impact sensitivity, relationships between the characteristics of detonation and ^{15}N NMR chemical shifts for nitramines [1, 4, 6, 10] and polynitro arenes and aza-arenes [9, 14] were studied. In contrast to the previously mentioned relationships for impact sensitivity, the characteristics of detonation (i.e. heat of explosion, Q, or the square of detonation velocity, D^2) correlate with the ^{15}N NMR chemical shifts, δ_N, of the nitrogen atoms of the first reacting nitro groups in the initiation process [1, 4, 6, 10]. It follows that the primary fission of a nitramine molecule is the same as that in the case of initiation by impact [1, 4, 6, 10]. Replacing the squares of detonation velocities by the Q values of nitramines gave equally good correlations [1, 6].

A closer relationship between the Q_{real} and δ_N values exists for polynitro arenes and aza-arenes [9]. The more complex intra-molecular interactions in these molecules result in more complex relationships. Two groups of substances differ by the presence of intra-molecular hydrogen bonds in one. Another group includes polynitro derivatives with a more distinct steric effect due to the interaction between the *ortho*-standing nitro group and this substituent (mediated by the electron pair at the oxygen atom) that participates in the primary chemical process of thermolysis. The last group represents substances with primary homolysis of the C–NO$_2$ bond, and C–S bond in the case of DMDIPS [9]. According to the relationship between the square of the detonation velocity and the δ_N values [14], two reaction centers are clearly identified for HNBP. 5,7-Dinitro-1-(2,4,6-trinitrophenyl)-1*H*-1,2,3-benzotriazine (BTX) correlates here through the δ_N value of the nitro group in position 7, while in the similar relationship for the E_{dr} values it is the nitro group in position 2 (of the 2,4,6-trinitrophenyl group) [14]. Similar dependencies exist for ^{13}C NMR shifts of carbon atoms – “bearers” of the primary reactive nitro groups in polynitro arenes [1, 4, 11, 12].

On the basis of the UB3LYP calculation, the values obtained for bond dissociation energies, *BDE*, of the weakest N–N bonds, and total energies, E_{total}, for 14 nitramines have been correlated (using the ratio BDE/E_{total}) with the logarithms of detonation velocities [27]. The ambiguity of the resulting relationships mainly lies in the real conformation of the respective molecules and intermolecular force effects in the real molecular crystal, which are included in the calculation methods [27]. However, partial relationships of this type can be used for evaluating the effectiveness of the method of classifying molecular structures of energetic cyclic nitramines in order to obtain products with the maximum possible performance.

8.6 Friction Sensitivity (Friction Reactivity)

Over the last 20 years, the main interest in high energetic materials has been studies of shock and impact sensitivities. However, no such attention focused on the characteristics of friction sensitivity (FS) for these materials. Our experience shows that the results of FS determination can be heavily influenced by “human variability.” Nevertheless, careful measurements by a single researcher provide results showing relationships that are also correlated with the output of other stability and physico-chemical tests [15, 40, 42, 43] and also with the output of DFT calculations [57].

The relationship between friction sensitivity (FS, shear slide with fixed volume) and impact sensitivity (IS, uniaxial compression) [43] can be described by a semi-logarithmic equation. The investigation of HMX fractions with different granulometric distributions showed that the lowest IS is connected with the highest FS and vice versa. There exists a relatively wide range of HMX granule sizes in which the FS is practically the same. Inclusion of a wider assortment of nitramines into the above-mentioned study results in their splitting into a number of partial groups, which are closely connected with the molecular-structural characteristics of the nitramines studied. Comparison of FS with heats of fusion shows that the increase in $\Delta H_{m,tr}$ values is more or less connected with a decrease in friction sensitivity.

The relationship between friction sensitivity and thermal reactivity of nitramines [40] is not unequivocal. It is possible to observe a general trend where a decrease in FS is connected with an increase in the N–NO_2 bond strength. This strength can be represented by the activation energies of monomolecular non-auto catalyzed thermal decomposition of the substances mentioned. Similarly, most of the nitramines studied exhibit a decrease in FS with increasing hypothetical initiation temperature. This temperature is taken as the temperature for a 5% conversion of the nitramine after 50 μs of thermolysis. However, this trend is opposite in the series of nitramines, which might be connected with the dominating effect of energy content of their molecules and the similarity of the effect of their intermolecular interactions upon the initiation reactivity of the nitramines. The relationships found made it possible to predict, and subsequently verify, the value of activation energy of non-autocatalyzed thermal decomposition of 2,5-dinitro-2,5-diazahexane (DMEDNA).

The relationship between friction sensitivity (FS) and the detonation parameters of nitramines [42] is also not unequivocal. There is a general trend of decreasing FS with increasing energy content of the nitramines studied. The character of intermolecular interactions and the initiation reactivity of structurally cognate nitramines may provide a reason for dividing the nitramines into groups on the basis of comparing their FSs with their detonation velocities. A better indicator of energy content of nitramines was found in the dimensionless ratio, $Q_{real}E_a^{-1}$, i.e. the ratio of heats of explosion to the activation energies of their non-auto catalyzed thermal decomposition. According to the relationship between FS and this ratio, the nitramines studied divided into groups on the basis of similarity and rigidity of their molecular skeletons. The presence of "acidic hydrogen atoms" in the molecule of 1,4-dinitro-1,4-diazabutane (EDNA) somewhat increases its FS as compared with structurally cognate secondary nitramines.

As in the case of other nitramine sensitivities, their FS also exhibit a relationship with the ^{15}N NMR chemical shifts of the nitrogen atoms in the nitramine groupings [15]. This relationship includes the ^{15}N shifts of those groupings (reaction center) that give the primary response in the process of initiation. In this respect, the nitramines studied can be divided into several groups in which there is a relatively close molecular-structural similarity. This classification is due to the extent of participation of the nitrogen atoms of the reaction center of the nitramine molecule in the intermolecular potential and electron configuration of this center. Using ^{15}N shifts of the nitrogen atoms in the nitro groups results in more sophisticated relationships than those resulting from the use of the shifts of aza-atoms. In this sense, the initiation by friction differs from initiation by impact and seems to be similar to initiation by shock, electric spark, and initiation in low temperature thermolysis.

The relationship between the maximum positive surface electrostatic potentials ($V_{S,max}$) and friction sensitivity (FS) [57] is again not unequivocal. In the groups of nitramines in which its increase is connected with a decrease (not very distinct) in FS, the dominant role in the initiation reactivity is most likely played by the bonds in the configuration of aza-nitrogen atoms; the conformation of molecules might perhaps play the dominant role in the group of nitramines exhibiting the opposite trend in the relationship of FS versus the $V_{S,max}$ values. The trend of the relationship between minimum negative surface electrostatic potentials ($V_{S,min}$) and the FS values stands in relatively good agreement with the evaluation of initiation reactivity by means of the net charges of nitro groups. In this case, FS more or less decreases with increasing $V_{S,min}$ values. It can be seen that the $V_{S,min}$ values correspond better than the $V_{S,max}$ values with the initiation reactivity. This conjecture agrees well with the fact that the nitro group is the center of initiation reactivity in nitro compounds.

8.7 Electric Spark Sensitivity

The University of Pardubice had two instruments for studying electric spark sensitivity [1, 23, 61]. They differ in the electrode configuration and circuit structure [1, 23, 45], particularly in the construction of their spark gaps. The discharge in the spark gap of the older instrument (code designation RDAD) goes through an air gap while the newer instrument (code designation ESZ KTTV) has its electrode in direct contact with the sample. The sensitivity values obtained by the two instruments differ in the order of magnitude [1, 23, 45]. The considerable electrical energy losses in the area between the upper electrode and the sample surface in the older system (RDAD) contribute to the difference mentioned above. Most likely a large part of the discharge is converted into the expressive thermal component [1, 23, 45]. However, the values for the measurements carried out with the RDAD instrument were comparable with those of Los Alamos National Laboratory [58].

An ESZ KTTV instrument was used to determine the electric spark sensitivity (E_{ES}) of 16 nitramines [1, 23]. From the results it is possible to conclude that the mechanisms for spark energy transfer into the reaction center of the molecule should be different using the two alternative instruments (RDAD and ESZ KTTV). The thermal component of discharge in the RDAD instrument may be one of the reasons for this difference. This assumption is also supported by the differences (in order of magnitude) between the E_{ES} values obtained from the instruments. Furthermore, the considerable electrical energy losses in the area between the upper electrode and the sample surface in the RDAD system measurements contribute to the difference. Most likely a large part of discharge is enacted in the air. Data from the ESZ KTTV instrument have a close relationship to the molecular structure of polynitro compounds measured [1, 23, 24]. In keeping with the knowledge about initiation reactivity of polynitro compounds [1, 23], the E_{ES} values correlate with those characteristics of the molecular structure that correspond to the primary reactive nitro group in the nitramine molecule. The reverse relationship between the E_{ES} values and dissociation energies *DH(N-N)* needs a detailed, preferably quantum chemical, interpretation. The E_{ES} values also correlate with heats of fusion of the nitramines studied, probably due to the influence of dislocations in their crystals on electric spark sensitivity. This assumption could be relevant to the significant influence of the shapes and size of the crystals on electric spark sensitivity of energetic compounds in general [23]

The results of measurements carried out with the ESZ KTTV correlate with the molecular structure of the polynitro arenes and their derivatives [24]. This structure was represented by the calculated

Mulliken net charges, Q_{NO2}, of the nitro group. These data should concern the nitro groups that would be the first to undergo chemical changes. In accordance with the findings of Ref. [23], it has been shown that intermolecular interactions play a non-negligible role in initiating polynitro arenes by electric spark [24]. The generally accepted assumption that the most positive Q_{NO2} value in the molecule represents its sensitivity cannot be regarded as universally valid. It would be useful to study the findings from crystallographic studies of the respective compounds to enable further understanding. In the case of polynitro compounds possessing more than one potential reaction center in their molecule, it has been shown [1, 4] that there can be selective initiation reactivity depending on the kind of impulse [24]. A reverse relationship between E_{ES} values and the thermostability threshold was found [38] that is analogous to the relationship between the E_{ES} and *DH(N-N)* values in nitramines [23].

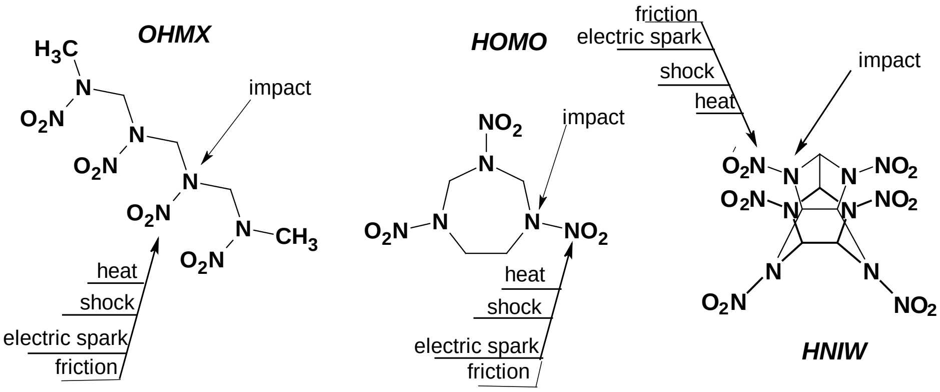
The E_{ES} values obtained from the ESZ KTTV instrument logically correlate with ^{15}N NMR chemical shifts of nitrogen atoms of the primary reactive nitro group and with the charges on these atoms [23]. In an attempt at classifying the reaction center in molecules of polynitro arenes by means of ^{13}C NMR chemical shifts of the “bearers” of primary reactive nitro groups, logical dependencies were observed, especially in the case of derivatives whose primary reactive nitro group is conjugated with the rest of the molecule [1, 4, 11].

A decrease in electric spark sensitivity (i.e. an increase in the E_{ES} values), when the grain size of nitramine crystals increase, confirms the French idea [59] about the mechanism of spark energy transfer into the powdered reactive solid, i.e. in this case to decrease the number of intergrain points per unit volume [59]. However, dislocations in the crystals should also have some effect on this type of energetic material initiation [23].

Artificially introducing fine and hard particles (nano-diamond, crushed glass) into the crystalline nitramines decreases the electric spark sensitivity of the resulting mixtures, i.e. the particles behave as a flegmatizing additive, where the number of intergrain contact points of the nitramines grains is decreased by introducing foreign particles [59].

8.8 Difference between Nitramine and Nitro Groupings in Molecules of EMs

From what has been given so far it follows that the aza-atoms carrying the primary reactive nitro groups play a key role in impact initiation [1, 4, 10]. The dominant factor in the initiation by shock, electric spark, friction and in low-temperature thermolysis should be the electron structure and proximity of the primary reactive nitro group [1, 4, 10, 15]. For those nitramine molecules whose nitrogen atoms are not isochronous, this is documented in Scheme 8.6 [1, 4, 10, 15]:



Scheme 8.6: Summary of the findings about initiation reactivities.

In Scheme 8.6, a summary of the findings about initiation reactivities can be presented as follows:

- dominating reactivity of “inner” nitramino groups of OHMX molecule in impact, shock and friction [1, 10]
- the most reactive nitramino group in HOMO molecule is the one at the 1 position of its molecule [1, 10] and in HNIW molecule at position 2 (where there is the longest N–N bond in a molecule of its ε–polymorph [10])

In the case of the 2,4,6,8-tetranitro-2,4,6,8-tetraazanonane (OHMX) molecule, the primary reactivity of “inner” nitramino groups (positions 4, 6) was confirmed using the molecular-dynamic simulation (see quotations in [1, 10]). A similar situation is encountered with polynitro arenes. Apart from the MO calculations, the inequality of nitro groups in the molecule is also indicated, especially in papers [1, 4, 9, 12, 14 - 16, 19, 20, 22, 24, 31]. All these inequalities are potential sources of initiation, i.e. one of the causes of sensitivity of individual EMs to stimuli.

As has already been mentioned, the complexity of the molecular structure of polynitro arenes (besides nitramines) makes the situation with their primary fission somewhat complicated. If a molecule contains several types of substituents, it can contain several potential reaction centers [1, 4]. Two potential reaction centers exist in the molecules of PYX, TMPM, DMDIPS, HNBP and others. A part of these possibilities is shown in Schemes 8.1-8.5.

More probable pathways for initiating the PYX molecule were estimated [28] from considerations involving the following relationships [1]: (1) between impact sensitivity and the ^{13}C NMR chemical shifts of some polynitro arenes; (2) between electric spark sensitivity and these shifts; (3) between Mulliken charges on nitrogen atoms of the primary reactive nitro group and onsets of thermal decomposition from differential thermal analyses of the said compounds [20]; and (4) with computations obtained using the DFT-B3LYP/3-21G methods in the GAUSSIAN 98/03 program. It was found that both reaction centers in the PYX molecule probably participate in the first fission caused by initiation stimuli, although primary participation of the picryl nitro group in position 2 (together with amino bridge) in this process seems to be the more probable (i.e. Channel I) [28]. The same approach to the TMPM molecule (see Scheme 8.2) [1, 28], i.e. primary participation of the nitro group in position 2 together with the methyl group in position 3 during initiation processes in this molecule, should be a unique reaction center (i.e. only Channel III). It may be stated that initiation proper can be achieved by the molecule simultaneously being activated by several centers (the detonation of TMPM) or always by a single center in a given type of initiation (the initiation of PYX by impact or shock versus its initiation by electric spark) [1].

8.9 Relationship between Data for Different Reactivities

8.9.1 Relationships between Initiation Reactivity and Detonation Characteristics

From what has been said so far, and from the published papers [1-4, 6, 7, 9, 10, 34, 39], it follows that logical relationships exist between the characteristics of low-temperature thermal decomposition and the characteristics of initiation and detonation. The homolytic character of primary fission in both the detonation and low-temperature thermal decomposition of energetic materials (for relevant quotations, see Refs. [1, 39]) was a reason for Zeman to use the Evans–Polanyi–Semenov equation (E–P–S) ([39] and references therein) to study the chemical micro-mechanism governing initiation of energetic materials [39]. A relationship similar to the E–P–S equation can also be obtained by comparison of the dependencies between thermolysis, or detonation characteristics, and NMR chemical shifts [1, 9]. It has the following form:

$$E_a = \alpha Q + \beta \qquad (1)$$

and, using the relationship defined between detonation velocities and explosion heats Q [138] in the form

$$Q = D^2\{2(\gamma^2 - 1)\}^{-1} \qquad (2)$$

where γ is the polytropy coefficient, this transforms eqn. (1) into the following form

$$E_a = \mathrm{a}D^2 + \mathrm{b} \qquad (3)$$

Zeman called equations (1) and (3) a modified E–P–S equation [39]. The original E–P–S equation describes a relationship between activation energies E of most substitution reactions of free radicals and the corresponding heats of reaction ΔH of narrow sets of substance structures. The equation shows that the strength of the bond being split is a decisive factor in the associated reaction. In both equations (1) and (3) the energy, E, can be the activation energy of thermal decomposition, E_a [1, 10, 39], the slope $E_a{\cdot}R^{-1}$ of the Kissinger relationship [1, 3, 34, 35, 60], the energy of electric spark, E_{ES} [1, 23], or drop energy, E_p [1, 22]. It may be substituted by the charge, q^{N}, at the nitrogen atom of the most reactive nitro group [1, 17] in the molecule, by the net charge of this nitro group [1, 22], or by half-wave polarographic potential [44]. The following paragraphs present several typical examples.

The validity of equation (1) has also been successfully verified for the thermal decomposition of inorganic azides and photolysis of fulminates [1, 39]. For azides, the literature gives activation energy values, E_a, for thermal decomposition within various temperature ranges. In the sense of equation (1), however, only those E_a values that correspond to the lowest experimental temperature ranges correlate well [39]. This is a very important finding.

The Q values can be taken as representative of energetic materials performance. Substitution of the activation energies E_a for highly thermostable polynitro arenes by drop energies in equation (1) shows how an increase of energy content in EMs corresponds to increasing sensitivity [1, 22]. For the analogous relationship for electric spark sensitivity of the technologically attractive nitramines, the same fact is valid, i.e. the increase in performance is related to increasing electric spark sensitivity [1, 59]. In the case of friction sensitivity, it appears that increased performance corresponds to a decrease in sensitivity [42]. From what has been said so far it is clear that the so called modified E-P-S equation corresponds to some well known facts: high performance is usually accompanied by enhanced sensitivity, which means that an insensitive explosive will not exhibit top performance (for relevant quotations, see Ref. [1]). This statement has not yet been proved by theory, and is waiting for quantum chemists to come up with an answer. However, exceptions from this statement exist, as is documented by Figures 8.2 and 8.3 (here a group RDX - β-HMX- α– and ε–HNIW which is described also in [36] as a part of study of PBXs)[61].

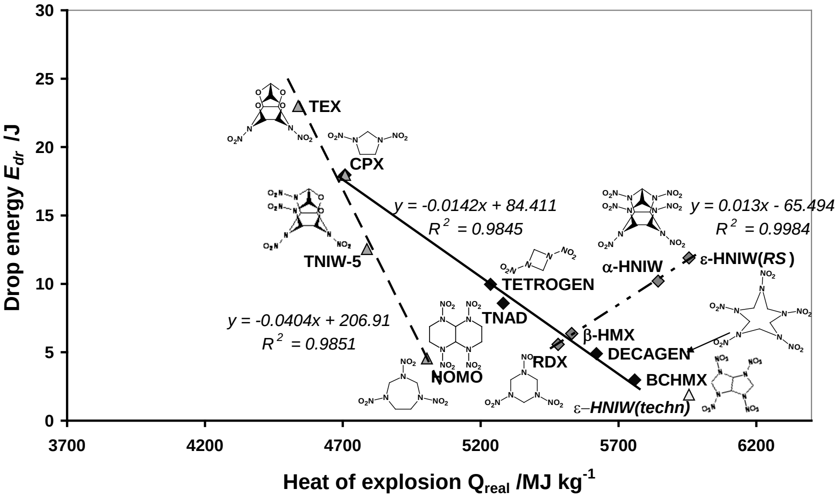


Figure 8.2: Relationship between impact sensitivity, E_{dr},, detected by sound, and heat of explosion, calculated according to Pepekin et al. (*the Q_{real} values should correspond to heats determined by calorimetric method for the given density*) [61].

Figures 8.2 and 8.3 again show the difference between "ordinary" quality ε-HNIW (technical grade CL20) and its pure variety (RS-CL20, i. e. with reduced sensitivity) [56].

Another form of equation (3) can be taken as a relationship between impact sensitivities, E_{dr}, and detonation pressure (represented by the product of the square of experimental detonation velocity and density of charge) of the plastic bonded explosives (PBXs) [41]. Here an increase in this pressure corresponds to an increase in the sensitivity. Technical grade CL20 is sharply differentiated from RS-CL20.

Equation (3), with the E_a replaced by the slope, E_aR^{-1} of the Kissinger relation, was used also in a study of explosive mixtures. Thermal reactivity of several oxidizing systems of emulsion explosives and some commercial explosives with different nitrate ester content have been specified in the literature [1, 34]. The main component of the oxidizing systems in all the materials studied was ammonium nitrate (AN). A critical amount of additives of nitric ester or nitramine type exists in the mixtures (i.e. about 30% by mass). Explosive decomposition is not influenced by the structure of the oxidizing system (solution or crystalline) of these fortified mixtures except in the case when the content of the additives is above the critical value. This effect is analogous to the well-known influence of shock pressure on initiation and growth of the detonation in which the critical pressure plays a decisive role. It was stated that in the explosive mixtures studied, the thermal reactivity of the oxidizing system and/or its mixture with a high explosive (for example: AN increases the thermal reactivity of RDX [21]) replaces the primary thermal reactivity of explosophore groups in the individual energetic materials [1, 34]. This form of equation (3) has been successfully used in the study of 10 nitramines [1, 3] and also plastic bonded explosives [36].

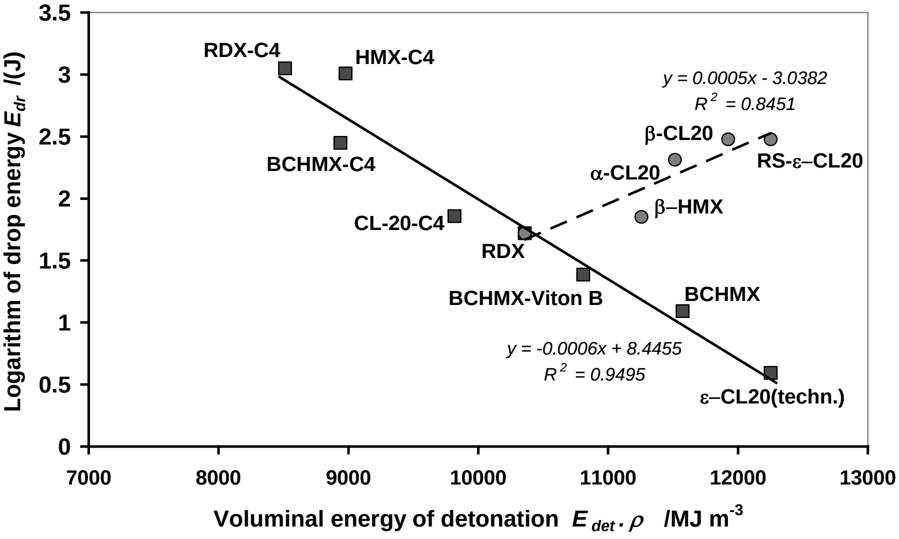


Figure 8.3: Semi logarithmic relationship between impact sensitivity, E_{dr},, detected by sound, and volume heat of explosion (calculation by EXPLO5); points with C4 means PBXs contained 9 % wt. of C4 matrix [61].

The same modification of equation (3) was used in a study of thermal and detonation reactivities of mixtures containing 1,3,5-

trinitroso-1,3,5-triazinane (TMTA or R-salt) [35], which might be the subject of criminal abuse (castable systems with a content over 70 % wt. of RDX [62]). Thermal reactivities of TMTA, 1,3,5-trinitro-1,3,5-triazinane (RDX), 2,4,6-trinitrotoluene (TNT), TNT/TMTA and RDX/TMTA mixtures and mixtures of 1,3,5-trinitrobenzene (TNB) with TMTA and TMTA/RDX were classified by means of differential thermal analysis with output evaluation by the Kissinger method. The reactivities, expressed as E_aR^{-1} slopes of the Kissinger relationship, correlate with the squares of detonation velocities of the corresponding explosive samples in the sense of modified Evans-Polanyi-Semenov equation. Taking this fact it is stated that detonation initiation of mixtures with TMTA content proceeds through initial fission of the TMTA molecule (here homolysis of the N-NO bond). If an ionic mechanism is dominant in thermal decomposition of some of the mixtures studied, then the resulting $E_a\ R^{-1}$values do not correlate in the sense of the equation. This is the case of the TNT/TMTA mixtures, where TNT has an acidic character toward TMTA. Also the TNB/TMTA/RDX mixture might give TMTA amine intermediates by thermal decomposition with RDX through an ionic mechanism [35].

8.9.2 Special Relationships

A semi logarithmic relationship was found between impact and friction sensitivities [41, 43]. In the case of ε-HNIW it was found that, while technical grade and RS-HNIW have very different impact reactivities, their friction sensitivities are practically the same [41, 43].

Taking detonation velocity as a zero-order reaction, a very important finding was obtained with Slovak commercial explosives [33]. Using a modification of the American vacuum isothermal stability test, the Czechoslovak system STABIL [33], in the study of the thermal reactivity of explosives, pressure-time curves over 300 minutes for thermolysis are often obtained corresponding to the zero-order reaction forming gaseous products. Then, a relationship between the corresponding zero-order reaction velocities and explosion (detonation) temperatures can be found [33]. This might indicate that the reaction rates of low-temperature thermolysis (with the occurrence of secondary reactions in the gaseous products formed) depend on the rate of conversion in the detonation reaction zone of the explosives [33].

Another paper deals with the characteristics of the processes in the detonation reaction zone [64]: it is well known that a trace admixture of a strong amine with nitromethane (NM) can change its detonation velocity from 6.3 km s^{-1} up to a value of 6.7 km s^{-1} and detonation pressure from 13 to 20 GPa [29]. There exists much greater discussion in the literature, not only about this fact but also about the mechanism of nitromethane initiation in general [1, 64]. We have commented on some thermodynamically, and sometimes also chemically, unrealistic conclusions in these discussions [64]. We have discussed [64] a well-known effect of amines, and also of water, on the detonation characteristics of the nitro paraffin, nitromethane (NM) from the point of view of the published knowledge concerning initiation reactivity. We also documented that bimolecular and higher interactions during the initiation of NM are impossible. The most widespread concepts of the primary steps of this initiation, i.e. formation of the *aci*-NM anion $[CH2=NO2]^{-}$ by intermolecular hydrogen transfer in the pure NM submitted to shock, and formation of this anion by action of an amine, have been scrutinized by the DFT B3LYP/cc-pVTZ+ method and judged to be thermodynamically disadvantageous. Also the 1,3-intramolecular hydrogen shift in the NM molecule was characterized as a higher-barrier process. Two favorable primary mechanisms of fission in the NM initiation and development of its detonation were investigated by DFT B3LYP/cc-pVTZ+ calculations: homolysis of the C–NO2 bond in the pure NM and homolysis of the N–OH bond in its *aci*-form. The second mentioned pathway was found to be the thermodynamically preferable mechanism of fission. Consequently, a detonation wave of NM with admixture of amine or water has a considerably reduced reaction zone length in comparison with the detonation of pure NM. The B3LYP/6-311++G(d,p) calculations of transition states revealed that an admixture of methylamine and/or water influences the conversion of nitromethane to its *aci*-form, and this effect is more feasible in the case of methylamine than with water [29].

8.10 Comparison of Splitting Polynitro Arenes by Heat and by Shock

In order to verify the hypothesis of identical primary fragmentation reactions in low-temperature thermolysis and detonation reaction of EMs, a group of polynitro arenes [49, 50] (with presumed mechanism of primary decomposition as given in Schemes 8.1-8.3) was submitted to a comparative study of splitting by heat and by shock wave. Paper [49] deals with 2,4,6-trinitrotoluene (TNT) that was exposed to heat or to shock and, afterwards detonation. The residues were analyzed chromatographically (LC-UV and LC/MS). It was found that the main decomposition intermediates identified are identical in all three cases. 4,6-Dinitro-2,1-benzoisoxazole and 2,4,6-trinitrobenzaldehyde are the most reactive of them. It has therefore been stated that the chemical micro-mechanism of the primary fragmentations of shock-exposed TNT molecules and/or its detonation transformation should be the same as in its low-temperature thermal decomposition. The first finding is in excellent agreement with the experimental results obtained recently by Bulusu and Autera in the field of using Deuterium Isotope Kinetics Effect (for relevant quotations, see Refs. [1, 29]).

In a second group of substances [50], the same investigation method was applied to *N,N´*-bis(2,4,6-trinitrophenyl)-3,5-dinitropyridine-2,6-diamine (PYX – see Scheme 8.1), 2,4,6-trinitroaniline (PAM), 2,4,6-trinitro-N-(2,4,6-trinitrophenyl)aniline (DPA), and *N,N´,N˝*-tris(2,4,6-trinitrophenyl)-1,3,5-triazine-2,4,6-triamine (TPM). Samples of these substances were also exposed to heat or to shock and then analyzed chromatographically (LC–UV and LC/MS). It was again found that the main decomposition products of these two incomplete initiations are identical for each of the compounds studied. Also in this case, it has been stated that the chemical micro-mechanism of the primary fragmentations of low-temperature decomposition should be the same as by shock initiation, including fragmentation during their detonation transformation.

8.11 Conclusions

Study of the sensitivity of energetic materials is inseparably connected with understanding the primary chemical processes of their initiation. However, over the last 22 years the study of such sensitivity (i.e. initiation reactivity) has accelerated thanks to theoretical methods based on quantum mechanics (quantum chemistry) [1]. Impact and shock sensitivities have been the main focus of this interest [1, 4]. A common feature of impact, shock, friction, electric spark and thermal sensitivities of organic polynitro compounds is the reactivity proper of the C–NO_2, N–NO_2 and O–NO_2 groupings in their molecules and/or molecular crystals. Besides the relationships between the characteristics of these various sensitivities [1 – 4, 7, 10, 11, 14, 23, 29, 33 - 35, 38 - 40, 42, 43, 49, 50] it is also possible to study the micro-mechanisms of their primary chemical processes with the help of ^{15}N and ^{13}C NMR chemical shifts of key atoms in the molecule’s reaction centers [1, 3 - 7, 9, 10, 11, 14,15, 16, 23], with the help of charges on the nitrogen atoms of the primary reactive nitro groups [1, 3, 13, 14, 17 - 23, 30] and/or of net charges of these nitro groups [1, 13, 14, 22 - 24]. However, it has been shown [13, 14, 30] that widely dispersed calculations on the basis of conformation of isolated molecules (i.e. DFT calculations) leads often to unrealistic results. This approach, however, can give acceptable results in the case of relatively simple molecules (nitramines) [13, 14, 30, 31, 57]. This is understandable because intermolecular interactions play a very important role in the initiation reactivity, as can be seen from the heats of fusion of energetic materials [1, 4, 7, 10, 43, 47] or the relationship between bond dissociation energies of the weakest N-N bonds and heats of fusion of nitramines [25]. The use of polarography to study this type of reactivity is limited by solvation effects of the polynitro compounds studied in aqueous solutions [44]. So far, NMR chemical shifts have appeared to correspond best to the real electron configuration and steric conditions of the key atoms in the reaction center of any given molecule. From the point of view of the physics of explosion, these atoms can be taken as “chemical hot spots” [1, 3, 10]. In the case of technologically attractive explosive mixtures with the oxidation system based on ammonium nitrate, these chemical “hot spots” represent a part of this system (or mixtures with high explosives, as the case may be – including explosives of the PBXs type [36]) [1, 34].

The relationships between detonation characteristics of energetic materials and the characteristics of their low-temperature decomposition and other characteristics of their mechanical and electric spark sensitivities [1 – 4, 7, 8, 10, 16, 33 – 43, 60, 61] show that:

- the primary fragmentation processes of energetic material molecules in low-temperature thermal decomposition should be identical with those in the impact, electric spark and shock initiations, which, in the case of shock, can also be documented by experimental results from initiation of TNT [49] and some of *N*-(2,4,6-trinitrophenyl)-substituted polynitrated aminoarenes [50], and in the case of zero-order low-temperature thermolysis by correlation of its reaction rate with the rate in the detonation reaction zone [33];
- the effect of temperature (*i.e. thermal decomposition*) in the classic sense is not applicable to the process of detonation initiation by shock, impact or electric spark [3];
- the primary fragmentation of EMs in their detonation transformation should proceed at milder conditions than those present at the front of a detonation wave or in its reaction zone, which means that the detonation transformation itself of the given substance should be preceded by an induction period [3, 10] (whose necessity is, however, also considered in the Non-Equilibrium Zeldovich–von Neuman–Döring theory of self-sustaining detonation - for relevant quotations, see Ref. [1]);

Electron configuration and steric effects at C or N-atoms, which are bearers of the primary reactive nitro groups in the molecule, should play a key role in initiation by impact. The dominant factor in the initiation by friction, shock, electric spark, and in low-temperature thermolysis should be the electron structure and proximity of the nitrogen atom of the primary reactive nitro group [1, 10, 15] (see Scheme 8.6).

The results mentioned are best demonstrated by secondary nitramines [1, 3, 10] which, in their molecular structure, are relatively simple polynitro compounds, and the mechanism of primary homolysis of these molecules is well understood (for relevant quotations, see Refs. [1, 10]). Polynitro arenes, on the other hand, have a more complex structure and have intra-molecular effects in their molecules. Here the mesomeric, inductive and steric effects on reactivity operate simultaneously. This fact also makes the problem of their primary fragmentation somewhat complicated [1, 4, 39] (see Schemes 8.1-8.4). If a molecule of these compounds contains several types of substituents, it can contain several potential reaction centers (e.g., the PYX and TMPM molecules, see Schemes 8.1 and 8.2). The initiation can then be realised by the molecule simultaneously participating with several centers or always by a single center in a given type of initiation (the initiation of PYX by impact or shock versus its initiation by electric spark) [1, 4].

As for electric spark sensitivity, which has also been assessed from the standpoint of development of the respective instruments [23, 45], this characteristic is also dependent upon the configuration of electrodes and structure of the circuit, which complicates the energy transfer from the electric spark to the reaction center of the molecule [23, 24]. In instruments exhibiting a large energy loss during electric discharge, the thermal principle of initiation predominates [4, 23, 45]. On the other hand, instruments with minimized energy losses still need to be investigated from the point of view of the energy transfer. So far, the operation of “hot spots” in this initiation has been confirmed (for relevant quotations, see Refs. [59]), i.e. the role of inter-grain contact points of the EM grains [59]. On the basis of this view, it is understandable that addition of fine, hard particles to EMs has a desensitizing effect in this type of initiation [59], while the same additives are well known to have a strong sensitizing effect in the initiation of EMs by mechanical stimuli.

With the already mentioned relationship between reaction velocities in the detonation reaction zone and low-temperature non-autocatalyzed decomposition of explosives [33], it should be remembered that there is a change in the chemical mechanism of the primary fission molecule in detonation of nitromethane (NM) [29]. There are two favorable primary mechanisms for this nitroparaffin initiation and its detonation development [29]: homolysis of the C–NO2 bond in practically pure NM and homolysis of the N–OH bond in its *aci*-form. The second pathway is thermodynamically the more preferable mechanism for fission; a detonation wave of nitromethane with admixture of amine or water has a considerably reduced reaction zone length, and thus increased detonation velocity, in comparison with the detonation of practically pure NM. An admixture of amine and/or water influences the conversion of nitromethane to its *aci*-form, and this effect is more noticeable in the case of amine than with water [29].

Differences between impact and friction sensitivities are a consequence of the intermolecular interaction in responding to a mechanical impulse: these interactions are inherent in the dipole-dipole contact of the oxygen and nitrogen atoms of nitro groups in neighboring nitramine molecules which act against the shear slide during friction [15, 40 - 42, 57]. As has been shown on the HMX samples with different granulometric distributions, the lowest impact sensitivity is connected with the highest fiction sensitivity and *vice versa* [43]. The example of *ε*-HNIW indicates that, while impact sensitivity depends markedly on the crystal quality of the nitramine, a similar dependency for friction sensitivity appears less pronounced and deserves additional investigation [41, 43].

A study of initiation reactivity should be performed on larger groups of energetic materials. In a search for molecular structural relationships with reactivity, it is not sufficient to rely on statistical methods, as these do not really provide the real results. The primary fission processes in initiation of these materials must also be fully considered.

8.11.1 Acknowledgement

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Chapter 9

Review and Analysis of Data on the Dislocation Mechanism of High Explosive Decomposition

Vladimir Y. Klimenko

9.1 Introduction

Our global task is to prepare a high-accuracy numerical detonation model that can describe all possible situations that happen in practice. We understand that detonation is a very complex process. It is governed by a combination of physical and chemical processes. The dominant physical or chemical process depends on the detonation pressure. We have shown elsewhere that the homogeneous mechanism (usually, it is the frontal mechanism) dominates at pressure $P > 200$ kbar and the hot spots mechanism dominates in region $20 < P < 200$ kbar. Figure 9.1 demonstrates this.

In practice there are many practical situations where pressure is < 20 kbar. These cases play an important role in applied detonation processes, for example in the initiation of explosive charges by penetrating fragments, and initiation of heavily confined explosive charges.

Haskins and Cook studied initiation of confined explosives by projectiles. They established that hot spot mechanisms do not explain initiation for sufficiently thick cover plates [1, 2]. They suggested [3] that it is a shear dominated mechanism [4].

The problem of initiation by shear was opened at the beginning of the 1980s. There were two approaches to the study of shear strain initiation mechanisms. The first is a continuous mechanics approach. The second approach considers shear process at the micro level.

Now we will discuss these two approaches.

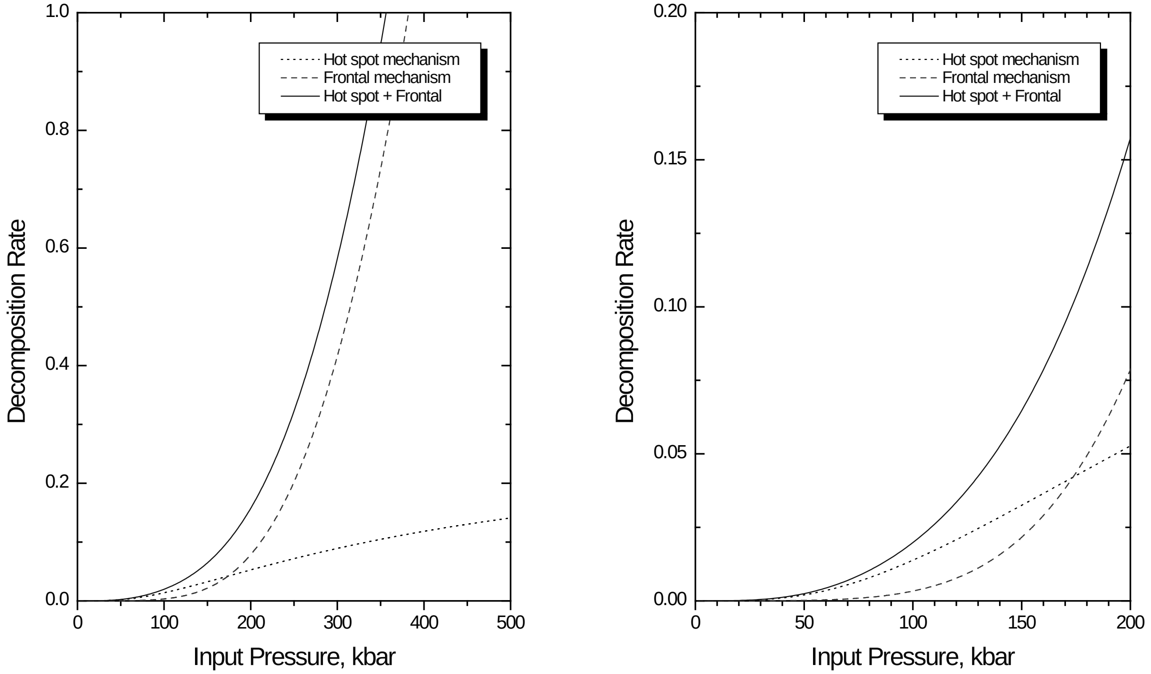


Figure 9.1: Parallel work of hot spots (….) and frontal (- - -) mechanisms.

9.2 Continuous Approach

The motivation to study explosive initiation mechanisms by shear came from two applied problems: (1) initiation in drop-weight impact tests and (2) initiation by projectile impacts.

Cambridge researchers headed by Field were pioneers in the study of shear initiation in drop-weight tests. They developed a unique drop-weight impact machine with transparent anvils that made possible real time observation of the process of shear band formation and explosive ignition (see Fig. 9.2).

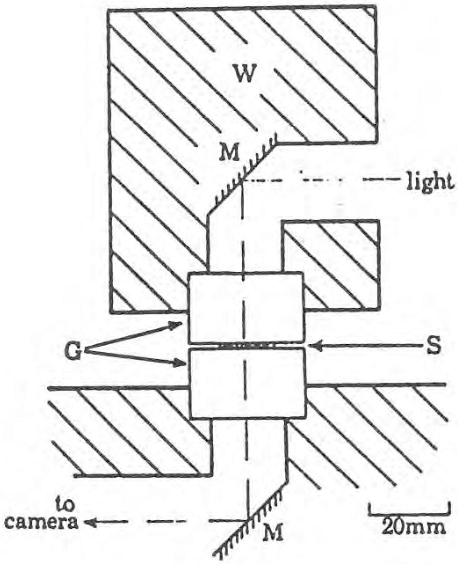
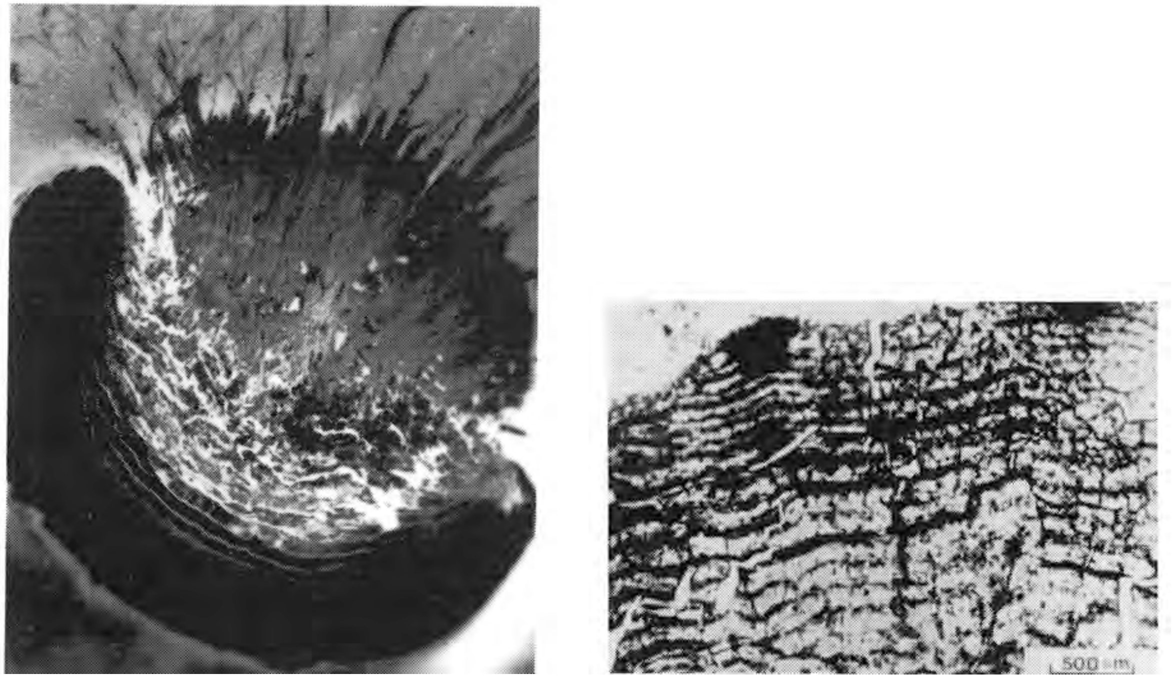


Figure 9.2: Setup for study of shear bands formation at drop-weight impact. A cross section of the C4 Drop-Weight System. W is the weight, M a mirror, and G the toughened glass anvils with S the specimen.

The most important results are presented in papers [5, 6], where it was shown that:

- explosive deformation proceeds by shear banding
- shear bands are hot-spot sites, which cause ignition of the explosive

Figures 9.3 and 9.4 show shear bands in PETN and HMX. The ignited regions are visible too.

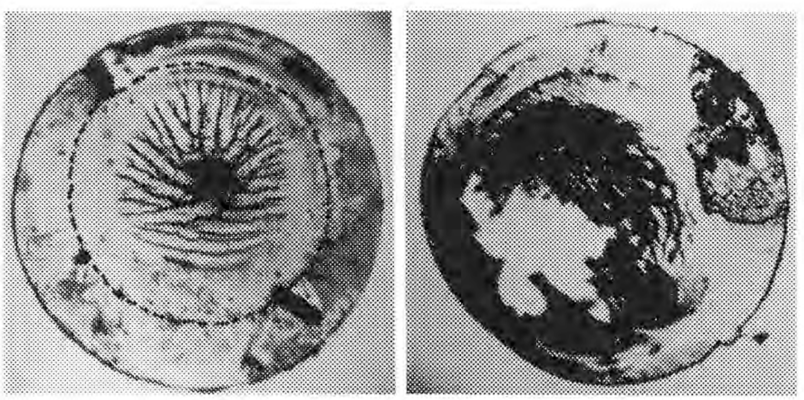


(a) (b)

Figure 9.3: Shear bands and ignition regions in PETN. (a) heat sensitive film record of an impact on PETN. Original in color. Clear evidence of shear banding and associated ignition. (b) shear banding in PETN after impact, where ignition failed to occur.

In these experiments, Field and coworkers did not try to understand the mechanism of this complex process. Indeed, it is a process with nonuniform pressure and strain distribution, which is difficult to analyze. Moreover, as a rule in drop-weight tests, tested explosives are mixtures of explosive grains with different size and shape. This further complicates interpretation of the results.

Therefore, Field et al. investigated single crystals of explosives [7]. The dropping ball (d=100 mkm) impacts a single crystal of PETN (or RDX, HMX) at velocity 150-200 m/s. The impact creates shear bands. Band width and spacing between bands is measured and analyzed.



(a) **(b)**

Figure 9.4: Shear bands and ignition region in HMX. (a) and (b) - two recovered discs of heat-sensitive film (HSF). The explosive has been removed: (a) The area that the HMX occupied after impact is indicated. The discoloration of the HSF appears as a pattern of both radial and parallel lines. The sample originally covered an area similar to the discolored area. (b) Partial reaction has occurred and part of the HSF disc has been consumed, but the band-like patter is still apparent near the center of the disc.

Grady and Kipp [8] derived expressions for shear bands' spacing and width based on the catastrophic growth model of unstable thermoplastic shear:

Band width $$a_o = \left(\frac{9\rho^3 {c_v}^2 k^3}{{\tau_y}^3 a^2 \dot{Y}} \right)^{1/4}$$

$$\text{Bands spacing} \quad b_o = 2\left(\frac{9\rho {c_v}^2 k}{\tau_y a^2 \dot{Y}^3}\right)^{1/4}$$

where ρ is density, C_v is specific heat, k is thermal diffusivity ($\lambda/\rho C_v$), λ is thermal conductivity, τ_y is flow stress, a is thermal softening coefficient in shear band and $\dot{Y}$ is shearing strain rate.

Field calculated band widths and band spacing at two strain rates, 2 x 10^5 s^{-1} and 10^6 s^{-1}, and obtained good agreement with the experiment.

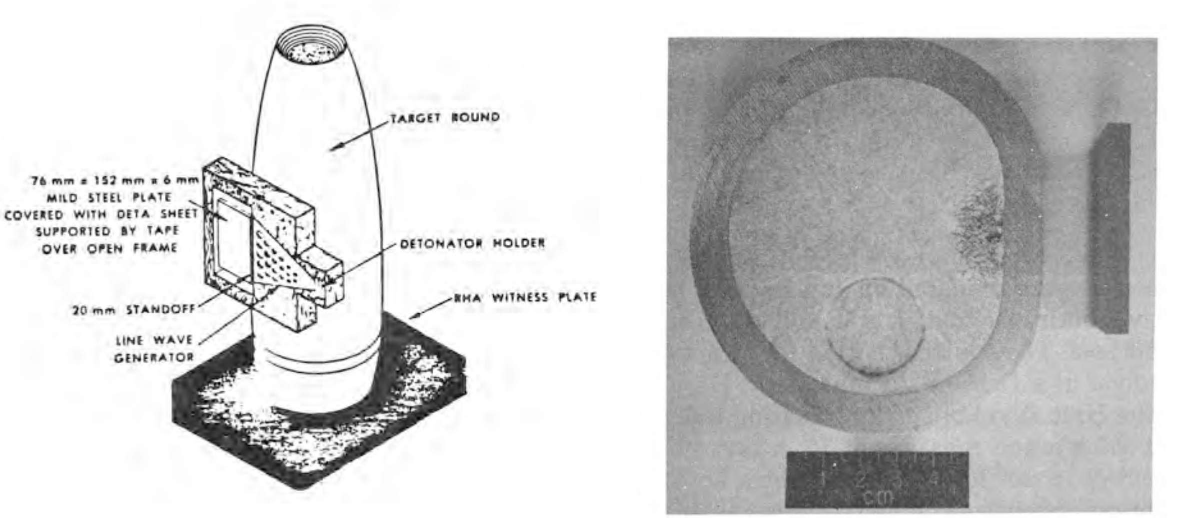
Table 9.1: Band spacing and band width for three explosives.

Band spacing, mkm					Band width, mkm	
Explosive	Calculated		Experimental		Calculated	
	2 x 10^5 s^{-1}	10^6 s^{-1}	Drop impact	Ball impact	2 x 10^5 s^{-1}	10^6 s^{-1}
PETN	255	76	250	75	0.12	0.08
RDX	237	71	-	50	0.08	0.05
HMX	321	96	400	-	0.20	0.14

Note that with an increase of impact intensity, the band width and band spacing decrease. At very high shock pressure the shear bands must merge.

Howe and coworkers at the United States Army Research Laboratory investigated initiation by projectile impact [9] (Figure 9.5). They impacted standard artillery shells with a flying plate and examined the damaged region of the explosive charge optically and with scanning electron microscopy. They detected (1) shear bands and (2) products of incomplete explosive decomposition, i.e., the beginning of ignition (see Figure 9.6). No conclusions were made about the reaction mechanism.

Other ARL researchers sought to discover the shear initiation mechanism. The 7th Detonation Symposium paper of Frey [10] is the cornerstone of the continuous approach to the study of shear ignition. Frey gives the following continuum mechanics explanation of shear band formation.



(a) **(b)**

Figure 9.5: Experimental setup (left) and damaged region in explosive after projectile impact (right) [9]. (a) Schematic of test setup for plate impact experiments; (b) Cylindrical cross section of impacted target. Corings were removed for microscopic examination. Top view.

One plane in the deforming block of material begins to shear faster than its neighbors. Extra heat generated by viscoplastic work weakens this plane due to thermal softening. The thermal weakening causes faster deformation of the plane. It is a process of spontaneous generation of the shear band. This model takes into account viscoplastic work and heating, heat transfer by heat conductivity, and heat generation by decomposition reaction. The model enables temperature estimation in a shear band.

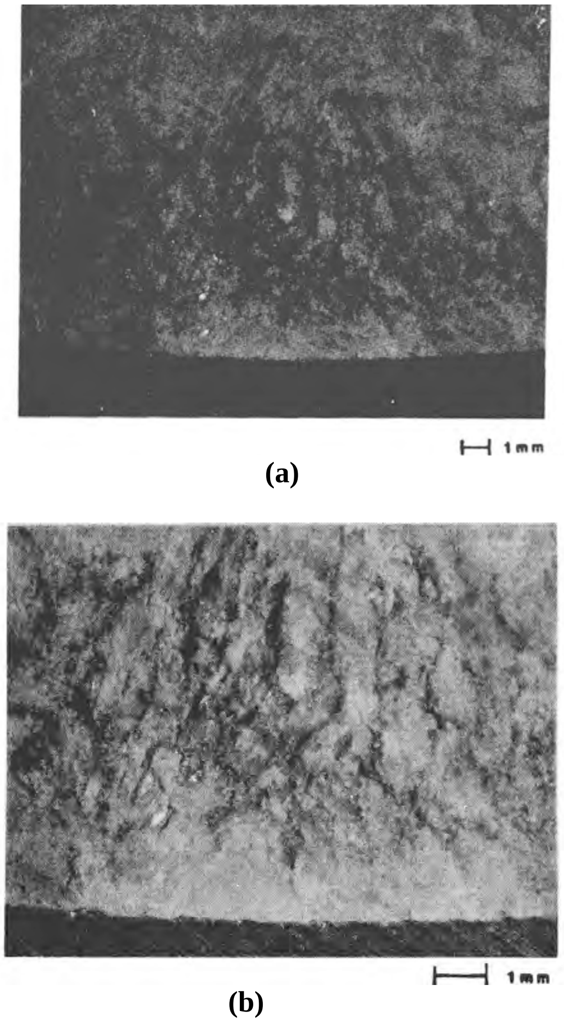


Figure 9.6: Damaged region with micro-regions of explosive decomposition. (a) Close up view of blackened region. Blackening is a result of chemical decomposition; (b) Blackened region at higher magnification. Note boundary between case and blackened region.

Viscosity is a key parameter of the model. The dependence of viscosity on pressure and temperature is calculated by

$$\mu = \mu_o \exp\left(\frac{P}{P_o}\right) \exp\left(\frac{E}{T} - \frac{E}{T_o}\right)$$

where P is pressure, P_o is an empirical factor, μ_o is viscosity at reference temperature, T_o is reference temperature, E is empirically determined activation energy for viscous flow divided by the universal gas constant.

Maximum temperature achievable in the shear band is limited by melting. The melt temperature is assumed to increase by 20 ^{0}C per kbar at pressure rise.

The Frey model was very useful in analysis of numerous experiments on explosive initiation by shear. In particular, Boyle and Frey used the model to study an ignition of Comp B, TNT and RDX compositions at combined action of pressure and shear [11]. It is necessary to note that Frey's model is very sensitive to the input parameter viscosity and therefore gives only a qualitative description of the ignition process. But, in any case, the model captures correctly the physics of the process. Frey's model is very useful in preparation and interpretation of experiments.

In [12] Boyle and Frey tried to find evidence of explosive decomposition reaction in experiments. They organized a parallel/oblique impact of a flyer plate on a thin explosive sample placed on a transparent base, and they detected a change of explosive state optically through the transparent plate (see Figure 9.7). Pressure in the high explosive sample varied from 3.3 to 13.1 kbar, and the time duration of compressed state was about 15 mks. To their great surprise, they did not detect any explosive reaction and concluded that the temperature increase in shear bands was too small ($\Delta T \approx 110$ ^{0}C) to induce reaction. But, we suspect that optical observation cannot detect the early stages of the decomposition process. Boyle and Frey could not detect decomposition with an extent less than 10 (or even greater) %. If they used the optical spectrum analyzer, then they could see the appearance and growth of reaction product concentration.

There were many attempts to observe evidence of a reaction in precise experiments. Chhabildas and Kipp [13] performed one-dimensional shear strain generation experiments with PBX-9404. They obtained precise velocity profiles, and after numerical analysis of these profiles (namely, comparison of calculated and experimental profiles), they concluded that no reaction took place during the experiment. But we feel the observation time was too short (about 1 mks) for a decomposition reaction to take place. The reactions at shear are very slow and have a characteristic time scale of about 10 mks.

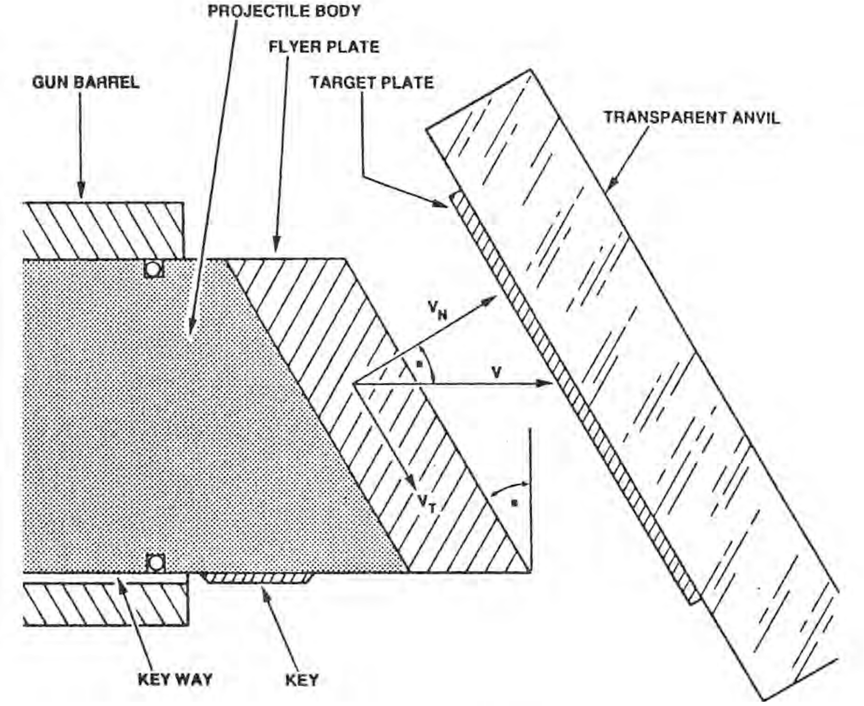


Figure 9.7: Experimental setup for creation combined pressure and shear in explosive sample [12]. Shows parallel/oblique impact of a flyer plate on a think explosive sample. The normal and tangential components of the flyer plate before impact are illustrated.

The continuous approach in different variants (for example, thermal softening, mechanical softening) is used for a description of the deformation behaviour of explosives in simulations of shock wave / detonation processes by hydrocodes. For example, Dey and Johnson [14] modeled the process of shear band formation in PBX-9501 at different deformation rates – 10-1000 s^{-1}. This is useful for improvement of the mechanical (not chemical) description of explosives by hydrocodes. But it is not a perfect description, because it does not take into account the real physics of the deformation process, which can be accompanied by a slow decomposition reaction.

The true nature of the process is to be seen at the micro-level. Events at the micro-level determine the overall process of shear band formation and the onset of reaction. Therefore, only the micro-level approach can give insight into the true nature of the shear band mechanism and ignition of the explosive.

9.3 Micro-level Approach

Coffey was the first to claim that it is necessary to consider deformation and ignition of crystalline explosive at the micro-level. He began his activity performing drop-weight test experiments [15]. The experimental results (at the beginning of 1980's) led him to develop his famous dislocation theory. This development continued about 20 years [16-19]. During this time Coffey received great support from the high-level experimental results of Sharma [20-23]. Sharma used a powerful Atomic Force Microscope, which made possible the observation of dislocations in impacted explosive (Figure 9.8).

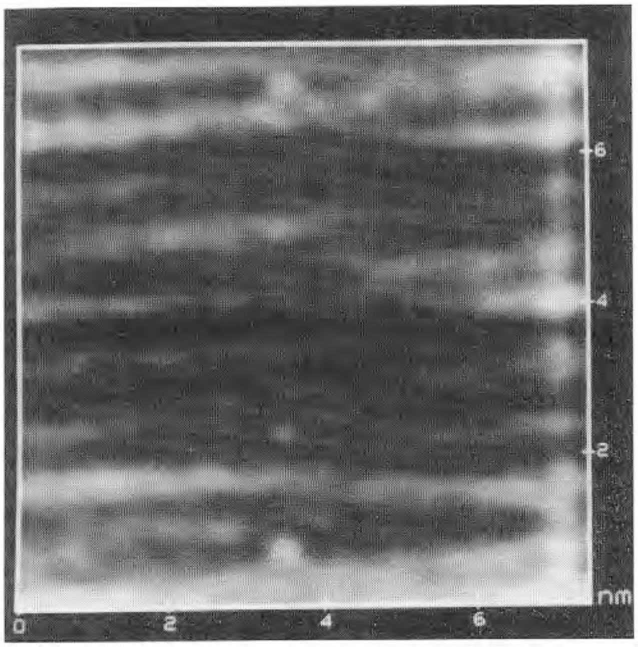


Figure 9.8: Molecularly resolved image of RDX crystal after impact [22]. A region of effected RDX showing a slip plane (vertical) and a few dislocations in horizontal rows.

The main points of Coffey's theory follow. Plastic deformation of solids (including explosive solids) occurs by generation and movement of dislocations. This is a classical theory (see, for example, [24]). The deformation often concentrates in narrow regions known as shear bands. These shear bands contain a high concentration of dislocations.

To understand the mechanism of plastic deformation of explosive crystals, it is necessary to study (1) generation and (2) moving of dislocations. Dissipation of energy takes place through dislocation motion. This dissipated energy induces decomposition of explosive molecules. The decomposition creates ignition sites that are detected in numerous experiments. Coffey gave a strong physical description of this multistep process.

The following process describes generation of dislocations. Any crystal contains some oscillator-like sources composed of a linear structure, such as a string of impurity atoms or molecules. The presence of this linear structure perturbs and distorts the local intercrystalline potential of the host lattice sufficiently so that, when a shear stress from a shock or impact is applied to the crystal across the impurity string, it is possible for local intermolecular bonds to be broken. In this process, a pair of oppositely oriented edge dislocations is created that, under the applied shear stress, are free to move away from the source region.

The dislocations are able to run along the slip plane until they encounter an obstacle such as a grain boundary, whereupon they stop and pile up behind the obstacle. Eventually, the number of dislocations in the pileup will increase to a level where it becomes energetically more favorable to transfer the newly created dislocations to an adjacent slip plane via the cross slip mechanism. In this way a shear band can be built up by the accumulation of many slip planes.

Thus, it is a physically perfect description of the process of generation of dislocations. Next, it is necessary to describe process of dislocation motion and energy dissipation.

Consider a dislocation moving at a speed V through a crystal lattice. Let d be the lattice intermolecular spacing. The lattice has some inter-crystalline potential. As the dislocation moves through the lattice it encounters this potential at a rate of V/d per second. The radial frequency of lattice perturbation near the core of the dislocation is $\omega=2\pi V/d$ rad/s. The maximum velocity at which a dislocation can move is nearly the shear wave speed $V \approx 2$ to 3×10^3 m/s. Typical intermolecular spacing in explosive crystal is about 10^{-9} m. Thus, maximum frequency is $\omega=10^{13}$ rad/s. It is a clear physical picture of the process.

Energy dissipation by rapidly moving dislocation is a quantum mechanical problem. Using a quantum mechanical approach, Coffey derived the following equation for the energy dissipation rate for N moving dislocations

$$\frac{dE}{dt} = \frac{4\pi \Gamma G^2 N}{d} \exp(-\tau_o / \tau) + N \sum_j \hbar \omega_{j,j-1}\, x \sum_{f,u} \left| \sum_{l=1} \frac{\langle f | H' | 1 \rangle \langle 1 | H' | u \rangle}{E_1 - E_u - \hbar \sum_{j=1} \omega_{j,j-1}} \right|^2 - K \frac{dT}{dx}$$

where $$\Gamma = \frac{1}{32\pi^3 \rho} \left(\frac{Rb}{1-v} \right)^2 \frac{1}{v_o d^2}$$

$$\omega_{j,j-1} = (2\pi V_o / d) \exp(-\tau_o / \tau)$$

Here

H' - the interaction Hamiltonian coupling moving dislocation with the internal molecular vibrational modes,
G - shear modulus,
b - the Burgers length,
ρ - density,
v_o - shear wave speed,
τ - applied shear stress,
τ_o - characteristic shear stress of the material.

This complex formula has a simple qualitative explanation. The first term is responsible for energy dissipation due to low and medium velocity dislocations. Consequently, it reflects the dissipation rate for impact and low level shock.

The following terms in the formula are mainly responsible for energy dissipation due to relatively large amplitude shocks. In this case the high-energy optical phonons are generated with large density. This creates conditions for multi-phonon resonant excitation of the internal vibrational modes of the molecules of the crystal located on or near the path of the moving dislocations. This results in an extremely fast process in which energy is transferred directly from the moving dislocations to excite the internal vibrational modes and even dissociate the molecules in the shear regions of the host crystal.

Coffey made a practical application of his theory. If we look at Coffey's formula, we can see that for impact and weak shocks the dissipated energy is proportional to the square of the shear modulus.

$$\frac{dE}{dt} \approx G^2$$

Standard explosives have the following shear moduli and sensitivities at drop weight test.

Table 9.3: Shear modulus and sensitivity of three explosives

Explosive	PETN	TNT	TATB
Shear modulus, dynes/cm^2	5 x 10^{10}	2 x 10^{10}	1 x 10^{10}
50% drop height test, cm	12	70	300

Coffey's dislocation model also accurately reproduces the dependence of explosive sensitivity to porosity. It is just for impact and low pressure shock waves.

Thus, Coffey's theory works well enough in the low pressure region, P < 20 kbar. This region has special interest for us because no other mechanism properly describes initiation of explosives at P < 20 kbar. That it works so well means that the dislocation mechanism truly is the control mechanism for explosives ignition at low pressures.

Unfortunately, Coffey does not give an explanation of the link between energy dissipation and decomposition reaction. Assume, for example, that all dissipated energy transfers into heat inside a shear band. In view of the fact that shear bands are very narrow, additional heat will be dissipated very quickly to surroundings due to thermo-conductivity. And reaction will not have time to grow. A thermal mechanism of decomposition will not be possible in this case. There must be a different initiation mechanism. But now we do not know the mechanism.

Thus, Coffey's theory does not give a complete explanation of explosive ignition by low amplitude shock waves (P < 20 kbar). We cannot use it as a complete model for HE initiation at P < 20 kbar. It is necessary to further study the physics of decomposition of explosive molecules subject to dislocation motion.

Coffey also demonstrates applicability of his theory for high-pressure shock waves, in particular, for detonation where pressure is 400-500 kbar. It is not right because at these pressures deformation of explosive crystals proceeds without dislocations. Klimenko studied this fundamental problem of mechanism of deformation in 1983-85. He used the method of molecular dynamics for simulation of shock waves in Ar and Cu single crystals and has concluded that there are three mechanisms of deformation:

1) If shock pressure is very high (compression = 20-30 %), deformation of crystal, i.e. 1D>3D transition, proceeds inside the shock front. This transition is similar to the martensite transition. No dislocations are formed in this case.

2) If shock pressure is intermediate (compression = 5-20 %), deformation proceeds through formation of dislocations that are distributed uniformly in all volume of crystal.
3) If shock pressure is low (compression = 1-2 %), deformation proceeds through formation of shear bands with large concentration of dislocations.

Thus, the dislocation mechanism cannot be used for high-pressure shock waves or for detonation waves. We know that the homogeneous mechanism (in some cases it is the frontal mechanism) works at high pressure $P > 200$ kbar. The hot spot mechanism works at pressure $20 < P < 200$ kbar. For this pressure range the hot spot mechanism is a more effective mechanism for energy localization than the dislocation mechanism. At low pressure $P < 20$ kbar, the hot spot mechanism does not work. In this pressure region only the dislocation mechanism is effective.

Armstrong (creator of the famous Zerilli-Armstrong model of plasticity for metals) together with Coffey developed in 1982 [25] the dislocation pile-up avalanche model, which describes adiabatic heating of shear bands. Using this model Armstrong derived dependence between the explosive grain size l and the drop-weight sensitivity for 50% probability of initiation H_{50}. It is a straight line in coordinates log H_{50} – log $l^{-1/2}$. And this line approximates experiments well enough. In his last paper [26], Armstrong extrapolates this dependence to nanometric-sized crystals (see Figure 9.9). We see that the avalanche model gives a good correlation.

We can explain Armstrong's observation by the following. The model gives a good estimation of the dissipated energy during plastic deformation of the explosive crystal. It means this first stage of the process is described and calculated well. However, the next stage (explosive decomposition) is not thermal. The dissipated energy is used in decomposition by some unknown manner. How? It is our task to understand this.

Our task is to study the dislocation mechanism so carefully that it will be possible to develop the numerical version of this mechanism, which would be suitable for incorporation into hydrocode. To understand the dislocation mechanism describing decomposition of explosive molecules, we must understand what happens at the molecular level during the motion associated with dislocation. It means we must change the investigation from the micro to the molecular level. At the molecular level we need to use quantum mechanics. Quantum mechanical simulation of molecular processes taking place during dislocation is necessary.

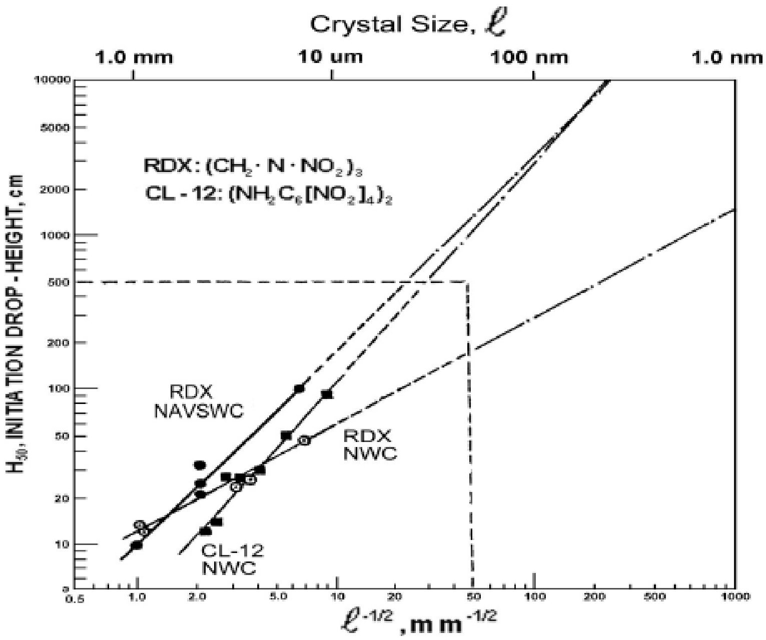


Figure 9.9: Initiation drop-weight height versus $l^{-1/2}$, extended to nano-scale crystal sizes [26].

9.4 Amazing Results from the 1970s

During the 1970's we asked questions at the Institute of Chemical Physics about the mechanism of decomposition of explosives during shock compression that relate to dislocation mechanisms. The problem was studied step by step, from the simple to the complex. At the beginning, more simple organic substances (than explosives) were investigated during shock and impact compressions.

Let us consider only impact experiments. We used the drop-weight machine presented at Figure 9.10. A great number of different substances were studied using this machine, but now we will consider the most amazing of those results.

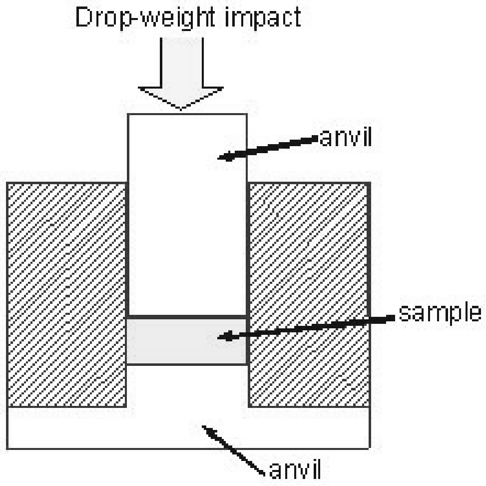


Figure 9.10: Setup for drop-weight impact experiments.

We performed experiments at liquid nitrogen temperature (T = -196^0 C). Benzene was selected for investigation, since its ring is at the core of a TNT molecule. Before impact the polycrystalline benzene was the color white. After impact its color changed to yellow (see Figure 9.11). Analysis determined that the yellow color corresponds to presence of a polymer $(-C=C-)_n$. It means that the benzene ring was broken. A bi-radical was formed. The bi-radical reacted to form the yellow colored polymer.

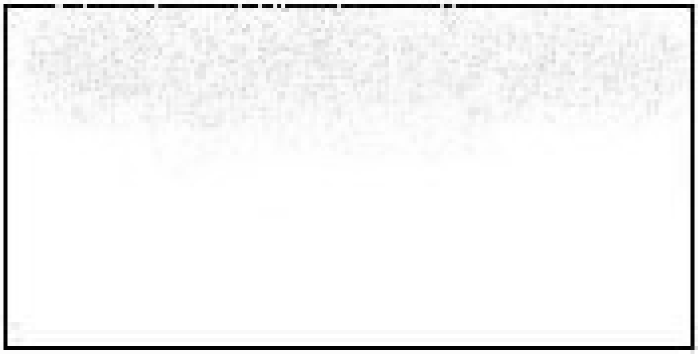


Figure 9.11: View of crystalline benzene sample after impact.

One can say that it is a result of local high temperature. We thought the same. To examine this we studied hexane, a molecule similar to benzene in weight and size (see Figure 9.12). But more important is that hexane has low thermal stability and benzene has high thermal stability. Impact experiments have shown that hexane does not decompose.

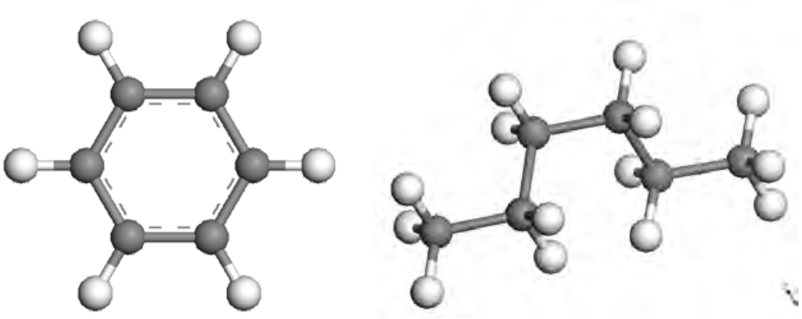


Figure 9.12: Molecules of benzene (left) and hexane (right).

It is an amazing observation. Thermally stable benzene decomposes at impact, but thermally unstable hexane does not. This means that the decomposition process at impact is an a-thermal process, in which temperature does not play the decisive role.

We have studied many substances. In particular, after impact of three-nitro-benzene, the following image was observed (Figure 9.13). Black sites are carbon atoms that arise at total decomposition.

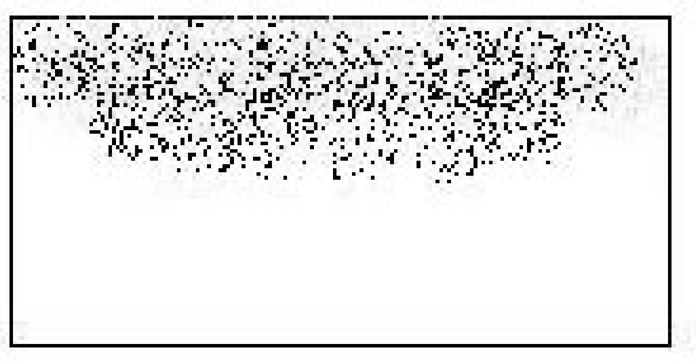


Figure 9.13: View of crystalline three-nitro-benzene sample after impact.

Thus, the impact mechanism of decomposition is not a thermal mechanism. What is the mechanism? Thirty years ago we did not know the answer to this question. We only detected an unknown mechanism we could not explain. Now we know it was the first mechanism in a new class of reactions – reactions induced by high pressure and shear.

This discovery stimulated deployment of new research directions in the Institute of Chemical Physics, but in a different department – the Department of Polymers, headed by Enikolopyan.

9.5 Reactions under Pressure and Shear

This new class of reactions was studied mainly in a special machine (Figure 9.14), where after compression of a substance in diamond anvils one anvil rotates and generates plastic shear. The maximum pressure in a compressed sample is about 100 kbar.

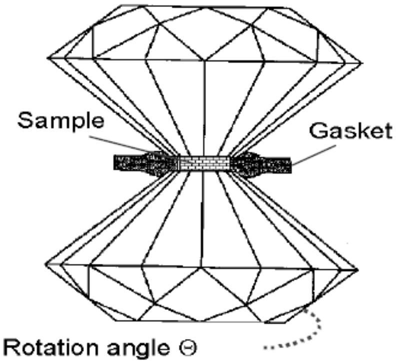


Figure 9.14: Rotational diamond anvil cell.

Through these experiments the main features of reactions under pressure and shear were established [27-29]. They are:

- high pressure alone does not induce reaction
- the extent of reaction is proportional to shear deformation, i.e. to rotational angle θ
- activation energy = 0
- reaction rate is several orders of magnitude greater than in solution (in liquid state)

These main fundamental results were obtained in 1980-1985. Now after 20 years we do not yet have a physically based mechanism to explain these reactions. There are only hypotheses. For example, Zharov proposed [29] the following mechanisms:

- a mechanically stressed chemical bond is chemically activated and reacts with other molecules under collision due to the plastic flow of the substance
- during relaxation, a high elastic bond energy is transferred into an oscillatory energy of molecule and increases its reactivity

Thus, even with great progress in experimental techniques and tremendous success in numerical simulations of molecular processes, the mechanism of reactions induced by high pressure and shear remains unknown. We can suggest why progress is slow. Only chemists (and sometimes, high level chemists) at the Institute of Chemical Physics studied the mechanism. But since these reactions proceed under shear, i.e. plastic deformation of substance, the investigation of the mechanism needs specialists in the mechanical plastic deformation of solids.

Plastic deformation proceeds through generation and motion of dislocations. The first elementary step of reaction occurs due to dislocation motion through the lattice. The main events take place in the dislocation core. It is a very complex process, especially for large explosive molecules. Even a static image of the dislocation core looks to be a complex molecular system (see Figure 9.15). Moreover, it is necessary to study this as a dynamic system using quantum mechanics.

9.6 Approach at the Molecular Level

In this chapter we have concluded that it is necessary to study the dislocation mechanism of explosive decomposition at the molecular level. To accurately describe the behavior of large molecules, quantum mechanics must be used.

At standard conditions (P = 1 atm), the distance between molecules is large (~4-5 Angstrom), and they interact by weak van der Waals forces. During compression (even as little as 20 kbar) the distance between molecules decreases and their electronic orbitals begin to interact. Overlapping of orbitals takes place, but not with so much overlap as to lead to chemical reaction. Geometrical and conformational factors become important in this case.

Now we will demonstrate quantum mechanical simulation of the effect of compression in a molecular crystal of aniline. Figure 9.16 shows aniline crystal at pressure P = 0. Figure 9.17 shows aniline crystal compressed by a 20-kbar shock wave.

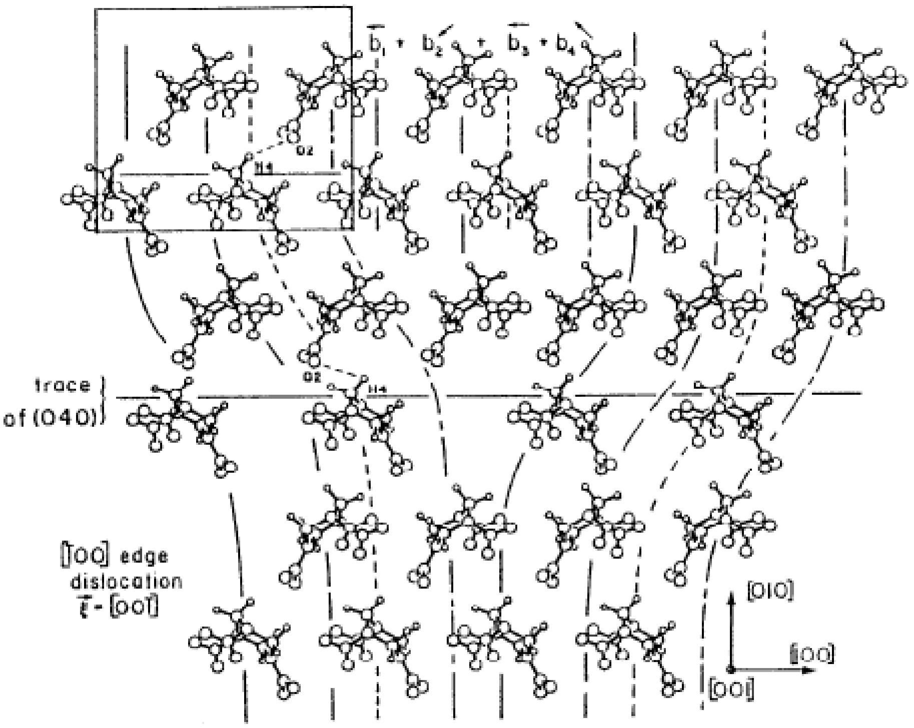


Figure 9.15: Schematic view of dislocation in RDX [26].

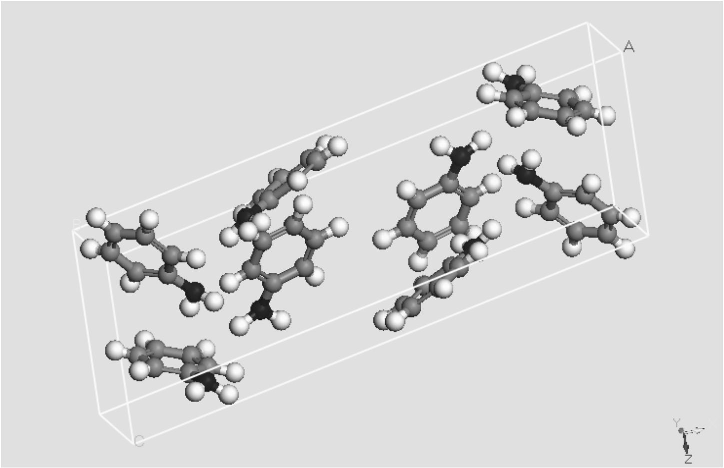


Figure 9.16: Aniline crystal at standard conditions (P=0 atm).

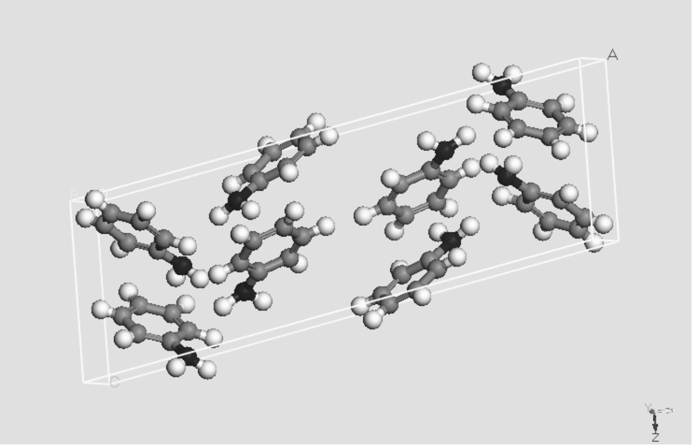


Figure 9.17: Aniline crystal after compression to 20 kbar.

We calculated the electronic structure of an aniline crystal before and after compression. Figure 9.18 depicts electronic clouds (electronic density) of molecules without compression. For simplicity we deleted all unnecessary molecules from the image, saving only three. One can see that molecules do not touch one another. In the shock compressed crystal (Figure 9.19), the electronic orbitals of these molecules overlap. The relative positions of these molecules have changed as a result of shock compression due to molecular dynamic equilibration of the crystal.

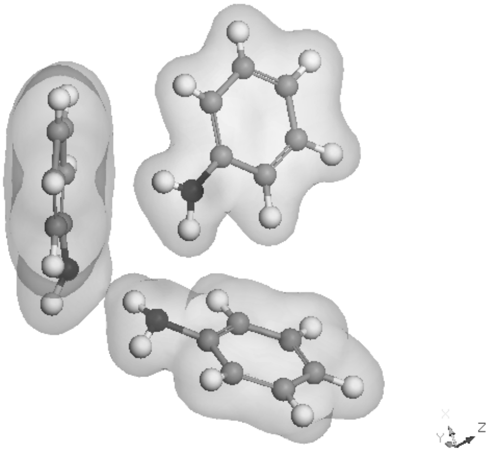


Figure 9.18: Electronic density in aniline crystal at standard conditions (P=0 atm).

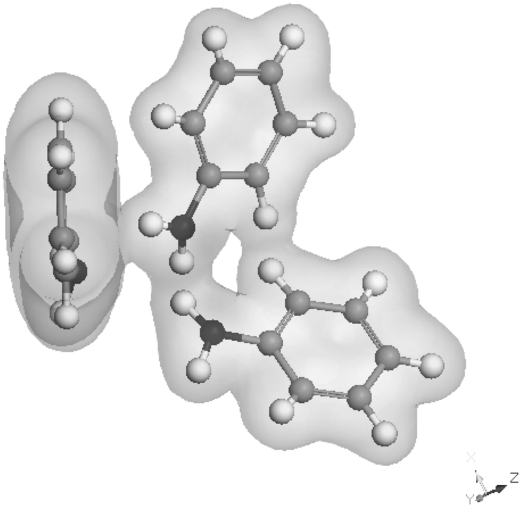


Figure 9.19: Electronic density in aniline crystal after compression to 20 kbar.

All these calculation were performed by the Density Functional Theory (DFT) quantum mechanical method.

9.7 Conclusions

We have analyzed important papers on explosive initiation due to plastic deformation and conclude that plastic deformation proceeds though generation and motion of dislocations. Interaction of moving dislocations with the crystal lattice stimulates decomposition reaction. The detailed mechanism of the decomposition process is still unknown.

Decomposition reactions initiated by impact and weak shock waves belong to a class of reactions induced by high pressure and shear. This research has collected useful data about the main features of reactions induced by high pressure and shear. For example, activation energy is equal to zero, and the reaction degree is proportional to the value of plastic strain. But detailed mechanisms for this reaction class are still unknown. Now we can say only that it is a dislocation mechanism.

To understand the dislocation mechanism of explosive decomposition, it is necessary to study decomposition at the molecular level using quantum mechanics. In particular, it will be important to investigate the dynamic process in the dislocation core. Next, we will study this elementary stage and develop a physical model for explosive initiation due to the dislocation mechanism. After that we will develop a numerical model.

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Chapter 10

Impacts on the Loss Factor Curve and Quantification of Molecular Rearrangement Regions from it in Elastomer Bonded Energetic Formulations

Manfred A. Bohn

The glass transition temperature of elastomer bonded composite rocket propellant and explosives formulations is an important property determining their in-service application. It is defined to be the main maximum of the loss factor tanδ (= ratio of loss modulus to storage modulus) of the elastomer. The loss factor as function of temperature is determined by DMA (dynamical mechanical analysis) measurements at some forced sinusodial deformation at lower frequencies in the range of 0.01 to 100 Hz. With the term transition, the center part of the molecular rearrangement process is meant, in which the transition from the energy elastic ('glassy elastic') to the entropy elastic ('rubbery elastic') behavior, or vice versa, occurs. Because the loss factor region of elastomers filled with rigid particles consists of several sub-transitions, which can change differently during ageing, a special modeling of the loss factor curve is presented using so-named exponentially modified Gauss distributions. Therewith a separation of the molecular rearrangement regions, corresponding to binder fractions with different mobility, is achieved after application of a suitable baseline correction to the loss factor curve.

10.1 The Loss Factor and Its Meaning

The loss factor is best determined with DMA measurements, in principle in any measurement mode, as torsion, bending, cantilever, tensile, shear. For elastomers highly filled with rigid particles as composite rocket propellants and PBX (plastic bonded explosive) materials, the torsion mode seems most useful. The measurement conditions for this mode can be found in [1], for example. The sample specimens are tested at several deformation frequency values, say 0.1, 1.0, 10, and 56 Hz, using a strain control in order to stay in the so-named linear visco-elastic range, which means the modulus should be independent of the strain. In torsion mode the measurement quantity is the dynamic torque M, from which the complex shear modulus $G^*=\tau^*/\gamma^* = G'+iG''$ is calculated. G' is the storage shear modulus; G'' is the loss shear modulus; τ^* is the complex shear stress and γ^* is the complex shear deformation. The loss factor tanδ is defined as given in Eq. (1).

$$\tan\delta = \frac{G''}{G} = \frac{E''}{E} = \frac{J''}{J} = \frac{\eta'}{\eta''} \tag{1}$$

It is the ratio between loss modulus G'' or E'' and storage modulus G' or E' or equivalently the definition with loss and storage compliance J or with the complex viscosity, whereby $\eta'=G''/\omega$ and $\eta''=G'/\omega$. The angle δ is called the phase angle and describes the phase shift between applied deformation phase and the phase registered from the instrument on the opposite side of the forced sample deformation, or in terms of mechanical quantities it is the angle between stress and strain vectors. The loss factor region defines the region of glass to rubber transition and vice versa, which is in short named glass transition. It is a temperature induced transition of an amorphous polymer phase from its energy elastic state to its entropy elastic state and vice versa. In other words, it is the region of molecular rearrangements of the polymer molecules from their enthalpy dominated interaction to their entropy dominated state. The glass transition always extends over a temperature region. It is often characterized by the temperature of the maximum in tanδ or of several maxima. However, it is better to use the areas and parameters of the subtransition regions of the loss factor as characteristic quantities, which is explained in this paper.

Table 10.1 gives the basic composition of the three energetic materials discussed in this chapter. All three have the same type of binder. The composite rocket propellant CRP1 uses a bonding agent for AP, which establishes primary (chemical) bonds to AP and to the binder. This creates around the AP particles a so-named rubbery shell, which is highly compact. HEC HX1 uses no bonding agent. In HEC HX2 a bonding agent was applied, but it is less effective than the one used in CRP1, because it establishes only secondary (physical) bonds.

Table 10.1: Basic composition of three energetic materials compared in this work. Composition in mass-%.

Material	Binder/elastomer	Filler	Plasticizer	Others (added to binder)
HEC HX1	HTPB-R45M IPDI, 12 %	RDX, 80 %	DOA, 8 %	Antioxidant
HEC HX2	HTPB-R45HT IPDI, 14%	HMX, 85 %	DOA, 1 %	Antioxidant, bonding agent for HMX
CRP1	HTPB-R45M IPDI, 12 %	Al, 6 % AP, 78 %	DOA, 4 %	Antioxidant, bonding agent for AP

HTPB: hydroxyl terminated polybutadiene
IPDI: isophorone diisocyanate (curing agent)
DOA: dioctyl adipate;
Al: aluminium powder
HEC: high explosive charge
HX: high explosive, general name
CRP: composite rocket propellant formulation
AP: ammonium perchlorate

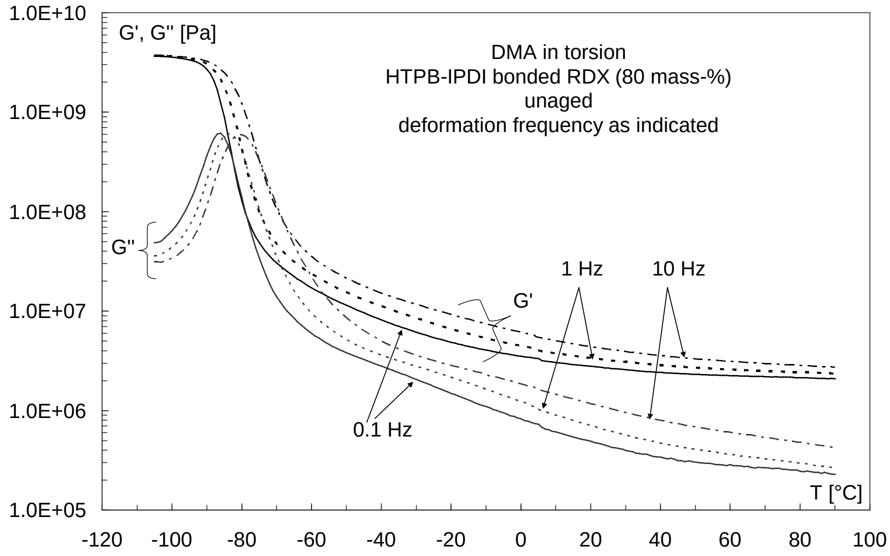


Figure 10.1: Storage shear modulus G' and loss shear modulus G'' of HEC HX1 as function of temperature at three deformation frequencies. The tensile modules E' and E'' show the same type of curves.

Figure 10.1 shows storage and loss shear modulus obtained by DMA in torsion mode at three deformation frequencies of HX1. In Figure 10.2 the typical loss factor curves tanδ=G''/G' of the PUR elastomer HTPB-IPDI bonded material can be seen, here for the HX1. The curves show clearly two maxima, and both are deformation frequency dependent. The first maximum is located between -80°C and -40°C (depending on the applied deformation frequency); the second maximum is broader than the first one and appears at higher temperatures, between -50°C and +20°C.

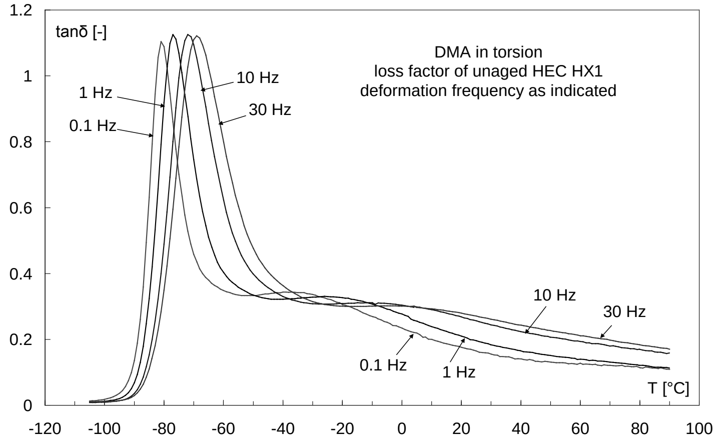


Figure 10.2: Loss factor tanδ vs. measurement temperature for HEC HX1 with 80 mass-% RDX. Evident are two maxima corresponding to two molecular rearrangement regions and processes.

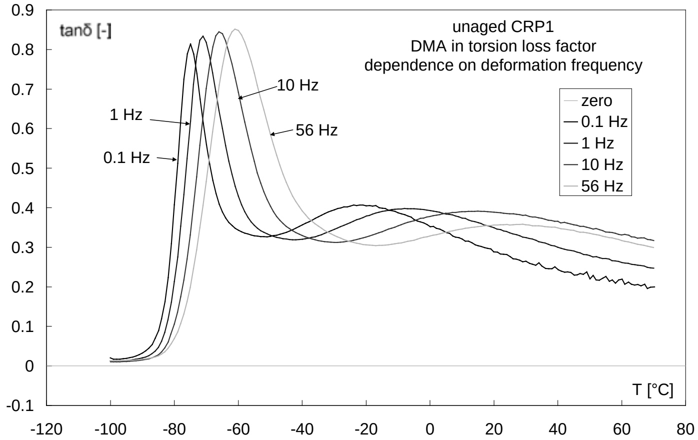


Figure 10.3: Loss factor tanδ vs. measurement temperature of CRP1 in which an active bonding agent for AP is used.

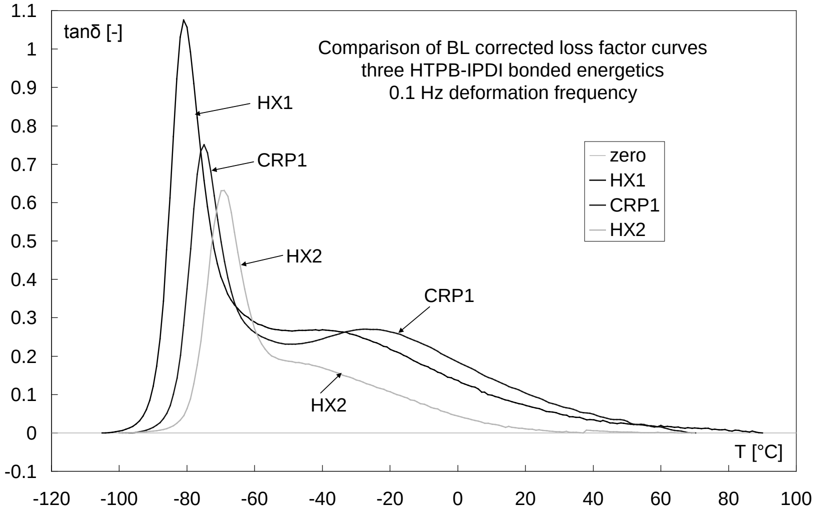


Figure 10.4: Baseline corrected loss factor tanδ vs. temperature for three energetic formulations made with the same type of binder, HTPB-IPDI. The basic structure of tanδ is the same for all three materials.

In Figure 10.3 the loss factor of a composite rocket propellant formulation CRP1 is shown. Principally the curves have the same features as the binder of the HEC HX1. Here the fillers are aluminium powder and ammonium perchlorate (AP) The CRP1 belongs to the type of formulations described and investigated in [1, 2, 3, 4, 5, 6]. In Figure 10.4 the baseline corrected (BLC) loss factor curves of the three formulations can be seen. All have the same binder type and therefore the same basic structure in the loss factor curve. The meaning of baseline correction is given in section 10.5.1 in this chapter.

10.1.1 Glass-rubber Transition Temperature

What is the glass transition temperature? There are several definitions and argumentations. One group of people says the maximum of the loss modulus (G’’ or E’’) is the glass transition temperature. If one takes this value then one is already in a glassy state of the elastomer binder, which means the free volume for the bigger chain segments of the elastomer polymeric material is already so small, that they can no longer rearrange in the material. But the motions of the bigger chain segments on mechanical impact are responsible for the behaviour and the response of the material: brittle or (residual) ductile. If no free volume is available for them the material reacts already brittle. From this view it is better to name the temperature at the maximum of the loss modulus as glass temperature, because the material is essentially already in the glassy state with respect to rearrangement possibilities for bigger elastomer chain segments.

The other choice for assigning a glass transition temperature is the maximum of the loss factor tanδ. At the maximum intensity of the loss factor, the molecular rearrangement process from glassy to rubbery and vice versa is at its maximum. Therefore, in order to characterize the transition between these two states, the maximum of the loss factor tanδ must be taken, which is then correctly named as glass (to rubber) transition temperature or rubber (to glass) transition temperature, in compact form best named as glass-rubber transition temperature. The loss factor is much more sensitive than the loss modulus in showing the different temperature regions of molecular rearrangements in order to change the basic state from energy to entropy elasticity. Especially with HTPB-IPDI binders, one has two apparent maxima. Both are equally important for assessing the properties of the material and its behaviour under load.

10.1.2 Principle Temperature Behavior of an Elastomer

Polymers, especially weakly cross-linked elastomers as the propellant and HEC binders, change from a glass-like to rubber-like behaviour by changing the temperature from low to high values. In the glassy state, at low temperature, the behaviour is related to the changes in the stored elastic energy by small displacements of the molecules from their equilibrium positions. In the rubbery state at high temperatures, the molecular chains have much more accessible free volume and can adopt a large number of conformations that lead to an increase in entropy. In scanning the temperature from one state region to the other, the material passes an in-between region, where transitions occur as change in molecular arrangements. Generally this phenomenon is named glass-rubber transition region. The loss factor is proportional to the part of applied deformation energy, which is consumed by the sample. The other part is transported elastically (means here loss free) through the sample and reaches the response detector. The driving force for this temperature induced transition from energy elastic to its entropy elastic state und vice versa, is to reach the lowest internal energy, given by the Gibbs free energy, when the variables controllable by the experiment are pressure and temperature, Eq.(2).

$$\Delta G(p,T) = \Delta H(p,T) - T \cdot \Delta S(p,T) \tag{2}$$

In the energy elastic state, the internal energy is controlled by lattice like energetic interactions between the polymer molecules. The enthalpy term ΔH controls the Gibbs free energy ΔG. Because of lower temperatures the distances between the polymer chain elements are small, mobility is restricted and local dipole-dipole interactions have a strong effect in lowering internal energy, so ΔH becomes appreciably negative. The entropy term plays nearly no role, because there is little change in configuration and conformation of the polymer chains. In the entropy elastic state the internal energy is not controlled by lattice like energetic interactions between the polymer molecules. Because of more free volume available at higher temperatures, the polymer chain segments have the possibility to form many configurations, which means that entropy is increased and the term T·ΔS gets more positive, but ΔG gets more negative. Therefore, the entropy term T·ΔS controls now the Gibbs free energy ΔG. ΔH increases, which means it is less negative than in the energy elastic state. It plays now nearly no role, because its value varies only little in changing the conformations of the binder chains. The cause is that the distances between the chain elements have increased. Further, local dipole-dipole-interactions are less effective because of the motions of the chain elements, which average this interaction down to small values, (see section 10.3)

Any effect that reduces the possibility of realisation of configurations of the polymer chains will reduce the entropy part and make the material less entropy elastic. In a not too large deformed state the polymer chains can adopt many conformations that lead to a maximum in entropy. But this is no longer the case at strong compression or strong elongation; it is also well above the glass transition temperature. In such cases the free volume is reduced, the polymer network gets more rigid, and the glass transition intensity is reduced or even disappears. The network can be transformed mechanically from a so-named mobile amorphous phase (MAP) to a rigid amorphous phase (RAP), which in the end is not able to show a glass transition. That means it no longer transforms to the entropy elastic state. Because only parts of the network are normally involved, the expression mobile amorphous fraction (MAF) and rigid amorphous fraction (RAF) are applied also. The interaction of fillers with the polymer matrix may be so strong that RAF regions can occur, especially with active fillers or fillers connected via bonding agents to the matrix.

10.2 Interpretation and Prognostic of Molecular Mobility

The molecular mobility of binders and plasticizers determines the temperature range of the glass transition. Further, it determines in part the sliding length along polymer chains. This is easily recognized with the fact that an unfilled HTPB binder has a much higher strain capacity than a filled one. The reason is that the filler particles – RDX, HMX, AP (especially if coupled by active bonding agents) and aluminium (this is per se a so-named active filler) – interact with the binder chains and reduce in this way the free length of the polymer.

Essential factors determining the molecular mobility of binder systems are: (1) chemical groups that create so-named free volume regions, (2) linear chains without side chains versus chains with intermediate long side chains, (3) sterical hindrance by cross-linking (not caused by curing), (4) sterical hindrance around curing cross-links, (5) short range interaction forces on molecular level between binder chains, (6) interaction forces between binder and plasticizer, (7) interaction forces between binder and filler particles. The changes in loss factor and their causes are described and compiled in the following. More details on these subjects can be found in [7, 8].

10.2.1 General Phenomena

- The more reorientation processes of the same type occur, the higher the value of the corresponding tanδ; more quantitatively said, the greater the corresponding area in tanδ;
- The higher the mobility of chain elements or structural elements of the polymer chains, the lower is the glass transition temperature
- The more free volume the polymer chains have for reorientation or rearrangement, the lower is the glass transition temperature

10.2.2 Effect of the Plasticizer

A good plasticizer penetrates between the polymer chains and breaks up the interaction between the polymer chains and sometimes also between chain sections of the same polymer chain. Therewith the mobility of the chains is increased, in part by reducing interaction energy between chains and in part by providing more free volume for the chains. The result is: Tg is shifted to lower temperatures and tanδ increases.

A plasticizer intrusion decreases also the mobility restrictions caused by cross-linking sites, by opening the molecular arrangements. However, if geometrical hindrance around the curing agent occurs based on sterical conditions of chemical bonds and atom arrangements, the plasticizer addition cannot remove this type of mobility restriction.

To be most effective, plasticizer molecules may not contain structural elements, which form rigid regions by intermolecular interactions (IIA). The plasticizer molecules should be short-chained or small molecules. The IIA between plasticizer molecules should be small in that the melting temperature is very low. If they show a glass transition, their Tg must be very low.

Diffusing away of plasticizer or any loss of plasticizer has the reverse effect: Tg is shifted to higher temperatures and tanδ decreases.

10.2.3 Filled Elastomers

Consider an elastomer with given filler content: The lower the mobility restrictions by the filler particles on the polymer chains the higher is tanδ and the lower Tg.

Comparison between unfilled and filled elastomer:

The area of tanδ is reduced by the filler. Mobility restrictions for the polymer chains are created by the filler particles (FP) already by geometrical conditions, even without any interaction forces. The more filler, the more the extent of mobility restrictions.

The more the filler is interaction-active, the stronger are the IIA between FP and polymer chain, the greater is the mobility restriction or the smaller the free accessible volume of the chain elements, and consequently the smaller is tanδ and the higher is the transition temperature. Mostly the main transition of the elastomer will be retained also with the presence of fillers, because some fractions of the elastomer binder are left undisturbed by the filler. It stays at the same transition temperature, but the intensity of the transition is much smaller than without filler. This may be quantified by area comparison of the corresponding transitions.

Active fillers create by interaction with the polymer matrix mobility restrictions in their nearer environment. If the mobility is reduced to such an extent that a more rigid layer (region) around the particle is formed, a new glass transition comes up caused by the mobility restricted polymer layer around the filler particles. Because the free volume of such polymer chains is smaller as in the undisturbed state, a higher temperature is necessary to initiate the molecular rearrangement from energy to entropy elastic state.

However, if the polymer chains a strongly fixed a glass to rubber transition of such binder fractions is no longer possible. An arrangement of the polymer chains with entropy elasticity will be prohibited by the intermolecular interaction. Such a region will stay in an energy elastic state also at higher temperatures. One has then a so-named rigid amorphous phase (RAP), or a rigid amorphous fraction (RAF), sometimes also named an immobilized fraction or phase. Highly active fillers as SiO2 and Al / Al2O3 and soot can form such RAPs around the particles. They are especially active in nano-scale size, because the active surface is great per unit filler amount.

10.2.4 Bonding Agents

Bonding agents (BA) or adhesive promoters, adhesive agents, are applied to increase the contact forces between filler particle (FP) and polymer matrix. The bonding agent forms, at least in part, a mobility restricted phase around the particle. This may create a new glass transition in such a phase, with higher Tg than the one of the unrestricted polymer binder.

Active bonding agents have strong but still physical bonding to the FP and/or good bonding to the polymer matrix. Mostly hydrogen bridge bonding is the base.

With chemical bonding agents the contact between BA and FP is by chemical bonding (primary bonding) and/or between BA and the polymer matrix.

Surface active substance as bonding agents (can be also named surfactants, but this term is used more in connection with tensides) normally perform bonding only by secondary bonds, which means bonding by so-named van-der-Waals type bonds. They have much less interaction energy, only about 3 to 10% of chemical bonds, which have typical values around 150 to 300 kJ/mol. However, van-der-Waals-based interactions may reach values of 70 to 130 kJ/mol and more, if many interacting molecular sites are present along a polymer chain (for example, see section 10.3).

10.2.5 Ageing

If with time (ageing) the bonding between FP and polymer matrix increases in strength, the mobility of chain elements will be restricted further. Consequently, the glass transition expressed in tanδ will become smaller in intensity, and the transition temperature is shifted to higher values. If a RAF is formed during ageing, the glass transition disappears. Reverse is the situation, if with ageing the bonding strength between filler and polymer matrix is reduced. The surrounding phase of the matrix gets more mobile. Then tanδ will increase and the transition temperature is shifted to lower values. This happens when no additional cross-linking has taken place and/or if no plasticizer loss occurred in the surrounding phase.

10.2.6 Cross-linking and Chain Scission of Polymer Chains

Additional cross-linking makes the polymer network more rigid, tanδ is reduced in intensity and Tg is shifted to higher temperatures. The reverse effect can be seen with chain scissioning. Cross-linking or chain scissions may occur in defined areas of the network, especially in the presence of fillers or special ingredients such as burning catalysts and polymerisation catalysts, which can foster an oxygen attack on the polymer chain. This is the case especially with transition metals able to change between two oxidation states, as Fe, V, Cu, Cr, Mn, Co, and Mo for example. Both types of network change may be caused by oxidative attacks on the polymer chain also without catalysts [1, 4, 9].

10.2.7 Hindrance by Sterical-geometrical Effects

It is evident that sterical hindrance reduces mobility of molecular polymers. But this simple effect can have significant impacts with elastomer binders. In the scope presented here this point is important with HTPB-IPDI binders, in that around the curing site the mobility of the binder is appreciably restricted. Figure 10.5 shows the situation with HTPB-IPDI binder around the cross-linking site formed by IPDI. The configuration was obtained by force field (FF) calculations with the Accelrys programme package Materials StudioTM, using the COMPASSTM FF [10] and is shown as ball-stick arrangement inside the darker volume, which gives the volume of the molecule using the van-der-Waals radii of the atoms. The lighter coloured volume represents the excluded volume, which is not reachable by the neighbouring molecules. By this effect the free volume for establishing configurations to increase entropy is significantly reduced. The glass transition temperature especially around the curing sites increases, which means HTPB-IPDI shows two transition regions in the loss factor curve, as was presented above.

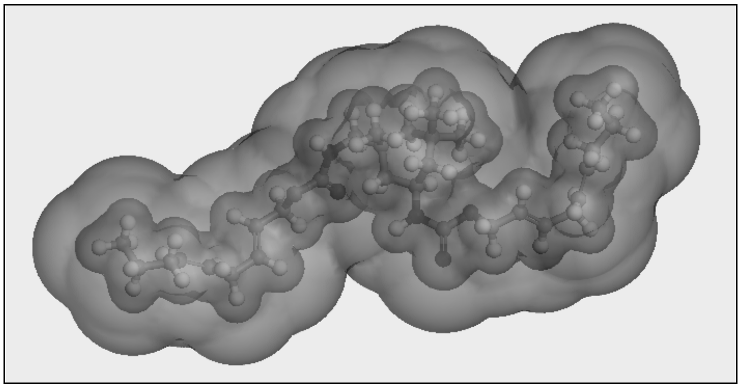


Figure 10.5: One of the energetically favored conformations of two HTPB chains (short simulates) cross-linked by IPDI.

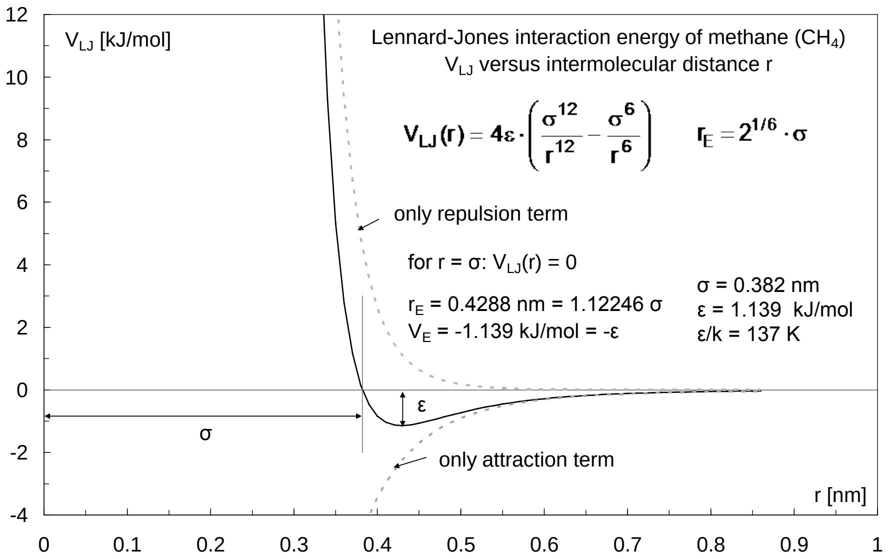
Figure 10.5 shows the ball-stick presentation of the molecules inside the darker blue volume based on the vdW-radii of the atoms. The lighter blue volume considers the excluded volume, which is not reachable by neighbouring molecules. The mobility restrictions in terms of available volume become evident in the range of the cross-linking by IPDI. The shown data have been obtained by atomistic simulation with the force field COMPASSTM of the Accelrys suite Materials StudioTM [10].

10.3 Intermolecular Interactions as Key Property for Glass Transition Temperature Ranges

Inter- and intramolecular forces between binder molecules and plasticizers as well as between binder and filler particles are decisive in determining the temperature range of the glass transition of binder molecules. Generally, one can say that binder molecules without polar groups, such as C-O-C, C=O, C-OH, C-N, have less interchain interaction energies than binder chains having such groups. This means HTPB-binder chains create less intermolecular energies than GAP binder chain molecules. Consequently, the glass transition of HTPB should occur at lower temperatures than the one of GAP, which is the case. A further aspect to consider is the difference in chain conformation between GAP and HTPB. GAP is linear and this facilitates close alignment of the chains. HTPB has cis and trans configurations and short side chains, which block good alignment and promote the increase of free volume. To estimate interaction energies, several intermolecular force types are in short discussed, which contribute essentially to the overall intermolecular energies. See also [7].

The Lennard-Jones (LJ) potential is the classical repulsive-attractive potential to describe so-named dispersion or van-der-Waals forces. It is a 12-6 potential, and the repulsive part has the power 12 for 1/r and the attractive part has the classical 1/r6 dependence for dispersion forces. From this form a lot of 'derivatives' have been established. Figure 10.6 shows the classical LJ potential in the insert. It has two parameters to be adjusted to the interaction data: ε as the energy value in the minimum and σ as the distance where V(r) becomes zero.

The LJ-potential or some variants as 9-6 in power of 1/r are used in the atomistic simulations with force fields, and also in COMPASSTM mentioned above. It is one of the most useful formulations to describe intermolecular interactions. Further useful potential functions are given in the Eqs. (3) to (8). They are used to describe dipole-dipole interactions and interactions between ionic charges and dipoles, whereby the dipoles can be permanent or induced.



V_{LJ}	intermolecular pair potential between two particles at a distance r
r	distance of the atoms / molecules
r_E	equilibrium distance between the atoms /molecules
σ	distance up to $V_{LJ}(r)=0$
ε	value of energy minimum at equilibrium distance r_E

Figure 10.6: Methane as example for a Lennard-Jones potential.

Permanent dipole - permanent dipole interaction; dipole orientations are averaged statistically by rotational thermal energy:

$$V(r) = -2 \cdot \left(\frac{p_1 \cdot p_2}{4\pi\varepsilon_0} \right)^2 \cdot \frac{1}{3 \cdot kT} \cdot \frac{1}{r^6} \tag{3}$$

Permanent dipole – induced dipole, dispersion type interaction:

$$V(r) = -p_1^2 \frac{\cdot \alpha_{V2}}{4\pi\varepsilon_0} \cdot \frac{1}{r^6} \tag{4}$$

Permanent dipole - permanent dipole, mutually induced dipolar interaction - dispersion type interaction:

$$V(r) = -\frac{p_1^2 \cdot \alpha_{V2} + p_2^2 \cdot \alpha_{V1}}{(4\pi\varepsilon_0)} \cdot \frac{1}{r^6} \tag{5}$$

Permanent dipole – permanent dipole, static orientations:

$$V(r) = -\frac{p_1 \cdot p_2}{(4\pi\varepsilon_0)} \cdot \frac{1}{r^3}\left(2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_2 - \phi_1)\right) \tag{6}$$

Ion - permanent dipole, static orientations:

$$V(r) = -\frac{p \cdot Q_{ion}}{4\pi\varepsilon_0} \cdot \frac{1}{r^2} \cdot \cos\theta \tag{7}$$

Ion – induced dipole, static orientations:

$$V(r) = -\frac{1}{2} \cdot \frac{\alpha_V \cdot Q_{ion}}{4\pi\varepsilon_0} \cdot \frac{1}{r^4} \cdot \cos\theta \tag{8}$$

V	interaction energy
r	distance between the two molecules (centre of gravity distance), assumed are spherical molecules
α_{v1}	polarizability volume of molecule 1 unit is in volume
α_{v2}	polarizability volume of molecule 2 unit is in volume
α_T	the true polarizability is connected to the polarizability volume
α_v	by the relation: $\alpha T = \alpha v\ 4\pi\varepsilon 0$
p	permanent dipole moment, unit is length*charge or Debye (D)
ε_0	absolute permittivity, vacuum permittivity
T	absolute temperature
θ, ϕ	dipole orientation angles
θ	inclination angles with axes between the dipoles
ϕ	azimuth angles
Q_{ion}	charge on ion

Important is the geometrical range of these forces. Some become active only if the atoms and molecules approach each other rather narrowly, especially the ones of induced dipole - induced dipole interaction and all potentials with 1/r6 dependence for the attractive interaction. However, also the permanent dipole - permanent dipole interaction is short ranged as long as rotational motions average out the interaction and no static mutual orientations can take place, Eq. (3). When, at lowering the temperature the rotational motions slow down and the distances between the chains are reduced, the rotational hindrances arise, and the much higher energy levels of oriented dipole - dipole interaction rapidly come to dominance and the transition to energy elasticity takes place. Now Eq. (6) is effective. In Table 10.2 the interaction energies caused by permanent dipole - permanent dipole in preferred orientation and thermally averaged orientation are compared. The former can be higher by a factor 10 and more.

The Eq. (7) and Eq. (8) can be applied with ionic or partial charges on the crystallite surface of ionic energetic materials as ADN. In Figure 10.7 the intermolecular potentials of HTPB, GAP and a polymer containing 35 benzene rings is shown. HTPB is simulated with the LJ interaction of methane and ethylene, standing for the CH2 and the -CH=CH-groups of HTPB. Even with these non-polar groups, the interaction energy per molecule or mol respectively reaches quite high values; up to 100 to 130 kJ/mol are possible. The polymer with benzene rings reaches the equilibrium distance at higher values, but the interaction energies are higher than those with methane or ethylene. Benzene rings act therefore as hard segment parts and lower the free volume and therefore the molecular mobility appreciably. The Tg values of such polymers are relatively high. Also, plasticizers having aromatic rings are less effective than aliphatic based ones. Polymer binders with polar groups as GAP cause much more interaction energy, but only if the dipoles can reach oriented interactions. As long as the mobility is high, the dipolar interaction is thermally averaged and in the range of normal dispersion interaction. This is clear to see in Figure 10.7. The transition from averaged orientation to more fixed orientations is reached by lowering the temperature. Because the relevant interaction distance is longer with fixed orientations, once this situation comes up the transition from an entropy to energy (enthalpy) dominated state happens quite fast, in a more narrow temperature range than with non-polar binders as HTPB. The further effect is that the transition starts already at higher temperatures.

Table 10.2: Interaction energies caused by permanent dipole – permanent dipole interaction according to Eq. (6) (preferred mutual orientation) and Eq. (3) (thermally averaged mutual orientation). Dipole moments: p1 = p2 = 1.5 Debye, T = 293 K.

r [nm]	Eq.(6) mutually preferred orientation [kJ/mol]	Eq.(3) thermally averaged mutual orientation [kJ/mol]	Eq.(6) / Eq.(3) [-]
0.40	-4.234	-1.227	3.5
0.42	-3.658	-0.915	4.0
0.4288	-3.437	-0.808	4.3
0.44	-3.181	-0.692	4.6
0.46	-2.784	-0.530	5.3

0.48	-2.450	-0.411	6.0
0.50	-2.168	-0.322	6.7
0.52	-1.927	-0.254	7.6
0.54	-1.721	-0.203	8.5
0.56	-1.543	-0.163	9.5
0.58	-1.389	-0.132	10.5
0.60	-1.255	-0.108	11.7
0.62	-1.137	-0.088	12.9
0.64	-1.034	-0.073	14.1
0.66	-0.943	-0.061	15.5
0.68	-0.862	-0.051	17.0
0.70	-0.790	-0.043	18.5

In Table 10.2, if preferred orientation between the two permanent dipoles happens, the interaction energy in the interesting distance range 0.46 to 0.6 nm differs by a factor of 6 to 11. All θ-values are assumed to be zero, which means alignment along the connecting axis of the dipoles.

Considered in Figure 10.7 are (i) two simulates for HTPB, built-up from 200 CH_2 group and 100 C_2H_4 groups, respectively. Between a distance range of 0.55 to 0.6 nm, the interaction energies are between 91 to 57 kJ/mol and 112 to 73 kJ/mol; (ii) GAP simulate with 120 permanent dipoles with 1.6 D each, with maximum interaction and with thermally averaged orientations; (iii): polymer with aromatic dispersion interaction, by 35 benzene rings.

10.4 Typical Glass Transition Temperatures of Some Binders Determined by DMA

Glass transition temperatures determined by DSC as the temperature of the half height in the step of the change of specific heat cP during the transition (the specific heat increases in going from energy to entropy elasticity) are often significantly lower than those determined by DMA. The reason is the ‘static’ determination by DSC, which means no mechanical deformation is applied. The volume change by thermal expansion is neglected. Increasing mechanical deformation rate leads to a pseudo increase in stiffness by inertia effects inside the material. This leads to a shift of the transition region to higher temperatures. An increase in the deformation rate means the material has less time to readjust the positions and orientations of molecular groups; and coming from the low temperature side, the energy elastic behaviour is retained longer as the deformation rate gets higher. Therefore, DSC glass transition temperatures correspond to very low deformation rates; this means very low deformation frequencies in case of forced sinusoidal excitation. To compare DMA-Tg with DSC-Tg, the deformation frequencies are in the range 0.001Hz and smaller. Therewith DSC glass transition temperatures give much too low values with respect to application loads, which can have deformation rates up to 1000 Hz and higher. Typical DMA-Tg values of cured and unfilled binders are compiled in Table 10.3.

Rule of estimation: with every increase in deformation frequency decade in DMA, the glass transition temperature Tg increases by 4°C to 5°C in the range 0.001 to 100 Hz. More precisely, the temperature at maximum changes nearly with the logarithm of deformation frequency. Tables 10.4, 10.5, and 10.6 list the maximum temperatures of the loss factor, the loss modulus and the temperature derivative of storage modulus of the tree formulations discussed here.

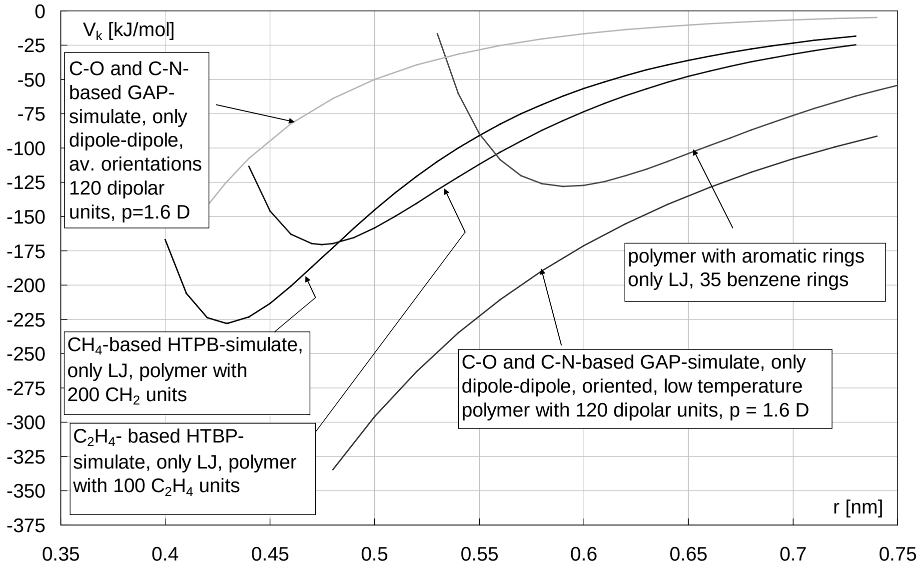


Figure 10.7: Interaction energies based on parameters for methane, ethylene, benzene and dipoles as function of distance r.

Table 10.3: Typical glass transition temperatures defined as temperature of the main maximum of the loss factor curve, determined by DMA at several deformation frequencies.

Binder (without plasticizer)	Tg [°C] byDMA at some deformation frequencies		
	0.01 Hz	0.1 Hz	10 Hz
HTPB (R45 M) – IPDI	- 75	- 70	- 62
HTPB (R45 HT) – IPDI	- 65	- 60	- 52
GAP (diol) – N100	- 41	- 36	- 28
GAP (diol, triol) – BPS	- 25	- 20	- 12
Desmophene D2200 – N3400	- 35	- 30	- 22

Table 10.4: Temperatures at maxima in loss factor, loss modulus and temperature derivative of storage modulus of unaged HEC HX1.

Maximum type	T_{max} [°C]				Max. difference
	0.1 Hz	1.0 Hz	10 Hz	30 Hz	
tanδ_max1	-80.9	-77.0	-71.8	-69.0	11.9
G"	-86.3	-83.8	-80.4	-78.8	7.5
dG'/dT	-86.5	-84.3	-81.2	-79.5	7.0
tanδ_max2	-41.4	-29.6	-15.1	-10.3	31.1

Table 10.5: Temperatures at maxima in loss factor, loss modulus and temperature derivative of storage modulus of unaged HEC HX2. The determination of the second maximum tanδ_max2 was not clearly possible.

Maximum type	T_{max} [°C]				Max. difference
	0.1 Hz	1.0 Hz	10 Hz	56 Hz	
tanδ_max1	-66.61	-62.56	-57.03	-51.75	14.86
G"	-72.1	-69.29	-65.86	-62.55	9.55
dG'/dT	-72.29	-70.11	-67.05	-63.81	8.48
tanδ_max2	-50.97	-43.73	-37.09	-	13.88

Table 10.6: Temperatures at maxima in loss factor, loss modulus and temperature derivative of storage modulus of unaged CRP1.

Maximum type	T_{max} [°C]				Max. difference
	0.1 Hz	1.0 Hz	10 Hz	56 Hz	
tanδ_max1	-74.9	-71.1	-65.8	-60.7	14.2
G"	-79.9	-77.1	-73.8	-70.8	9.1
dG'/dT	-80.1	-77.4	-74.3	-72.2	7.9
tanδ_max2	-21.8	-6.6	14.4	26.2	48.0

10.5 Modeling of Loss Factor Curve to Quantify Mobility Regions

10.5.1 Baseline Correction of the Loss Factor Curve

The deformation energy applied on the sample during the DMA measurements is in part transmitted loss free from the donor to the acceptor and in part used up by the sample, especially in the glass transition region. This second phenomenon has two contributions: a purely dissipative one in which the energy is transformed to heat by frictional effects, and a contribution used for the molecular rearrangements, which needs energy to separate the molecules. Energy is also needed when going from the rubbery to the glassy state in order to reduce the entropy of the system. Outside the glass transition regions only dissipative consumptions occur, which are usually small, particularly in the energy-elastic state. Considering unfilled elastomers, they are small also in the entropy-elastic state. Indeed, with filled elastomers the dissipative effects become significant. In order to extract the information concerning the molecular interpretation of the loss factor, these dissipative effects must be separated from the wished information. A visual sign for the dissipative part is the baseline offset between the start and the end point of the loss factor distribution (see Figure 10.2 and 10.3). The separation of the dissipative part can be done geometrically by applying a suitable iterative baseline correction function (BLC) of the form shown in Eq. (9), using a transient function $\alpha(T)$, Eq. (10), which is a cumulative partition variable, to adjust the baseline weights along the loss factor curve. This baseline function regards that on both sides normally the loss factor curve ends in plateau values. However, there can be difficult situations in that on the high temperature side a minimum in loss factor appears. Then consistent evaluations are necessary in ageing courses or in considering deformation frequency dependence.

$$BL_{\alpha}(T) = \left(1-\alpha(T)\right)\cdot \tan\delta(T_A) + \alpha(T)\cdot \tan\delta(T_B) \tag{9}$$

$$\alpha(T) = \frac{\int_{T_A}^{T} \tan\delta(T)dT}{\int_{T_A}^{T_B} \tan\delta(T)dT} \tag{10}$$

$$D_k = \sum_{T_A}^{T_B}\left(\tan\delta\_I_{k-1}(T_i) - \tan\delta\_I_k(T_i)\right)^2 \tag{11}$$

$BL_{\alpha}(T)$	base line correction function based on $\alpha(T)$ between T_A and T_B;
$\alpha(T)$	normalized cumulative partition function of $\tan\delta(T)$, in [-];
T_A	lower baseline setting temperature, in [°C];
T_B	upper baseline setting temperature, in [°C];
T	measurement temperature between T_A and T_B, in [°C]
$\tan\delta(T_A)$	value of uncorrected $\tan\delta(T)$ at temperature T_A, in [-]
$\tan\delta(T_B)$	value of uncorrected $\tan\delta(T)$ at temperature T_B, in [-]
D_k	assessment parameter for the k^{th} iteration cycle, k = 1, 2, 3,…
$\tan\delta\_I_{k-1}(T_i)$	loss factor at temperature T_i in $(k-1)^{th}$ iteration cycle
$\tan\delta\_I_k(T_i)$	loss factor at temperature T_i in $(k)^{th}$ iteration cycle

The iterative procedure to find the final baseline is as follows.

Iteration cycle k=1

(1.1) Calculation of $\alpha(T)$ from the uncorrected curve, $\tan\delta\_I_0(T_i)$. (1.2) Establishing the BL according to Eq. (9). (1.3) first BL correction of the uncorrected curve, formation of $\tan\delta\_I_1(T_i)$. (1.4) Calculation of the assessment parameter D_1.

Iteration cycle k=2

(2.1) Calculation of $\alpha(T)$ from the first corrected curve, $\tan\delta\_I_1(T_i)$. (2.2) Establishing the BL. (2.3) second BL correction of the **un**corrected curve, formation of $\tan\delta\_I_2(T_i)$. (2.4) Calculation of the assessment parameter D_2.

Iteration cycle k=n

(n.1) Calculation of $\alpha(T)$ from the n-1 corrected curve, $\tan\delta\_I_{n-1}(T_i)$. (n.2) Establishing the BL. (n.3) nth BL correction of the **un**corrected curve, formation of tanδ_$I_n(T_i)$. (n.4) Calculation of the assessment parameter D_n.

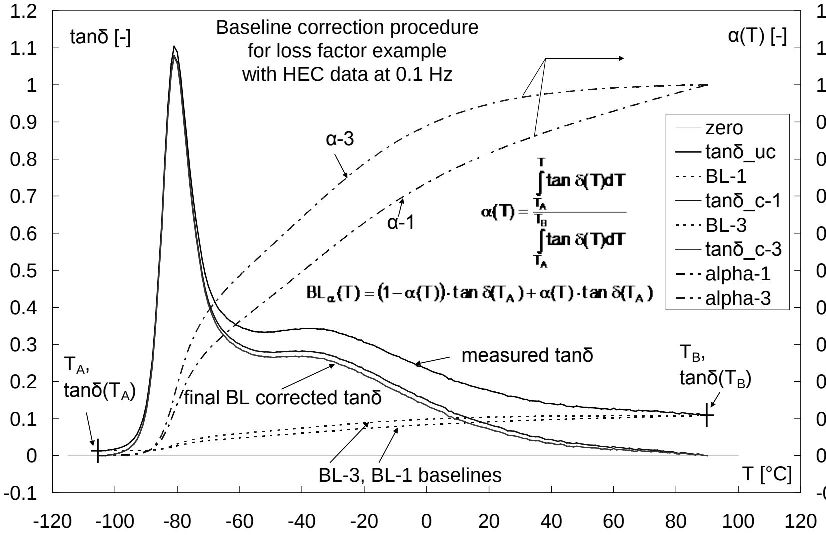


Figure 10.8: Example of a baseline correction of the loss factor of HEC HX1. Shown are the iteration steps 1 and 3. After 3 iterations the calculations already reached convergence.

During iteration the value of D_k, becomes smaller. In defining the sentencing value $D_{k\text{-limit}}$ for the limit of D_k, the iteration is stopped when D_k falls below $D_{k\text{-limit}}$. Mostly 0.01 to 0.001 are good choices for $D_{k\text{-limit}}$. In Figure 10.8 the course of the BLC is presented. The iteration procedure is fast and stable. Mostly after 3 to 6 cycles the final baseline corrected curve has been reached. Figure 10.8 shows also the course of the $\alpha(T)$. Figure 10.9 and 10.10 show examples of baseline corrected loss factor curves of HEC HX1 and an ageing series of CRP1.

10.5.2 Modeling of the Loss Factor Curve

After the baseline correction a suitable fit function must be chosen in order to evaluate the areas under the peaks of the loss factor curve. The function must describe the experimental data and extract from it the indications for the different regions of molecular rearrangement processes corresponding to different binder fractions. If the values of the interaction energies and the molecular docking regions are randomly distributed in the isotropic material, a Gauss distribution, Eq. (12) should describe the processes. But, as clearly visible in Figure 10.9 and 10.10, the shapes

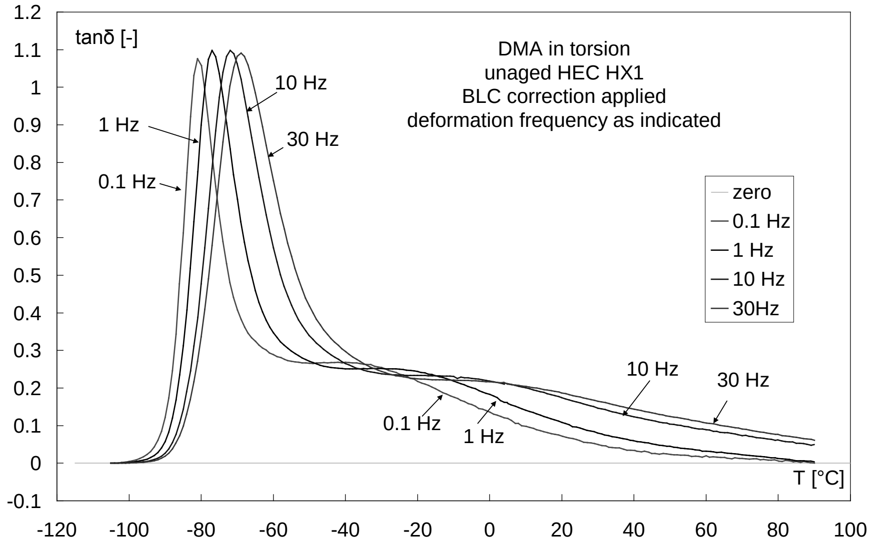


Figure 10.9: Baseline correction of the loss factor of the HEC HX1. The Figure 10.2 shows the not BL corrected curves.

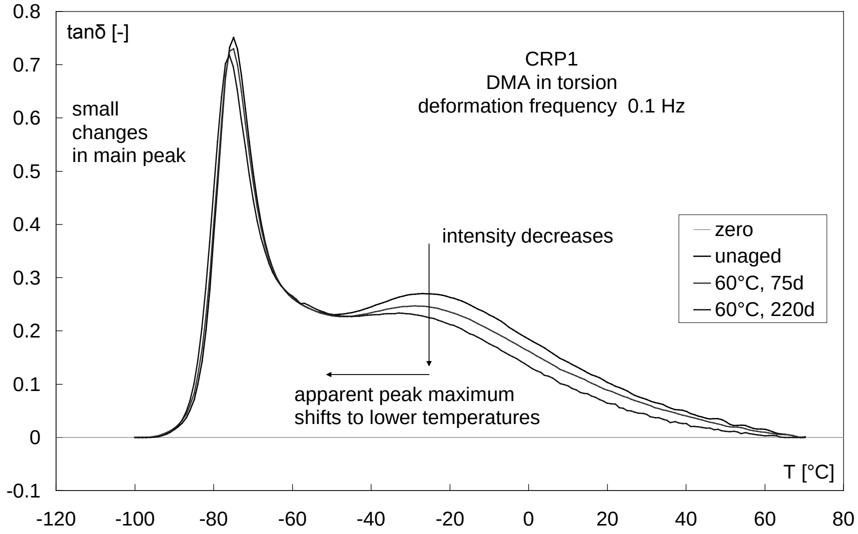


Figure 10.10: Baseline corrected loss factor curves at different ageing times of CRP1. Ageing temperature was 60°C. For interpretation see [1, 3, 4, 6, 13].

of the loss factor curves are not symmetrical as a Gauss distribution, meaning that some dissipative parts still remain in the experimental data. These dissipative effects can be described with relaxation curves, which mostly can be represented with exponentially decreasing functions, see Eq. (13). The combined processes are described by an exponentially modified Gauss distribution function (EMG), shown in Eq. (14), which is mathematically a convolution between Eq. (12) and Eq. (13). In Eq. (15) a sum of EMGs is given, because the whole loss factor curve is composed of several transition processes.

$$f_G(T) = \frac{A}{w \cdot \sqrt{2\pi}} \cdot \exp\left[-0.5 \cdot \left(\frac{T - Tc}{w}\right)^2\right] \tag{12}$$

$$f_E(T) = \exp\left(-\frac{T}{To}\right) \tag{13}$$

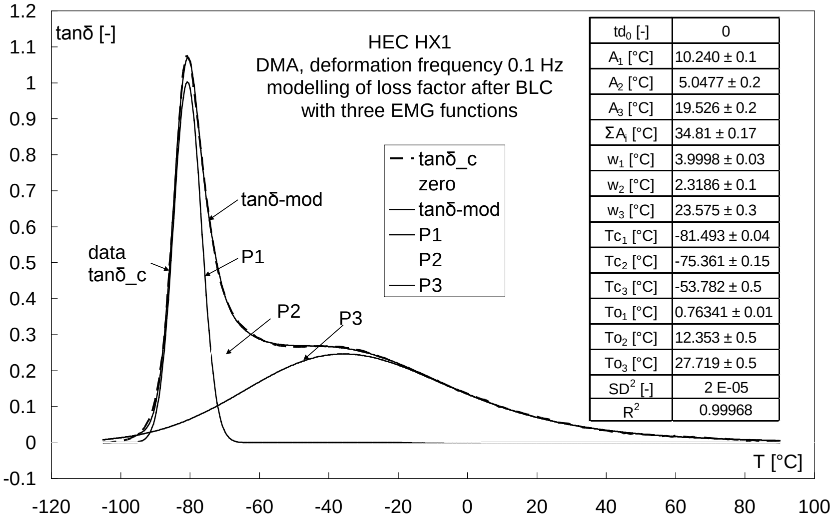
$$\begin{aligned} f_{EMG}(T) = \frac{A}{To} \cdot \frac{1}{2} \cdot \exp\left[0.5 \cdot \left(\frac{w}{To}\right)^2 - \frac{T - Tc}{To}\right] \cdot \\ \left\{1 - \operatorname{erf}\left[-\frac{1}{\sqrt{2}} \cdot \left(\frac{T - Tc}{w} - \frac{w}{To}\right)\right]\right\} \end{aligned} \tag{14}$$

$$\begin{aligned} \tan\delta_{BLC} = td_0 + \sum_{i=1}^{N} \frac{A_i}{To_i} \cdot \frac{1}{2} \cdot \exp\left[0.5\left(\frac{w_i}{To_i}\right)^2 - \frac{T - Tc_i}{To_i}\right] \cdot \\ \left\{1 - \operatorname{erf}\left[-\frac{1}{\sqrt{2}}\left(\frac{T - Tc_i}{w_i} - \frac{w_i}{To_i}\right)\right]\right\} \end{aligned} \tag{15}$$

T	measurement temperature, in [°C];
$\tan\delta_{BLC}$	loss factor as function of T after the BLC, in [-];
A_i	peak areas of the EMG peaks, also equivalent to the area of the corresponding Gauss peaks alone, in [°C];
w_i	half peak width at half height of only the Gaussian part, in [°C];
Tc_i	temperature at peak maxima in the Gaussian part of EMG (not the peak maxima of EMG), in [°C];
To_i	relaxation parameter in exponential part of EMG, in [°C];

td_0	used to consider an eventually residual offset in tanδ data, in [-];
N	number of EMG fit functions;
erf	error function.

In [11] EMGs have been applied also to loss factor curves. The Eq. (15) with a value of N equal to the extractable mobility ranges is adjusted to the baseline corrected experimental data by non-linear fit algorithms. Here a Levenberg-Marquardt algorithm was used provided by the programme package Origin^{TM} [12].



td_0 [-]	0
A_1 [°C]	10.240 ± 0.1
A_2 [°C]	5.0477 ± 0.2
A_3 [°C]	19.526 ± 0.2
ΣA_i [°C]	34.81 ± 0.17
w_1 [°C]	3.9998 ± 0.03
w_2 [°C]	2.3186 ± 0.1
w_3 [°C]	23.575 ± 0.3
Tc_1 [°C]	-81.493 ± 0.04
Tc_2 [°C]	-75.361 ± 0.15
Tc_3 [°C]	-53.782 ± 0.5
To_1 [°C]	0.76341 ± 0.01
To_2 [°C]	12.353 ± 0.5
To_3 [°C]	27.719 ± 0.5
SD^2 [-]	2 E-05
R^2	0.99968

Figure 10.11: Modeling of tanδ with three EMG functions. The description is very good with high correlation coefficient.

In Figure 10.11 the modeling of the loss factor of HEC HX1 at 0.1 Hz deformation frequency is presented. The description of the data is very good, with high correlation coefficient. In comparison, Figure 10.12 shows the modeling with pure Gauss functions. It is clearly recognizable that this description is only approximate and qualitatively usable. But it can help to identify the positions of the first two peaks P1 and P2 for the EMG fits. It is obvious now that the residual dissipative effect must be regarded in the description, as it is achieved with the EMG functions.

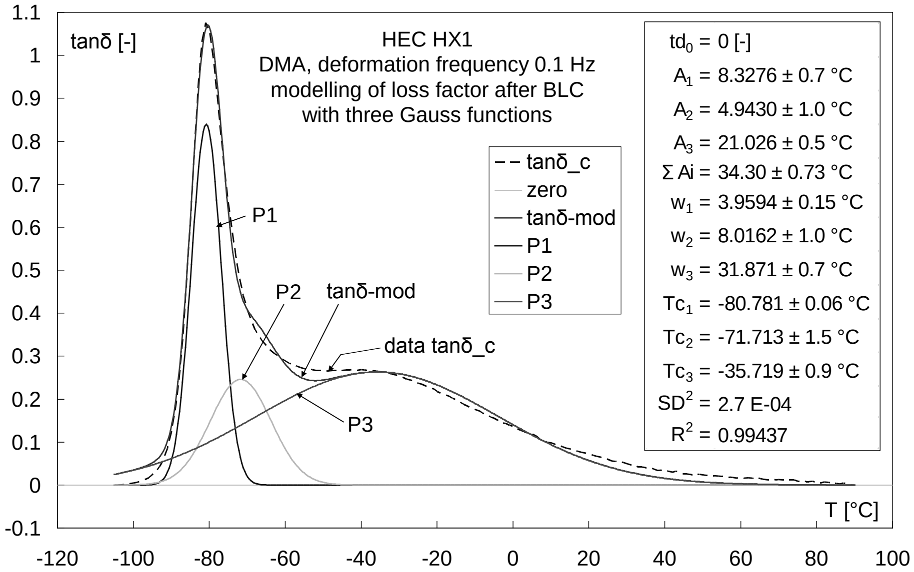


Figure 10.12: Modeling of loss factor of HEC HX1 with three Gauss distributions. The description is only approximate.

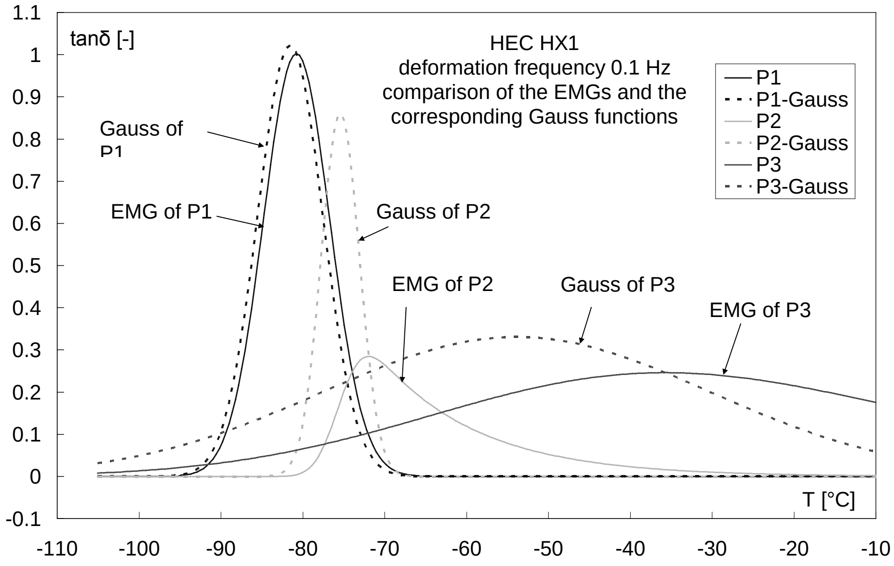


Figure 10.13: Detailed representation of the formal Gauss peak and EMG peak of the main, second and third transition. The maximum of an EMG lies on the corresponding Gauss function.

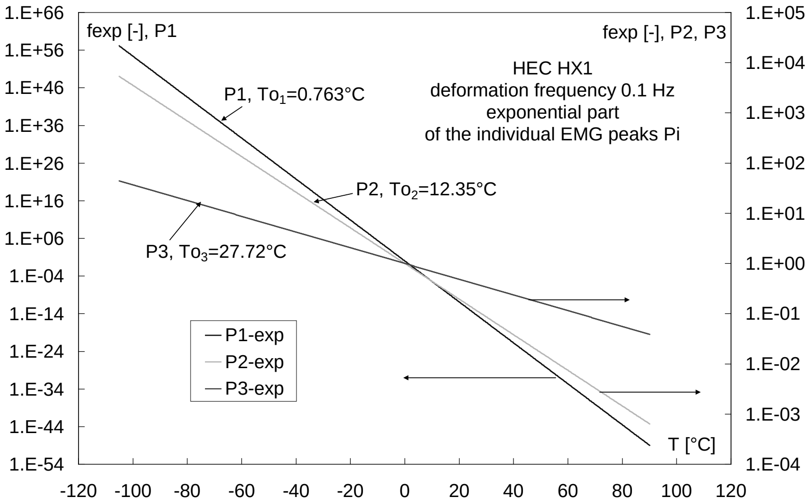


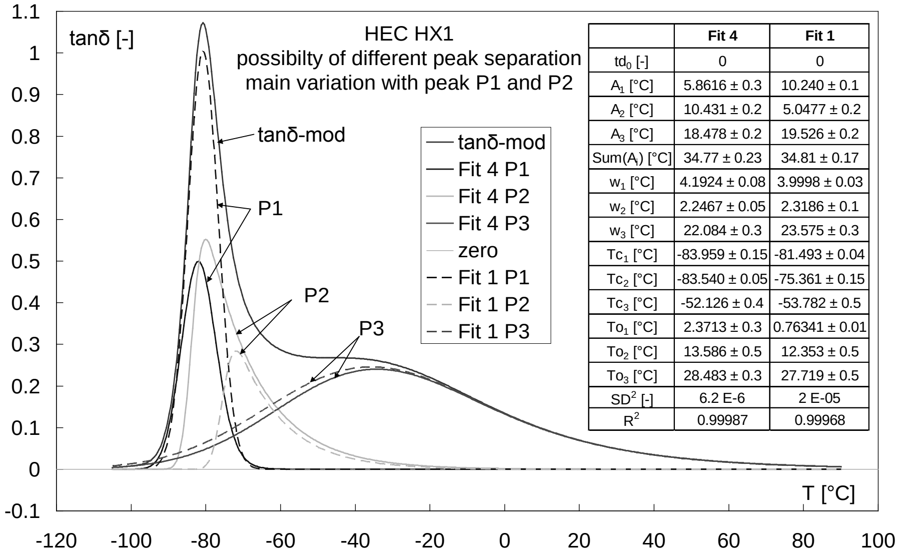
Figure 10.14: Exponential parts of the EMGs of the example used in Figure 10.13.

Figure 10.13 shows an example of EMG peaks together with their Gaussian parts. The maxima of the EMG peaks lie always on the corresponding Gaussian curves. Depending on the relative weight of the dissipative part, the EMG functions are moving from the maximum of the Gauss curves to the base, meaning from non-dissipative to totally dissipative behavior. The exponential parts of the EMGs in the example of Figure 10.13 can be seen in Figure 10.14.

A note to the number of fit parameters used should be given. The number of fit parameters is equal to N*4, and with N=3 EMGs one has to find 12 parameters in a unique way. This is possible because of the limitations of the EMG function in reproducing the shape of functions or curves. This means the EMG contains the constraints by its mathematical structure and cannot describe any shape. However, one must have the necessary structure in the data to determine the parameters uniquely. The following examples, all based on the data of HEC HX1, 0.1 Hz deformation frequency, illustrate this aspect. In Table 10.7 four sets of parameter determinations are compared. The parameters of fits 1 to 3 are all in the standard deviation for each fit. The initial parameter settings have been varied by about 1% to 3%. With fit 4 this variation was about 10% from the values of fit 1 to 3. The search procedure has found another solution, which has even a slightly higher correlation coefficient. These data are compared in Figure 10.15. The main variation is with peak 1 and peak 2, whereby peak 3 stays quite similar in both fits. The explanation is that two peaks are definitely given in the structure of the curve. The third peak is more or less ‘hidden,’ which means for its presence the total curve gives no unique part in its shape. This gives for the fit algorithm some freedom for choosing the values in size, shape and position. In principle both solutions are correct, if one has no additional information or knowledge about the probable structure of the third peak, here named P2. Such problems can also arise with not well defined experimental data, which means they contain noise and scattering. Then it becomes useless to try a description with three peaks, even if three processes are really happening. The way out is to use less peaks in the description. The present loss factor curve is structured in such a way to support clearly and even uniquely the parameter fit with two peaks. The result is shown in Figure 10.16. Peak 3 is nearly the same in both determinations. Peak 1 from two EMGs comprises the peak 1 together with peak 2 from three EMGs. Only a part of peak 2 from 3 EMGs is represented by peak 2 from 2 EMGs, which corresponds to peak 3 from 3 EMGs. In this way the two main structural features of the loss factor curve are described and an evaluation of data obtained with parameter variation as deformation frequency or ageing is easily possible.

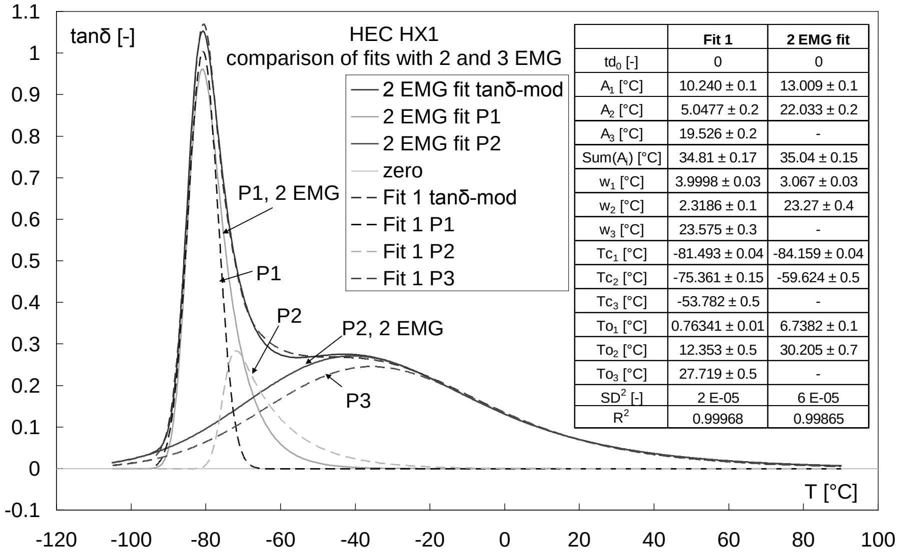
Table 10.7: Comparison of fits and their parameters obtained with HEC HX1 at 0.1 Hz deformation frequency. R^2: correlation coefficient; SD: standard deviation.

	Fit 1	Fit 2	Fit 3	std.dev.	Fit 4	std.dev.
td_0 [-]	0	0	0	-	0	-
A_1 [°C]	10.24	10.254	10.157	0.1	5.8616	0.3
A_2 [°C]	5.0477	5.0621	5.0591	0.2	10.431	0.2
A_3 [°C]	19.526	19.47	19.575	0.2	18.478	0.2
$\sum A_i$ [°C]	34.81	34.79	34.79	0.17	34.77	0.23
w_1 [°C]	3.9998	4.0035	3.9767	0.03	4.1924	0.08
w_2 [°C]	2.3186	2.3027	2.3658	0.1	2.2467	0.05
w_3 [°C]	23.575	23.545	23.564	0.3	22.084	0.3
Tc_1 [°C]	-81.493	-81.488	-81.522	0.06	-83.959	0.15
Tc_2 [°C]	-75.361	-75.35	-75.485	0.15	-83.54	0.05
Tc_3 [°C]	-53.782	-53.727	-53.917	0.5	-52.126	0.4
To_1 [°C]	0.76341	0.76231	0.76321	0.03	2.3713	0.3
To_2 [°C]	12.353	12.427	12.152	0.5	13.586	0.5
To_3 [°C]	27.719	27.721	27.758	0.5	28.483	0.3
SD^2 [-]	2 E-05	2 E-05	2 E-05	-	6.2E-06	-
R^2	0.99968	0.99967	0.99967	-	0.99987	-



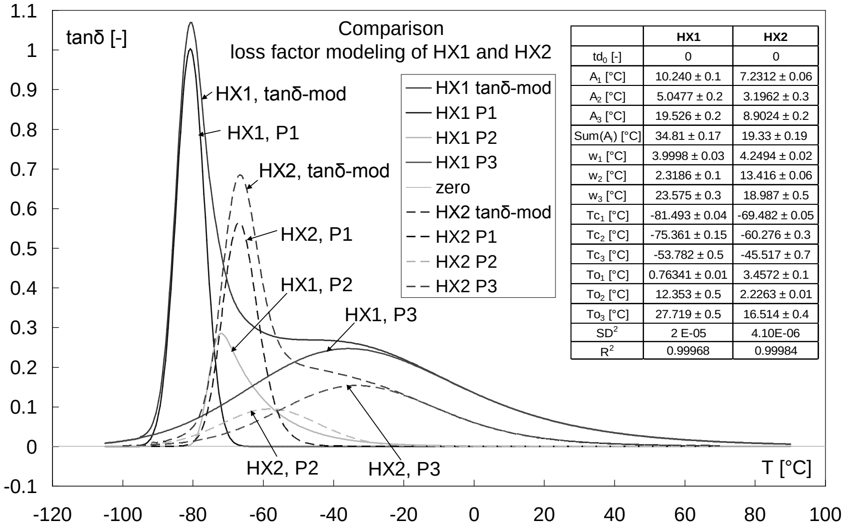
	Fit 4	**Fit 1**
td_0 [-]	0	0
A_1 [°C]	5.8616 ± 0.3	10.240 ± 0.1
A_2 [°C]	10.431 ± 0.2	5.0477 ± 0.2
A_3 [°C]	18.478 ± 0.2	19.526 ± 0.2
Sum(A_i) [°C]	34.77 ± 0.23	34.81 ± 0.17
w_1 [°C]	4.1924 ± 0.08	3.9998 ± 0.03
w_2 [°C]	2.2467 ± 0.05	2.3186 ± 0.1
w_3 [°C]	22.084 ± 0.3	23.575 ± 0.3
Tc_1 [°C]	-83.959 ± 0.15	-81.493 ± 0.04
Tc_2 [°C]	-83.540 ± 0.05	-75.361 ± 0.15
Tc_3 [°C]	-52.126 ± 0.4	-53.782 ± 0.5
To_1 [°C]	2.3713 ± 0.3	0.76341 ± 0.01
To_2 [°C]	13.586 ± 0.5	12.353 ± 0.5
To_3 [°C]	28.483 ± 0.3	27.719 ± 0.5
SD^2 [-]	6.2 E-6	2 E-05
R^2	0.99987	0.99968

Figure 10.15: Comparison of two descriptions with three EMGs. The main difference is found with peak 1 and peak 2.



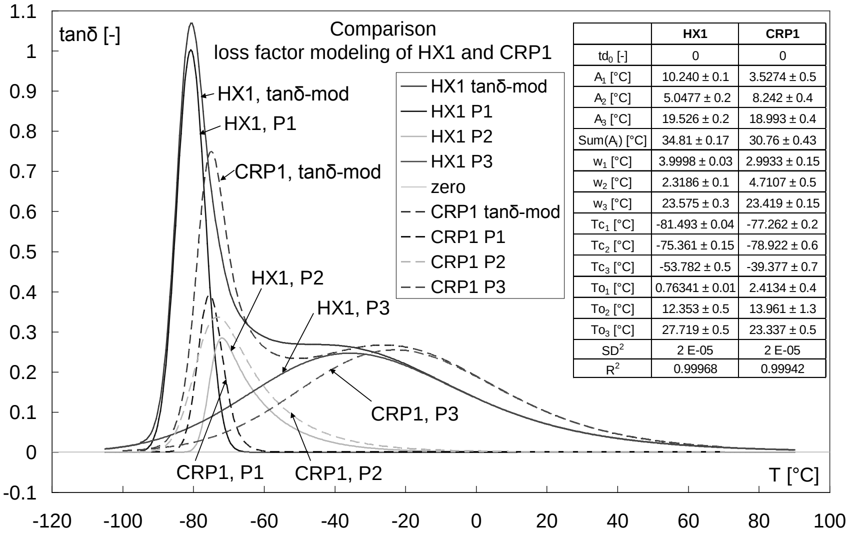
	Fit 1	**2 EMG fit**
td_0 [-]	0	0
A_1 [°C]	10.240 ± 0.1	13.009 ± 0.1
A_2 [°C]	5.0477 ± 0.2	22.033 ± 0.2
A_3 [°C]	19.526 ± 0.2	-
Sum(A_i) [°C]	34.81 ± 0.17	35.04 ± 0.15
w_1 [°C]	3.9998 ± 0.03	3.067 ± 0.03
w_2 [°C]	2.3186 ± 0.1	23.27 ± 0.4
w_3 [°C]	23.575 ± 0.3	-
Tc_1 [°C]	-81.493 ± 0.04	-84.159 ± 0.04
Tc_2 [°C]	-75.361 ± 0.15	-59.624 ± 0.5
Tc_3 [°C]	-53.782 ± 0.5	-
To_1 [°C]	0.76341 ± 0.01	6.7382 ± 0.1
To_2 [°C]	12.353 ± 0.5	30.205 ± 0.7
To_3 [°C]	27.719 ± 0.5	-
SD^2 [-]	2 E-05	6 E-05
R^2	0.99968	0.99865

Figure 10.16: Comparison of two descriptions: one with three EMGs, the other with two EMGs. The main difference arises in the range of the main peak.



	HX1	HX2
td_0 [-]	0	0
A_1 [°C]	10.240 ± 0.1	7.2312 ± 0.06
A_2 [°C]	5.0477 ± 0.2	3.1962 ± 0.3
A_3 [°C]	19.526 ± 0.2	8.9024 ± 0.2
Sum(A_i) [°C]	34.81 ± 0.17	19.33 ± 0.19
w_1 [°C]	3.9998 ± 0.03	4.2494 ± 0.02
w_2 [°C]	2.3186 ± 0.1	13.416 ± 0.06
w_3 [°C]	23.575 ± 0.3	18.987 ± 0.5
Tc_1 [°C]	-81.493 ± 0.04	-69.482 ± 0.05
Tc_2 [°C]	-75.361 ± 0.15	-60.276 ± 0.3
Tc_3 [°C]	-53.782 ± 0.5	-45.517 ± 0.7
To_1 [°C]	0.76341 ± 0.01	3.4572 ± 0.1
To_2 [°C]	12.353 ± 0.5	2.2263 ± 0.01
To_3 [°C]	27.719 ± 0.5	16.514 ± 0.4
SD^2	2 E-05	4.10E-06
R^2	0.99968	0.99984

Figure 10.17: Comparison of the loss factor modeling with three EMGs of HX1 and HX2.



	HX1	CRP1
td_0 [-]	0	0
A_1 [°C]	10.240 ± 0.1	3.5274 ± 0.5
A_2 [°C]	5.0477 ± 0.2	8.242 ± 0.4
A_3 [°C]	19.526 ± 0.2	18.993 ± 0.4
Sum(A_i) [°C]	34.81 ± 0.17	30.76 ± 0.43
w_1 [°C]	3.9998 ± 0.03	2.9933 ± 0.15
w_2 [°C]	2.3186 ± 0.1	4.7107 ± 0.5
w_3 [°C]	23.575 ± 0.3	23.419 ± 0.15
Tc_1 [°C]	-81.493 ± 0.04	-77.262 ± 0.2
Tc_2 [°C]	-75.361 ± 0.15	-78.922 ± 0.6
Tc_3 [°C]	-53.782 ± 0.5	-39.377 ± 0.7
To_1 [°C]	0.76341 ± 0.01	2.4134 ± 0.4
To_2 [°C]	12.353 ± 0.5	13.961 ± 1.3
To_3 [°C]	27.719 ± 0.5	23.337 ± 0.5
SD^2	2 E-05	2 E-05
R^2	0.99968	0.99942

Figure 10.18: Comparison of the loss factor modeling with three EMGs of HX1 and CRP1.

In Figure 10.17 the EMG description of HEC HX1 and HEC HX2 is compared. The total loss factor intensity of HX2 is only about the half of the intensity of HX1. The position of the first maximum in tanδ is at significantly higher temperature. The cause is the lower content in plasticizer (1 mass-% against 8 mass-%) and in using the type HTPB R45HT, which results in a higher cross-linking density. This reduces the mobility of the binder chains. The EMG maximum of the second apparent transition of HX2 has nearly the same temperature as the one of HX1. This information could not be obtained from the total loss factor curves alone by determining maximum temperatures. Only by modeling is this recognizable. A further interesting comparison is made in Figure 10.18 between HX1 and CRP1. The total intensities of the loss factors are similar, but the contributions to it are different. With HX1 the two lower temperature transitions contribute about 44 %, and with CRP1 this is only 38%. The second apparent peak of CRP1 is more intense and positioned at higher temperatures. The reason is the binder shell around the AP particles created by the used reactive bonding agent for AP. This forms an elastomer network with higher glass transition temperature, and the transition intensity of this region is increased.

10.6 Modeling of Loss Factor Curves Subjected to Change of One Experimental Quantity

In this section the modeling of loss factor curves is presented, when one experimental parameter is changed, which is here the deformation frequency. In other papers [1, 3, 13] the influence of ageing is discussed. Figures 10.19, 10.20 and 10.21 show the modeling of HX1 loss factor at 1 Hz, 10 Hz and 30 Hz deformation frequencies; the one at 0.1 Hz was shown above. The curves change systematically, which can be seen in the overview given with Figures 10.22. The maximum temperatures Tc_i shift to higher temperatures, the individual intensities A_i increase, the peak widths w_i increase and the relaxation parameters To_i increase. The quantitative data are given in Table 10.8. Some of the changes in going from 0.1 Hz to 30 Hz are highlighted. The peak 2 changes most significant in A_2 and w_2, whereas peak 3 shows the greatest changes in the Tc_3 and the To_3. The increase in the relaxational part (To_i) indicates the increasing dissipative effects, mainly by ‘molecular friction.’ The strong increase in maximum temperature with deformation rate indicates the possibility of high energy dissipation and therefore a heating up of the material already at moderate low temperatures. This effect has importance with rocket motor propellants; it is dominant in the mobility range of the hindered binder, expressed in peak 3. Peak 2 is seen to represent the restricted binder by the filler particles, here RDX. Peak 1 gives the behavior of the unrestricted binder. With regard to general peak broadening by increasing deformation rate, peak 1 stays constant in intensity.

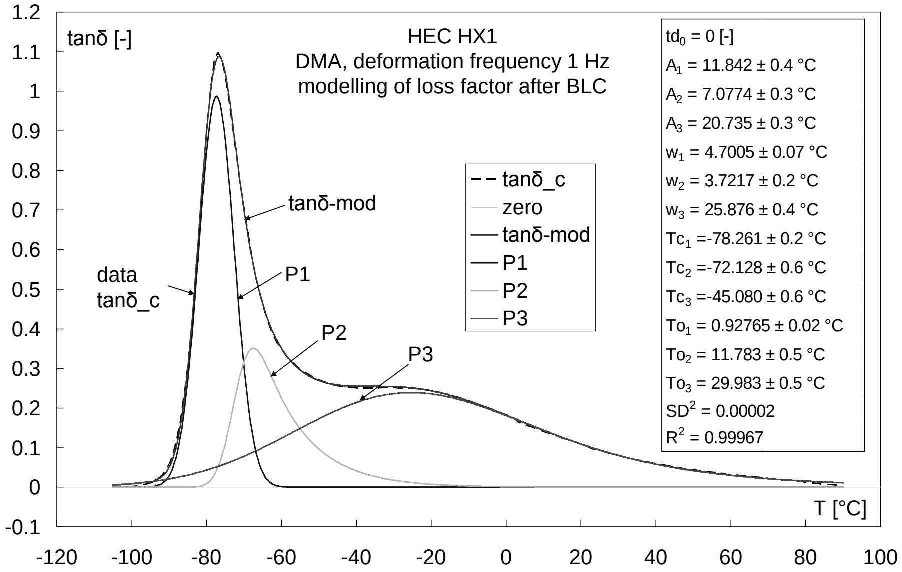


Figure 10.19: Description of the loss factor of the unaged HEC HX1 with three EMG functions at 1 Hz deformation frequency.

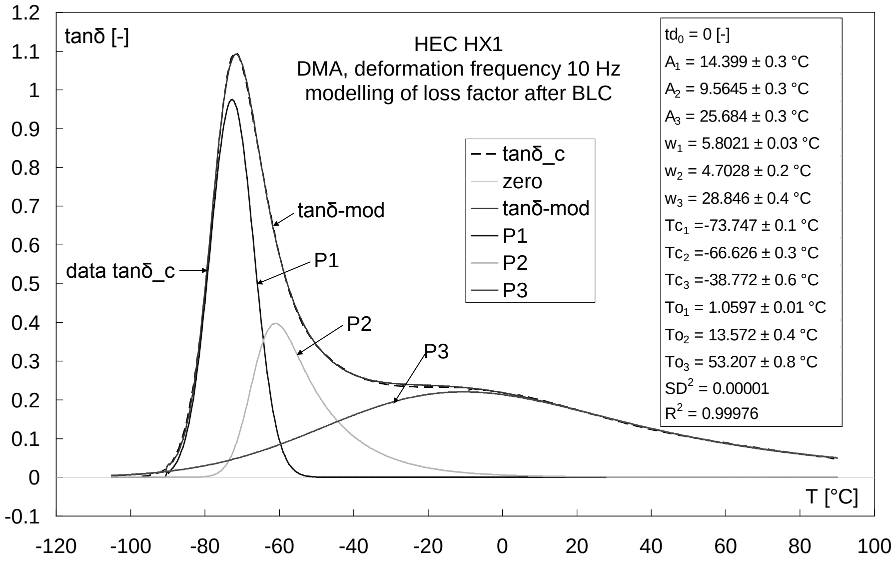


Figure 10.20: Description of the loss factor of the unaged HEC HX1 with three EMG functions at 10 Hz deformation frequency.

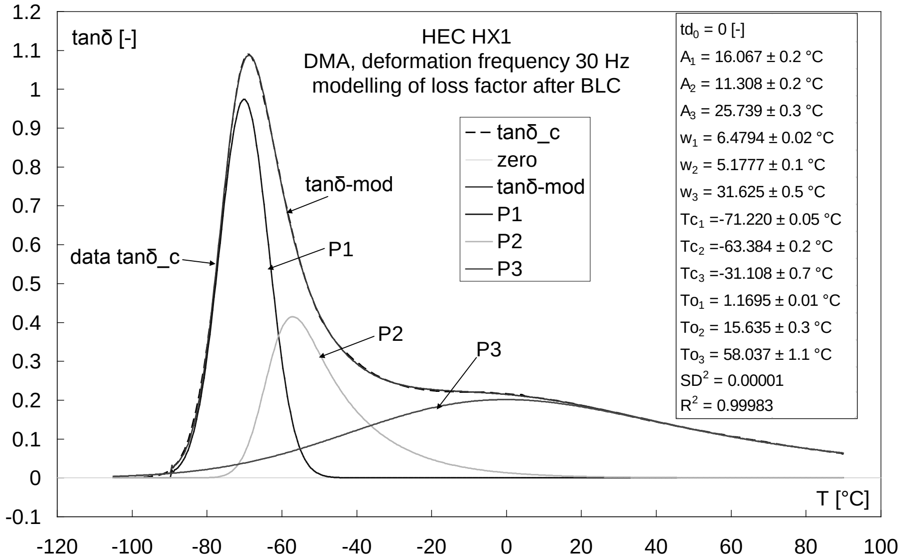


Figure 10.21: Description of the loss factor of the unaged HEC HX1 with three EMG functions at 30 Hz deformation frequency.

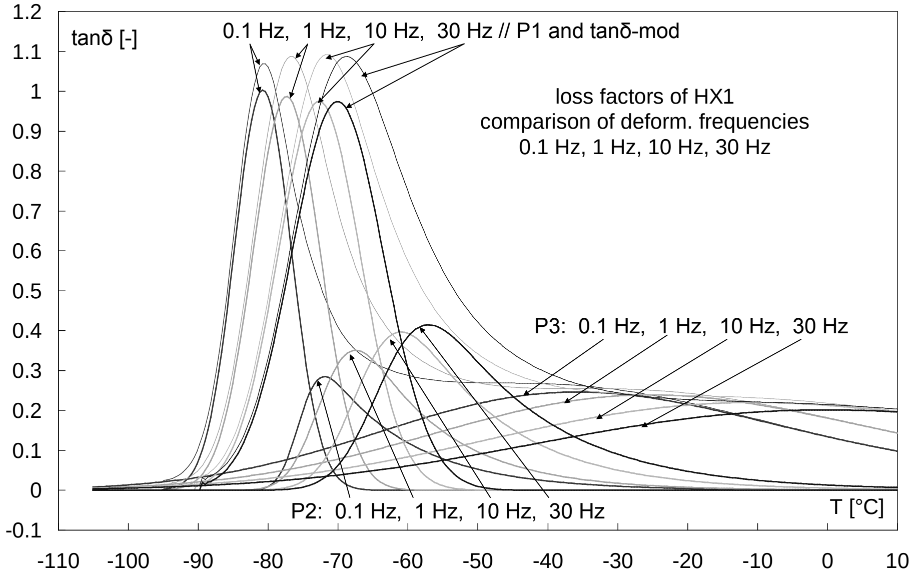


Figure 10.22: Overview of the description of the loss factor of the unaged HEC HX1 with three EMG functions at four deformation frequencies.

From the total behavior it becomes now clear that the essential information about the influence of a parameter change is contained in peak 2 and peak 3. Peak 1 contains no information about such an influence. This was also found with ageing of composite rocket propellant formulations based on HTPB-IPDI, see [1, 2, 3, 13]. The following Figures 10.23 to 10.26 show the parameterization of the frequency dependence of the fit parameters of the EMG functions. In Table 10.9 the equations found are compiled. The quantities A_i, w_i, Tc_i have logarithmic dependence on deformation rate, and the relaxation quantities To_i could be described best by linear dependency.

Table 10.8: EMG parameters of the description of loss factor curves of HEC HX1 at several deformation frequencies. R^2: correlation coefficient; SD: standard deviation.

	0.1 Hz	1.0 Hz	10 Hz	30 Hz	Change
td_0 [-]	0	0	0	0	0
A_1 [°C]	10.24 ± 0.1	11.84 ± 0.4	14.40 ± 0.3	16.07 ± 0.2	1.57
A_2 [°C]	5.048 ± 0.2	7.077 ± 0.3	9.565 ± 0.3	11.31 ± 0.2	2.24
A_3 [°C]	19.53 ± 0.2	20.74 ± 0.3	25.68 ± 0.3	25.74 ± 0.3	1.32
$\sum A_i$ [°C]	34.81 ± 0.17	39.65 ± 0.33	49.65 ± 0.3	53.11± 0.23	-
w_1 [°C]	4.00 ± 0.03	4.701 ± 0.07	5.802 ± 0.03	6.479 ± 0.02	1.62
w_2 [°C]	2.32 ± 0.1	3.723 ± 0.2	4.703 ± 0.2	5.178 ± 0.1	2.23
w_3 [°C]	23.58 ± 0.3	25.88 ± 0.4	28.85 ± 0.4	31.63 ± 0.5	1.34
Tc_1 [°C]	-81.49 ±0.04	-78.26 ± 0.2	-73.75 ± 0.1	-71.22 ±0.05	10.3
Tc_2 [°C]	-75.36 ±0.15	-72.13 ± 0.6	-66.63 ± 0.3	-63.38 ± 0.2	12
Tc_3 [°C]	-53.78 ± 0.5	-45.08 ± 0.6	-38.77 ± 0.6	-31.11 ± 0.7	22.7
To_1 [°C]	0.763 ±0.01	0.928 ±0.02	1.060 ± 0.01	1.170 ± 0.01	1.53
To_2 [°C]	12.35 ± 0.5	11.78 ± 0.5	13.57 ± 0.4	15.64 ± 0.3	1.27
To_3 [°C]	27.72 ± 0.5	29.98 ± 0.5	53.21 ± 0.8	58.04 ± 1.1	2.09
SD^2 [-]	2 E-05	2 E-05	1 E-05	1 E-05	-
R^2	0.99968	0.99967	0.99976	0.99983	-

Table 10.9: Description of the fit parameters of the EMGs modeling the loss factors of HX1 as function of deformation frequency f in Hz. For the relaxation parameter To_3 a two step behavior was found. Part one comprises 0.1 to 10 Hz and part two 10 Hz to 30 Hz.

Quantity	function type	Equation	correl. coeff. R^2
A_1 [°C]	logarithmic	$A_1 = 1.0844*\ln(f) + 11.813$	0.8827
A_2 [°C]	logarithmic	$A_2 = 1.0621*\ln(f) + 7.4516$	0.9781
A_3 [°C]	logarithmic	$A_3 = 1.2387*\ln(f) + 21.792$	0.9154
w_1 [°C]	logarithmic	$w_1 = 0.4470*\ln(f) + 4.7975$	0.9645
w_2 [°C]	logarithmic	$w_2 = 0.4734*\ln(f) + 3.6964$	0.9346
w_3 [°C]	logarithmic	$w_3 = 1.3434*\ln(f) + 26.408$	0.9655
Tc_1 [°C]	logarithmic	$Tc_1 = 1.8352*\ln(f) - 77.910$	0.9840
Tc_2 [°C]	logarithmic	$Tc_2 = 2.2024*\ln(f) - 71.792$	0.9271
Tc_3 [°C]	logarithmic	$Tc_3 = 3.7982*\ln(f) - 45.632$	0.9753
To_1 [°C]	linear	$To_1 = 0.0119*f + 0.84398$	0.7801
To_2 [°C]	linear	$To_2 = 0.1395*f +11.607$	0.8709
To_3 [°C]	linear, part 1	$To_3 = 2.5848*f + 27.348$	0.9999
To_3 [°C]	linear, part 2	$To_3 = 0.2415*f + 50.792$	(1.00)

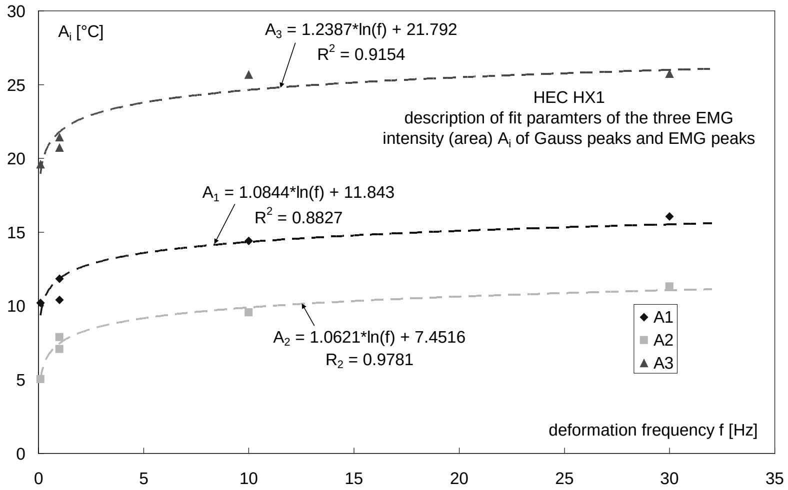


Figure 10.23: Parameterization of the intensities A_i of the three mobility ranges of loss factor of HX1 as function of deformation frequency.

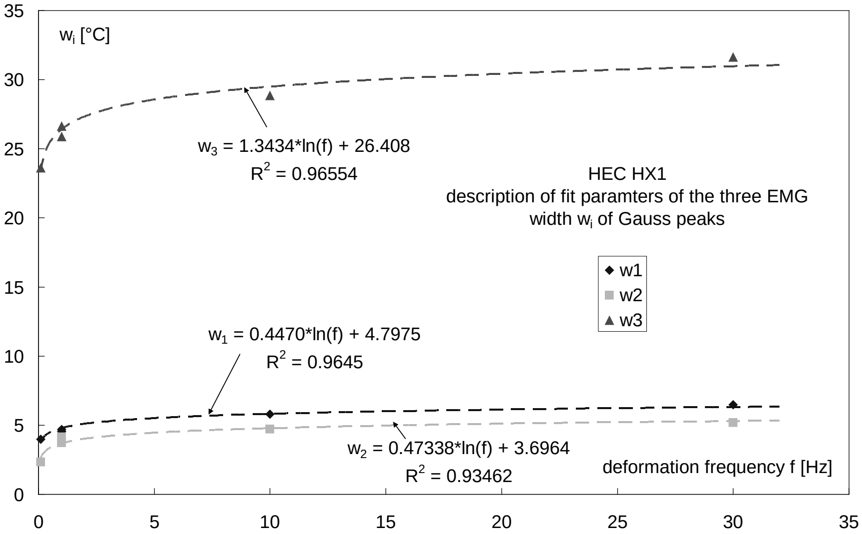


Figure 10.24: Parameterization of the Gaussian half peak widths w_i of the three mobility range peaks of the loss factor curves of HX1 as function of deformation frequency.

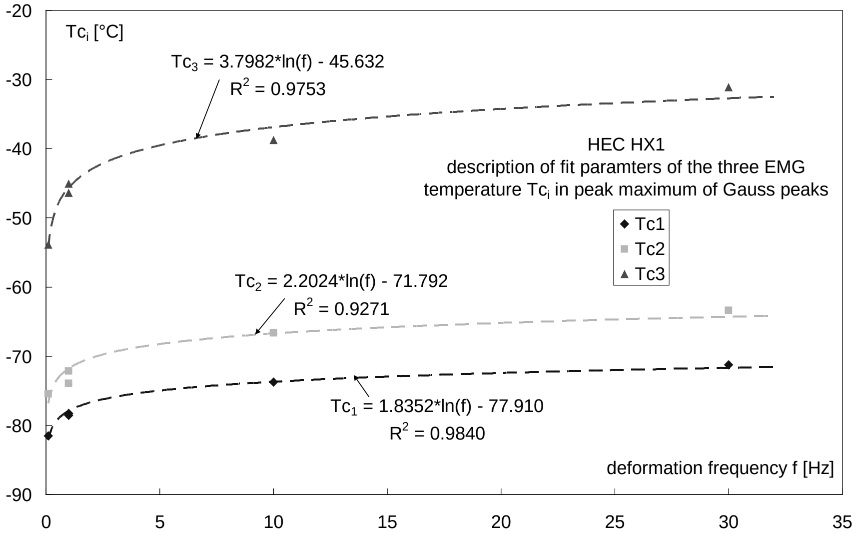


Figure 10.25: Parameterization of the peak temperature Tc_i of the Gauss part of the three mobility range peaks of the loss factor curves of HX1 as function of deformation frequency.

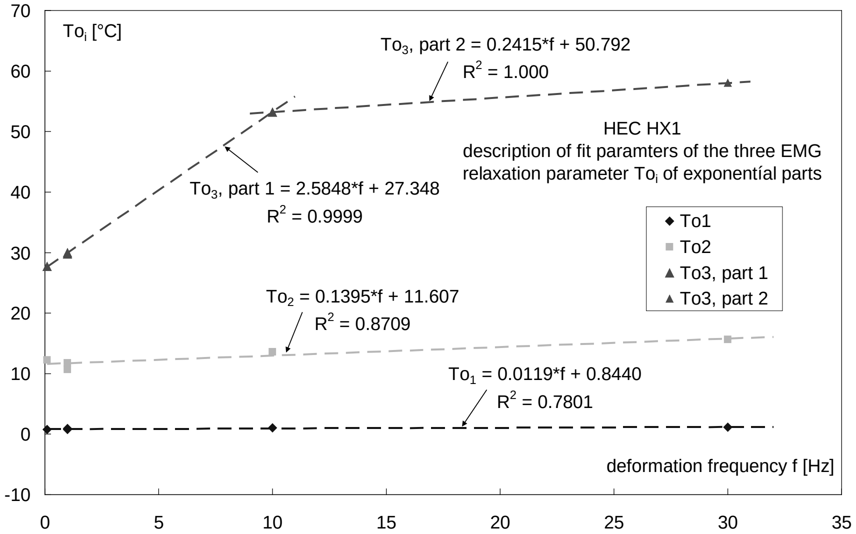


Figure 10.26: Parameterization of the exponential relaxation parameter To$_i$ of the three mobility range peaks of the loss factor curves of HX1 as function of deformation frequency.

10.7 Summary and Conclusions

The loss factor tanδ obtained by DMA measurements contains important information on the mobility phases or fractions of the binder of elastomer bonded energetic materials, which have different molecular mobility. With HTPB-IPDI binders often used, the loss factor curve contains two apparent peak regions and therefore at least two mobility fractions of the binder. Glass transition temperatures Tg are here defined as maximum temperatures of the maxima in the loss factor curve. A discussion of main influences on the loss factor curve was given. Essential for low Tg values are the effects that increase the free volume for the chain motions and all features that reduce the interaction energies between the chains of the elastomer and the plasticizer. Because the binder GAP has a lot of polar groups in the polymer chain, which is also linear, the glass transition must be at higher temperatures compared to the HTPB binder, which has no polar groups and is non-linear. An estimation of intermolecular interaction energies between HTPB chains and GAP chains has been presented.

The loss factor curve contains the information about the transition from energy elastic state to entropy (rubber) elastic state by molecular rearrangement processes. These processes are affected by external impacts as strain, deformation rate and ageing. To extract the information about these processes and their dependence on these external impacts, the modeling of the loss factor curve has to be achieved. For this a procedure was worked out and is presented here. The loss factor is a measure of the energy consumption needed to perform the molecular rearrangement processes. Beneath this part of energy use, parts with energy dissipation are also contained. With filled elastomers this expresses as an offset of the curve in the rubbery state. To eliminate the dissipative part a baseline correction has to be applied on the loss factor curve. A special iteration procedure was developed to achieve the baseline correction. The baseline corrected loss factor is subjected to a modeling in order to separate the mobility fractions. For this so-named exponentially modified Gauss (EMG), distribution functions have been used. The undisturbed rearrangement processes should follow a Gauss distribution. But the loss factor curves are not purely symmetrical as Gauss functions, because there is still a dissipative part included. This is handled by exponential relaxation, and in combination with Gauss function the EMG results. One EMG function has four parameters to be determined: peak intensity A, half peak width w of the Gauss part, maximum temperature Tc of the Gauss part, and the relaxation parameter To of the exponential part. Modeling of the loss factor curves of HTPB-binders with EMGs revealed three transition regions or mobility fractions in the complete loss factor curve instead of only two, as it is evident from the shape structure of tanδ of HTPB-IPDI binders. These three regions seem typical for this binder, because it was found already with several types of materials containing this binder type. By variation of the external impact on the material as deformation rate or ageing, it was found that the three mobility fractions belong to the (i) mobility of unrestricted binder fraction with the lowest glass transition temperature, (ii) mobility of restricted binder fraction with intermediate glass transition temperature, (iii) hindered binder fraction or stronger mobility restricted fraction with the highest glass transition temperature. The intensity of the unrestricted binder fraction is little affected by the external impact deformation rate and ageing. The other two fractions show clearly a dependence on deformation rate and ageing effects, especially in intensity, peak broadness and relaxation parameter. The conclusion is that these two mobility parts reflect essential changes in the binder and in the binder-filler interaction on external impacts. The maximum temperature of the main peak in the loss factor curve is not enough as assessment quantity. Further work will elucidate the behavior of the mobility fractions of HTPB-IPDI binders, including investigations with small rocket motor configuration using embedded stress sensors.

10.8 Abbreviations

Al	aluminium, fuel
AP	ammonium perchlorate, oxidizer
ADN	ammonium dinitramide, oxidizer
BA	bonding agent
BLC	baseline correction
BPS	Bis-propargyl succinate
COMPASS	Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies force field from Accelrys, San Diego, CA, USA
CRP	composite rocket propellant, based on binder, AP, Al
DMA	dynamic mechanical analysis
DOA	dioctyl adipate, plasticizer
DSC	dynamic scanning calorimetry
EMG	exponentially modified Gauss distribution
FF	force field, used in atomistic simulation calculations
FP	filler particle (as Al, AP, RDX)
GAP	glycidyl azide polymer (energetic binder)
HEC	high explosive charge
HTPB	hydroxyl terminated polybutadiene, binder
HX	high explosive
IIA	intermolecular interaction
IPDI	isophorone diisocyanate, curing agent for PUR elastomers
LJ	Lennard-Jones (John Edward Lennard-Jones), intermolecular potential
PBX	Polymer bonded explosive
PUR	polyurethane
RP	rocket propellant
N100	Desmodur$^{\mathrm{TM}}$ N100, curing agent for PUR elastomers
N3400	Desmodur$^{\mathrm{TM}}$ N3400, curing agent for PUR elastomers
Tg	glass transition temperature defined as temperature in a maximum of $\tan\delta$ (loss factor) curve
vdW	van-der-Waals (Johannes Diderik van der Waals)
vdW radii	the vdW-radii are the ones in the minimum of the Lennard-Jones potential. They are the half distance between equal atoms in a crystal lattice without chemical bonding; only the dispersion interaction exists.
MAP	mobile amorphous phase

MAF	mobile amorphous fraction
RAP	rigid amorphous phase
RAF	rigid amorphous fraction
G'	storage shear modulus
dG'/dT	temperature derivative of G'
G"	loss shear modulus
E'	storage tensile modulus
E"	loss tensile modulus
tanδ	loss factor, tanδ = G"/G' = E"/E'
tanδ_max1	main maximum of loss factor, unrestricted binder
tanδ_max2	second maximum of loss factor, hindered binder
δ	phase angle
α	normalized cumulative partition function of tanδ(T)
T	temperature

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Chapter 11

Industrial Explosives in Polish Mining

Andrzej Maranda

The development of many economic sectors depends on extraction of minerals. This is true in Poland. The demand for metal ores as well as for energetic raw materials and crushed aggregates is increasing. That is why big quantities of blasting explosives, which have very different functional properties, are used in the Polish mining industry. Emphasis is put on the use of safe explosives and initiators as well as safe loading of materials into shot-holes. Solutions adopted in Polish mining industry are described in the article.

11.1 Introduction

In Poland, as in other European countries, the beginnings of the use of explosives are connected with black powder. The first document that testifies to the use of firearms and black powder in Poland is the Wiślica Statutes, a collection of laws issued by King Casimir the Great in 1347. The description of the Battle of Grunwald between the Order of Teutonic Knights and the allied Polish and Lithuanian armies, which took place in 1410, mentions that the Polish army used 60 cannons. One of the first gunpowder mills was opened in Legnica in 1348 [1].

Black powder was used in a kind of terrorist attack that took place in 1582 when the Polish army besieged the fortress of Psków (now in Russia). During talks concerning a cease-fire necessary to organize the burial of killed Russian soldiers, Polish negotiators were shot at. In revenge, a Polish commander, Jan Ostromęcki, sent to the enemy camp a casket where he placed an explosive device. The constructor *put into an iron casket twelve tubes which he arranged in rows; the tubes were purposely thinned, so that they could crack easily. He filled up the casket* *and the tubes with the finest powder. He installed also inside the lock of a harquebus the cock of which was raised. Then, he placed the casket in a wooden chest and attached the cock to the bottom of the chest and to the lid of the casket with two strings* [2]. The opening of the casket caused the explosion of the device. However, the attack did not succeed. The explosion did not kill the commander of the fortress, Russian prince Ivan Szujski.

Another explosive, dynamite, was produced – very soon after its invention by Alfred Nobel – in the regions that form the current Polish territory. According to T. Rogalski, the first dynamite factory in Poland was built about 1870 in the area of Bytom. There were many coal mines in the region at that time. The factory was mentioned in a letter of October 8th 1877. The author makes reference to an explosion that happened in 1870. More sources confirm the construction of a dynamite factory at Bieruń Stary. According to a document of July 1st 1871, the merchant-industrial group Guttmann & Company from Bytom was allowed to build a dynamite factory in the boundaries of Bieruń Stary town. The new factory was called Schlesische Sprengstoff Fabryk. It was situated, similarly to the first A. Nobel`s nitroglycerin factories, on inaccessible land, between two small rivers, Gostynia and Mleczna. The factory buildings were raised quickly, and the first batches of dynamite were produced a year after getting the building permit. Also in this factory were registered explosions − in 1872 and 1875 [3].

Another explosives manufacturing factory was situated on the current territory of Krupski Młyn town. In 1870, the Berlinian company Lignose Sprengstoffwerke GmbH bought terrains at the riverside of Mała Panew from Count Thiele-Winckler. The first buildings were built in 1872. Two years later the factory reached its planned production capacity. Initially, black powder and guncotton for grenades were manufactured. Next the production of dynamite was launched. In addition to the factories mentioned above, which continue to operate within the NITROERG company, a factory in Pionki was another big producer of mining explosives. The factory was built in 1922-1923 by the State Factory of Powder and Brisant Materials in Zagożdżon. After the II World War, it was known as the Plastic Materials Factory, PRONIT, in Pionki.

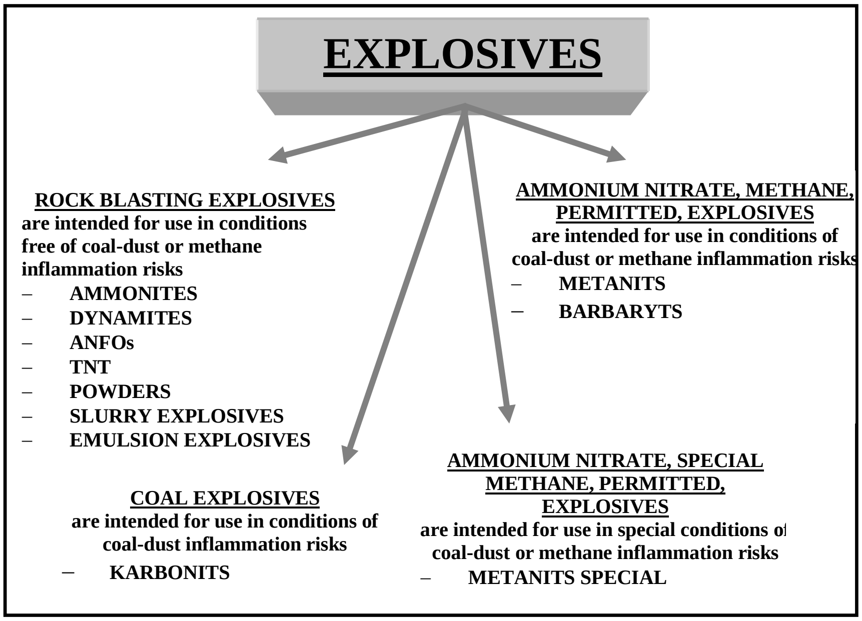
The period of the constitutional transformation after 1989 was crucial for the mining explosives industry because of the inflow of foreign capital to the Polish explosives market. Westspreng was one of the first western companies to open a branch in Poland − Blastexpol in Duninów. Currently, almost all world potentates producing blasting explosives operate in Poland.

11.2 Classification and Use of Mining Explosives

In Poland, the classification of mining explosives was published in the Polish Standard PN-C-86067:1997. It was replaced in 2006 by the European Standard PN-EN 13631-1:2006. However, classification, labeling, and requirements set by the Polish Standard are still in force. Mining explosives can be divided into:

- groups, depending on safety degree in contact with mixtures of methane and coal dust with air
- subgroups, depending on their physical features and chemical composition
- sorts, depending on their additional properties
- types, depending on the form in which they are used

Classifications in groups (Figure 11.1) and subgroups (Figure 11.2) are of fundamental importance:



EXPLOSIVES

ROCK BLASTING EXPLOSIVES
are intended for use in conditions free of coal-dust or methane inflammation risks
- **AMMONITES**
- **DYNAMITES**
- **ANFOs**
- **TNT**
- **POWDERS**
- **SLURRY EXPLOSIVES**
- **EMULSION EXPLOSIVES**

AMMONIUM NITRATE, METHANE, PERMITTED, EXPLOSIVES
are intended for use in conditions of coal-dust or methane inflammation risks
- **METANITS**
- **BARBARYTS**

COAL EXPLOSIVES
are intended for use in conditions of coal-dust inflammation risks
- **KARBONITS**

AMMONIUM NITRATE, SPECIAL METHANE, PERMITTED, EXPLOSIVES
are intended for use in special conditions o coal-dust or methane inflammation risks
- **METANITS SPECIAL**

Figure 11.1: Classification of mining explosives by safety degree in contact with mixtures of methane and coal dust with air.

In the last two decades, serious changes in the use of explosives in Polish mining have occurred. In 1996 manufacturers offered more than 70 types of explosives. However, in the Polish mining industry mainly cartridged and loose explosives were used. They were put into shot-holes manually. Figure 11.3 illustrates the structure of the use of explosives in Poland in 1996.

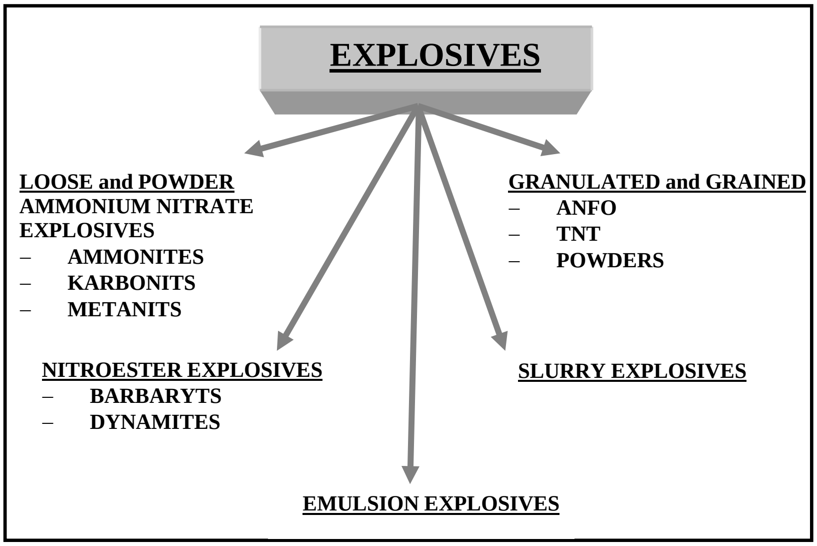


Figure 11.2: Classification of mining explosives by physical features and chemical composition.

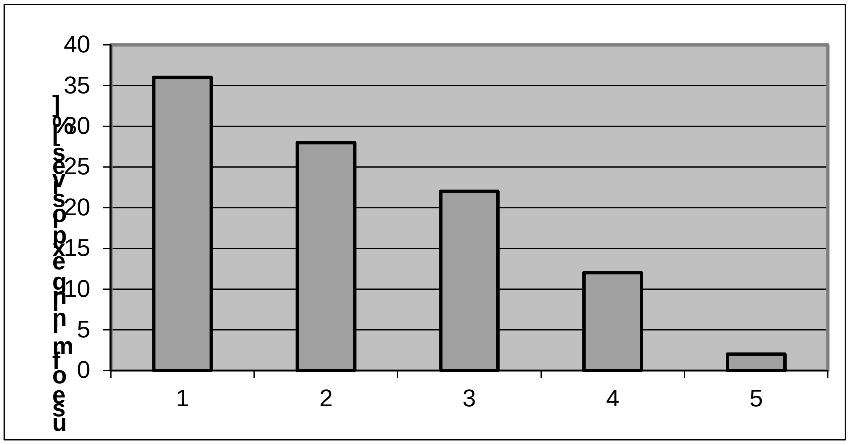


Figure 11.3: Explosives in Poland in 1996: 1 – plastic explosives cartridged, 2 – granulated, 3 – grained explosives cartridged, 4 – trotyl, 5 – loose explosives bulk [3].

In 2010, 36,800 tons of explosives were used in the Polish mining industry. ANFOs and emulsion explosives were the most popular blasting explosives (Table 11.1).

Table 11.1: Use of explosives in the Polish mining industry in 2010.

Explosives	Dynamites	Ammonites	Karbonits	Metanits	Metanits Special	ANFOs
Use [%]	16.47	1.52	0.09	0.43	1.71	23.39
Explosives	Emulsion explosives bulk	Emulsion explosives cartridged	Slurry explosives bulk	Slurry explosives cartridged	Trotyl	Powders
Use [%]	44.76	11.22	0.04	0.05	<0.01	0.30

The above data show that mainly explosives sold in bulk are used. Therefore, in many cases, the most advanced loading and mixing systems are used for preparing *in situ* and loading blasting explosives into shot-holes.

The State Mining Authority allows the use of blasting explosives on areas subject to mining law and keeps a register of them.

11.3 Profile of the Individual Groups of Mining Explosives

11.3.1 Ammonites

In the mid-1990s, ammonites were still one of the most used blasting agents. The popularity of ammonites was due to their accessibility, the low price of raw materials, and relatively simple production technology. Investigations of mining explosives, conducted at Polish scientific institutes, especially at the Military University of Technology in Warsaw, aimed to determine the explosive properties of mixtures of ammonium nitrate (V) with trotyl, aluminum dust and various organic fuels. Other research focused on the description of the mechanism of the detonation of systems: oxidizer − combustible component [4-15]. Researchers examined also ammonium nitrate explosives containing homogeneous fuels [16-20].

During the 20th century more than several dozen ammonites were developed, which differed, i.e., in sensitizing additives. Nitroglycerine – nitroglycol system was applied most often as a sensitizer. Trotyl and aluminum dust were also used as sensitizers and simultaneously acted as combustible components. Other combustible components were: powdered shove harl, wood flour, slack wax, solid hydrocarbons or ethylene glycol. Ammonites contained additional modifiers, which, among others, increased their water resistance, e.g. carboxymethylcellulose or guar gum. The State Mining Authority register dated September 19, 2011 lists 8 ammonites. The general composition and some parameters of ammonites applied in Polish mining are shown in Table 11.2.

Table 11.2: Composition, detonation and thermodynamic parameters of selected ammonites [3].

Component or parameter	Ammonites							
	45H	49H	53	54H	55H	56	60	61H
	Composition [%]							
Ammonium nitrate(V)	84.8	53.0	80.98	81.45	80.4	56.1	83.0	80.38
Sodium nitrate(V)	-	-	-	-	-	20.0	-	-
Nitroglicerine	-	-	1.2	3.6	1.2	-	-	3.6
Nitroglycol	7.75	-	4.8	2.4	4.8	-	-	2.4
Nitrocellulose	0.25	-	-	-	-	-	-	-
Trotyl	-	40.0	-	-	8.0	12.0	11.0	10.0
Fuels	7.1	4.0	7.0	5.7	4.5	3.9	6.0	2.5
Aluminium powder	-	2.0	6.0	6.0	-	7.0	-	-
Modifiers	0.1	1.0	0.02	0.85	1.1	1.0	-	1.12
Density [g/cm^3]	1.05	1.00	1.08	1.11	1.04	1.01	0.97	0.85
Oxygen balance [%]	+0.37	-29.70	+1.09	+1.41	+1.51	-2.91	+1.60	+3.20
Strength								
- Trauzl test [cm^3]	296	339	384	392	348	331	253	350
- ballistic mortar [% Hx]	82	81	87	80	73	76	76	82
Critical diameter [mm	18	15	15	13	10	25	40	15
Detonation velocity [m/s]	2925	3991	3174	3256	2631	2339	1314	3300
in diameter charge [mm]	36	80	36	36	36	80	40	36
Transmission of detonation [cm]	13	3	10	5	6	-	-	6
Volume of gas products [dm^3/kg]	943	894	842	845	913	819	906	903
Heat of explosion [kJ/kg]	4004	4004	4900	4934	4082	3428	4112	4090

11.3.2 Karbonits

Explosions of coal dust and methane are the most common hazard in mining. They cause many mine catastrophes. In the 18th century and during a considerable part of the 19th century, all the explosions that occurred in mines were associated with so called ”mine gas”, identified as methane. J. Buddle first took into consideration the possibility of the explosion of coal dust. He testified that during the explosion in the British mine in Wallsend in 1803, sparks of burning coal dust were observed. The first researcher to acknowledge the danger of a coal dust explosion was M. Faraday. His opinion was referred to after the catastrophe in the mine in Haswell in 1844.

In Poland, research into explosive materials that would be safe in a coal dust and methane environment were conducted on a large scale by Prof. Wacław Cybulski [21-23]. This research constituted a basis for elaborating the composition of karbonits and methanits. Other studies concerned systems ammonal−inert salt (sodium chloride, barium sulphate (VI)) [24].

Karbonits contain similar components as ammonites and additionally have about 10% sodium chloride. At present, there is only one karbonit on the State Mining Authority register. Compositions and parameters of karbonits are shown in Table 11.3.

11.3.3 Metanits and Special Metanits

In contrast to karbonits, metanits allowed for use in Polish mining are more numerous. There were two metanits and nine special metanits in the State Mining Authority register of September 19,^{h} 2011. An emulsion is among them. The chemical composition of metanits is similar to karbonits. However, metanits contain more sodium chloride. Some typical compositions, as well as detonation and thermodynamic parameters of metanits, are presented in Table 11.4.

11.3.4 Dynamites

After black powder, dynamites were the second group of explosives manufactured in Poland. Their composition changed over the years. Today explosives are considered dynamites if they contain more than 10% of nitroesters. Polish research on dynamites has a long history. One of the findings was that the intensity of excitation has an influence on detonation parameters and the content of toxic substances in explosion products [25].

The register of the Polish State Mining Authority lists 22 dynamites. Table 11.5 shows the composition and parameters of chosen ones.

Table 11.3: Composition, detonation and thermodynamic parameters of karbonits [3].

Component or parameter	Karbonits					
	1H	D7G	D8G2	D10H	D11H	D12H
	Content [%]					
Ammonium nitrate(V)	76.0	74.98	76.5	77.0	81.8	80.8
Nitroglicerine	3.0	3.0	-	-	-	-
Nitroglycol	2.0	2.0	4.0	6.0	3.0	4.0
Nitrocellulose	-	-	-	-	0.2	0.2
Fuels	7.5	10.0	9.0	5.0	5.0	5.0
Sodium chloride	10.0	10.0	10.5	10.0	8.0	8.0
Modifiers	1.5	0.02	-	2.0	2.0	2.0
Density [g/cm^3]	1.18	1.04	0.96	1.02	1.07	0.99
Oxygen balance [%]	+2.81	+2.03	+3.40	+0.75	+1.64	+1.44
Strength						
- Trauzl test [cm^3]	281	281	279	273	261	281
- ballistic mortar [% Hx]	62	82	63	69	75	72
Critical diameter [mm]	15	15	-	-	-	15
Detonation velocity [m/s]	2385	2622	2570	2458	2493	2000
in diameter charge [mm]	36	36	36	36	36	36
Transmission of detonatio [cm]	5	5	6	5	4	3
Volume of gas products [dm^3/kg]	836	793	833	847	872	870
Heat of explosion [kJ/kg]	3583	3549	3534	3490	3491	3553

In the 1980s and 1990s, the pneumatic loading of long shot-holes was used, among others, in coal mines: Staszic, Katowice, Śląsk and Zabrze-Bielszowice. After the access to the European Union, Poland implemented Directive 93/15/WE on placing on the market and supervision of explosives for civil uses, as well as the European harmonized standards related to it. The standard PN-EN 13631-1, “Explosives for civil uses – High explosives – Part 1: Requirements,” introduced more rigorous safety conditions concerning mechanical loading of explosives.

The standard sets the minimal shock sensitivity of explosives used for mechanical loading at 30 J. None of the nitroglycerine based explosives (dynamites, barbaryts) nor ammonium nitrate based explosives (ammonites, karbonits, metanits) fulfills this condition. Emulsion explosives are the only type of explosives that comply with the shock sensitivity level set by the standard. If an explosive is advertised by the producer as suitable for mechanical (including pneumatic) loading, it should meet sensitivity requirements, determined during tests according to the standards:

– PN – EN 13631-3 (friction): more than 160 J,
– PN – EN 13631-4 (shock): more than 30 J.

Table 11.4: Composition, detonation and thermodynamic parameters of metanits [3].

Component or parameter	Metanits				Special Metanits	
	1	D6G2	D8GH2	D12H	1H	2H
	Composition [%]					
Ammonium nitrate(V)	65.0	66.0	65.99	63.4	63.0	60.48
Nitroglycerine	3.6	-	1.0	0.8	-	6.0
Nitroglycol	2.4	3.0	4.0	3.2	5.0	4.0
Nitrocellulose	-	-	-	-	0.2	-
Trotyl	-	3.5	-	-	-	-
Fuels	7.0	3.5	2.5	5.0	4.7	2.3
Sodium chloride	22.0	24.0	22.0	26.0	25.0	27.0
Modifiers	-	-	1.51	1.5	2.3	1.22
Density [g/cm^3]	1.29	0.98	1.09	1.00	1.10	1.12
Oxygen balance [%]	+3.92	+5.20	+3.35	-	+0.41	+3.95
Strength						
- Trauzl test [cm^3]	223	204	228	209	223	194
- ballistic mortar						
[% Hx]	48	47	50	-	50	40
Critical diameter [mm]	-	-	-	-	13	15
Detonation velocity [m/s]	2249	2061	228	2168	2380	2201
in diameter charge [mm]	36	36	36	36	36	36
Transmission of detonation [cm]	10	3	4	-	6	5
Volume of gas products [dm^3/kg]	718	704	723	-	700	683
Heat of explosion [kJ/kg]	3026	2897	2982	-	2926	3025

Taking into account the above-mentioned standards, as well as several accidents which cannot be considered as necessarily related to the use of pneumatic loading, the State Mining Authority prohibited this method of charging shot-holes in the case of nitroesters explosives (i.e., dynamitesand barbaryts). They have a low shock sensitivity (ca 10 J).

Table 11.5: Composition, detonation and thermodynamic parameters of dynamites [3].

Component or parameter	Dynamites					
	1G6	3G4H	12G5H	14G5	15G5	16G5H
	Composition [%]					
Ammonium nitrate(V)	73.1	60.0	58.5	71.29	53.8	58.0
Sodium nitrate(V)	4.0	2.0	6.0	-	10.0	4.0
Nitroglicerine	7.8	18.6	5.0	13.2	16.8	16.2
Nitroglycol	5.2	12.4	20.0	8.8	11.2	10.8
Nitrocellulose	0.3	1.5	1.0	0.7	0.7	0.9
Trotyl	3.0	-	-	-	3.0	-
Fuels	6.0	1.0	7.0	6.0	4.2	5.6
Modifiers	0.6	4.5	3.5	0.01	0.3	3.6
Density [g/cm^3]	1.36	1.46	1.46	1.43	1.48	1.53
Oxygen balance [%]	+6.50	+9.88	+4.65	+6.61	+7.81	+5.53
Strength						
- Trauzl test [cm^3]	312	360	309	349	343	369
- ballistic mortar [% Hx]	83	80	90	94	78	78
Critical diameter [mm]	-	25	30	20	-	20
Detonation velocity [m/s]	2645	2244	2381	2587	4472	5715
in diameter charge [mm]	32	32	32	32	25	50
Transmission of detonation [cm]	5	8	5	7	3	9
Volume of gas products [dm^3/kg]	862	853	802	842	822	841
Heat of explosion [kJ/kg]	4022	4273	3942	3935	3273	3821

11.3.5 Barbaryts

Barbaryts are a group of dynamites that can be used in a coal dust and methane environment because of sodium chloride content. In spite of the fact that at present there are 3 barbaryts in the State Mining Authority register, they were not actually used in 2010 (as is shown in Table 11.1). Composition, as well as detonation and thermodynamic parameters of barbaryts used in the past few years in Polish coal mining, are shown in Table 11.6.

11.3.6 ANFOs

In the Polish mining industry, as elsewhere, ANFOs have been one of the most popular mining explosives for many years. In Polish research centres, especially at the Military University of Technology and Institute of Industrial Organic Chemistry in Warsaw, a number of investigations of the influence of various factors on detonation and practical parameters of ANFOs were carried out [26-39]. For a long time, ANFO was produced with agricultural ammonium nitrate (V). At present, in accordance with the relevant directive of the State Mining Authority, only porous ammonium nitrate is used in the production of ANFOs.

Detonation parameters of selected ANFOs used in the Polish mining industry are shown in Table 11.7.

Both production and loading of ANFO to shot-holes require the use of self-propelled units with mixer-loading equipment. The system used by the firm Orica Poland is shown in Figure 11.4.

Table 11.6: Composition, detonation and thermodynamic parameters of barbaryts [3].

Component or parameter	Barbaryts				
	1H	2	N1	N2	3H
	Composition [%]				
Ammonium nitrate(V)	34.0	34.5	44.5	36.09	36.0
Sodium nitrate(V)	-	4.5	-	-	5.0
Nitroglicerine	13.2	16.2	4.2	12.6	16.2
Nitroglycol	8.8	10.8	16.8	8.4	10.8
Nitrocellulose	0.4	1.0	0.4	0.4	1.0
Fuels	2.5	-	2.5	2.5	-
Sodium chloride	40.0	31.0	30.0	40.0	29.0
Modifiers	1.1	2.0	-	0.01	2.0
Density [g/cm^3]	1.48	1.50	1.44	1.44	1.44
Oxygen balance [%]	+3.12	+8.00	+4.33	+4.64	+8.04
Strength					
- Trauzl test [cm^3]	192	204	186	184	213
- ballistic mortar [% Hx]	43	78	54	38	42
Critical diameter [mm]	15	15	-	-	-
Detonation velocity [m/s]	2424	3020	2143	2192	2215
in diameter charge [mm]	32	32	32	32	32
Transmission of detonation [cm]	8	9	5	4	3
Volume of gas products [dm^3/kg]	506	568	648	522	586
Heat of explosion [kJ/kg]	2795	2397	3745	2712	2480

Table 11.7: Detonation and practical parameters of ANFOs [3].

ANFOs	Parameter				
	Density $[g/cm^3]$	Detonation velocity [m/s], in cartridge [mm]	Initiator	Strength	
				Trauzl test $[cm^3]$	Ballistic mortar [%]
2	0.829	1997 (70)p	Cartridges AS and DS, T-50, HT-14	198	57
6	0.738	1678 (60)p	Cartridges AS and DS, T-50, HT-14	351	80
7H	0.713	2415 (70)p	Cartridges AS and DS, HT-14, HT-75	204	63
10	0.738	2031 (60)p		330	65
8	0.739	2800 (60)p	Cartridges AS and DS, T-50, HT-14	348	68
Hanal 3	0.732	2973 (40)p	Cartridges AS, DS and emulsion explosive, HT-14 HT-75	336	70
Ammonex	0.712	1282 (50)p		259	71
Prillex 3	0.707	1925 (40)PCV		238	74
Prillit	0.809	1320 (60)p	Cartridges AS and DS, T-50, HT-14	274	67

11.3.7 Slurry Explosives

The investigation of the physicochemical properties and detonation parameters of slurry explosives was initiated in the middle of the 1970s at Military University of Technology in Warsaw in cooperation with the Main Mining Institute (GIG) in Katowice [40-51]. Two series of slurry explosives were studied: SBA (sensitized with aluminum dust) and SE (containing trotyl). Their parameters and compositions are presented in Tables 11.8 and 11.9.

Figure 11.4: Self-propelled unit with mixer-loading equipment.

Table 11.8: Composition and parameters of slurry blasting explosives [3].

Component or parameter	Slurry blasting explosives			
	HS-2	HS-3	HS-5	HS-8
	Composition [part by weight]			
Aluminum powder	8.0	8.0	9.0	8.0
Water	20.0	17.0	18.0	20.0
Ammonium nitrate(V)	67.0	58.0	55.4	55.0
Sodium nitrate(V)	-	5.0	5.7	10.0
Calcium nitrate(V)	-	4.0	4.5	-
Fuels	5,0	7.0	6.6	4.0
Thickener	0.5	1.0	0.7	2.4
Modifiers	-	-	0.1	1.25
Density [g/cm^3]	1.15 ÷ 1.25	1.10 ÷ 1.25	1.10 ÷ 1.25	1.10 ÷ 1.25
Consistence	semi-fluid	gel	semi-fluid	gel
Sensitiveness to plane [g]	0.5	0.5	0.2	1.2
Detonation velocity [m/s]	3500	3300	3500	4220
Strength, Trauzl test [ml]	252	280	315	266
Cartridge diameter [mm]	90	70, 90	loose	70, 90

Table 11.9: Composition and parameters of slurry explosives [3].

Component or parameter	Slurry explosive		
	HS-6	HS-T1	HST-2b
	Composition [part by weight]		
Water	20.0	16.0	12.0
Ammonium nitrate(V)	28.0	25.2	26.8
Sodium nitrate(V)	27.5	26.0	26.9
Calcium nitrate(V)	4.6	-	-
Fuels	5.0	2.0	3.0
Aluminium powder	12.0	-	-
Trotyl	5.0	30.0	30.0
Thickener	1.0	1.0	1.3
Modifier	-	0.5	-
Density [g/cm^3]	1.30	1.30	1.30 ÷ 1.35
Consistence	gel	semi-fluid	gel
Sensitiveness to plane [g] [g]	Detonator ZnT	HT-14	HT-14. T-75
Detonation velocity [m/s]	4000	4000	4470
Strength, Trauzl Test [ml]	320	102	148
Cartridge diameter [mm]	70. 90	bulk	80, 90, 140

In the first stage of investigations in 1976-1981, slurry explosives containing flaked aluminum as sensitizer were developed. The elaboration of hydroamonit HS-6, which can be considered a transitory explosive as it contains both aluminum dust and trotyl, was the next step. Later, in order to meet the mining industry demand for explosive material of higher density and also because of the high price of aluminum dust, slurry explosives sensitized with shell trotyl were developed. Slurry explosives were produced in two forms: cartridged and in bulk. The second type, produced by Zakłady Tworzyw Sztucznych (Plastic Materials Factory, or PRONIT) in Pionki, could be used for mechanical loading of the shot-holes, which was a revolutionary solution on the national scale. That is why two types of loaders were designed and produced: for SBA and SE.

Political and economic changes after 1989 stopped the construction of production lines for slurry explosives in PRONIT. In the 1990s, foreign companies entered into the Polish market and started to introduce more modern mining explosives − emulsion explosive materials.

However, for several years, the Spanish firm MAXAM Corp. AU, which has its branches in Poland, has been promoting slurry explosives. The company currently offers many types of slurry explosives. Some are listed in Table 11.10.

Table 11.10: Slurry explosives distributed by MAXAM Polska company [3].

Parameter	Slurry explosive name			
	Riogel® Troner	Riogel® Troner Plus	Rioflex® U	Rioflex® OC
Density [g/cm^3]	1.25	1.30	1.10 ÷ 1.30	1.10 ÷ 1.20
Detonation velocity [m/s]	5000	5500	4500 ÷ 5500	>3000
Heat of explosion [MJ/kg]	3.5	4.3	2.84	3.33
Temperature of explosion [K]	-	-	-	2608
Energy of explosion [kJ/kg]	-	-	-	934
Volume of gas products [l/kg]	886	886	1006	965
Initiator	Detonator, min. 0.6 g PETN content			Pentolite booster, min. 29 g
	Detonating fuse, 12 g/m		-	
Cartridge diameter [mm]	32 ÷ 100	32 ÷ 90	bulk	
Cartridge weight [g]	260 ÷ 6000	278 ÷ 4000		
Range of temperature [°C]	+10 ÷ +60		+5 ÷ +40	+5 ÷ +40

Figure 11.5: Self-propelled shooting carts – SWS MORA 14.

Slurry explosives listed in Table 11.10 can be used in opencast and non-coal and non-methane underground mines. The Rioflex® type explosive materials are produced and loaded into shot-holes by mixer-loading units. In the case of Rioflex® U explosive, which is designed mainly for underground use, blasting utility vehicle – e.g. SWS MORA 14 (Figure 11.5) and SWS MAX 17W – can be used. Conversely, the mixer-loading unit UMS-2000-6 (Figure 11.6) is designed for the production and loading of Rioflex® OC and Rioflex® QY slurry explosives.

Figure 11.6: Mixer-loading unit UMS-2000-6.

Employment of the aforementioned mixer-loading systems enables the adjustment of the density of slurry explosives, which means matching their detonation and thermochemical parameters to the local requirements of the blasting pattern.

11.3.8 Emulsion Explosives

The first investigations of emulsion explosives in Poland were carried out in 1986 [52]. They made it possible to obtain an emulsion explosive that received a positive opinion from the Experimental Mine Barbara, a part of the Main Mining Institute in Katowice. A prototype line for its production on a semi-technical scale was constructed in Plastic Materials Factory ERG in Bieruń. Further research was carried out at the beginning of the 21st century at The Military University of Technology in cooperation with Blastexpol company, which belonged to the German concern Westspreng at that time [53-62]. Table 11.11 shows the parameters of some emulsion explosives offered by Blastexpol company (taken over by the Spanish concern MAXAM several years ago).

Table 11.11: Emulsion explosives parameters [3].

Emulsion explosives	Parameter				
	Density [g/cm^3]	Detonation velocity [m/s], in cartridge [mm]	Initiator	Strength	
				Trauzl test [cm^3]	Ballistic mortar [% Hx]
Emulgit 22P	1.12	2698 (60)PCV	detonator ZnT, electric detonator, nonelectric detonator	154	-
Emulgit 42GP	1.19	4888 (65)		295	60
Emulgit 82GP	0.96 ÷ 1.16	4079 (40)		299	53
Emulgit 85P	1.12	2897 (60)PCV		199	-
Emulgit LWC ALAN1	1.101	3700 (32)		358	66
Emulgit LWC ALAN3	1.060	3900 (36)		325	68
Emulgit LWC AN20	1.105	3300 (32)		331	53
Emulgit TX	1.096	3706 (32)		355	53

At present, there are about 50 emulsion explosives in the State Mining Authority register. They are applied in opencast as well as in underground mines, in the both forms: cartriged and in bulk. Explosives sensitization during the mechanical loading of shot-holes is both cost-effective and maximally safe. Mixer-loading systems, such as UMS-2000-6 (Figure 11.6) and RP-T type (Figure 11.7), are used for this purpose.

System UMS-2000 is installed on a triaxial car underbody and is suitable not only for the production of emulsion explosives but also for ANFO and heavy-ANFO.

The RP-T type mixer-loading unit of dimensions 1100x1890x700 mm and capacity up to 600 kg was designed to work in special conditions of the Polkowice-Sieroszowice mines, where excavations are no more than 1.5 m high. The system was constructed on blasting utility vehicle of 1400 mm height. Its optimal efficiency comes to 50-70 kg/min.

Figure 11.6: Mixer-loading system UMS-2000.

Figure 11.7: Mixer loading unit RPT.

11.4 Summary

The mining industry is one of the most important sectors of the Polish economy. It makes possible the extraction of energetic raw materials, crushed aggregates and metal ores. The technical solutions used comply with the highest world standards. The newest blasting agents – emulsion explosives (including *Low Water Compositions*) and nonelectric and electronic detonators – are used, which guarantee effectiveness and safety of blasting works.

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