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Insensitive High-Performance Energetic Materials – Applied Research for Optimized Products

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Dedicated to Professor Dr. Hiltmar Schubert on the Occasion of his 70th Birthday

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1. Introduction

The Fraunhofer-Institut für Chemische Technologie (-Institute for Chemical Technology - ICT) in Pfinztal-Berghausen near Karlsruhe is a unique German research facility orientated to product development. Therefore, it uses all necessary processes in order to be able to represent and qualify the product requested; if necessary, it has to develop its own methods of investigation. The ICT was established to include many different processes in order to fulfil customer's demands settled either by the German Ministry of Defence or by the defence industry.

2. Research Tasks of the Fraunhofer ICT

The Fraunhofer ICT researches into two main areas and therefore is being divided into the main sections

- Defence research and
- Commercial application, e.g. polymer technology

Both sectors consider the product related solution to customer's requests to be central to their work and provide complete solutions. Polymers are the starting point of research for both sectors.

3. Defence Research

The defence research of the Fraunhofer ICT is dedicated to problems within the framework of chemical energetic materials and systems such as solid rocket propellants, gas generators, gun propellants, and high explosives.

The ICT was founded in 1959 with the aim to develop polymer compounds for modern rocket propellants not based on nitrocellulose and nitroglycerin. Initially, the only client has been the German Federal Ministry of Defence (BMVg). In time the ICT was the only research institute in Germany which expertly advised the BMVg and then also the relevant industry, and which pushed ahead with new developments and, on behalf of the BMVg and in agreement with them, represented the international cooperation in this sector. Accordingly, the ICT's research targets must be given high priority.

4. Research Orientation on Insensitive, High-Performance, Chemical Energetic Materials

The applied research carried out by the Fraunhofer ICT is being orientated as follows:

- customer's demand, i.e. in this case the BMVg and the defence industry
- self designed projects for future developments and international cooperation.

One of the current high priority tasks deals with insensitive environmentally conscious high performance chemical energetic materials.

The attention is focused equally on insensitiveness in relation to temperature and mechanical impact as well as on environmental consciousness with regard to reaction products and components. But the demand for high performance still remains as a most important priority.

These requirements seem to be a contradiction in terms—at least to a certain extent—and therefore have to be balanced and optimized.

Further requirements make research more difficult as sometimes they show contradictory characteristics. Examples are:

- simple, safe and environmentally conscious production processes
- mechanical and chemical stability
- long service life both in operation and on stock
- safe handling and storage
- weak signature and controllability after firing
- recovery potential and safe disposal.

For example the opposite requirements between weak signature and controllability after firing are typical. In order to get away from these apparently contradicting requirements, the development process must take into consideration:

- products are made of components
- the suitability of the specific properties requested of the products is checked
- the environmentally conscious disposal of products not required and the possible recovery or re-use of their components is considered.

5. Selection of Constituents and Components

Component selection contributes to a significant amount towards the final product's properties. Constituents of chemical energetic materials are mainly:

- polymeric binders
- energetic substances

- oxidizing agents
- energy-rich plasticizers
- stabilizers
- burning modifiers.

As mentioned, most of the known pre-products and components, respectively of the chemical energetic materials contradict in its overall quality the required final properties. An example of this are the components ammonium perchlorate (AP) and ammonium nitrate (AN) as oxidizing agents:

- AP increases performance and regulates the burning process but does not comply with the requirements for the environment and for the lack of signature.
- AN can be regarded as environmentally conscious and leads to a weak signature but has a lower performance than AP which is depending, e.g. on humidity and temperature.

In order to be able to use AN instead of AP and still achieve high performance, additional measures are required when selecting components:

- AN must be phase stabilized in order to be temperature independent
- High energy binders or plasticizers have to be used to its equal performance.

The conclusion of these considerations is: new, creative developments are necessary to balance out the disadvantages of the components. Replacing AP by AN requires, as mentioned, energy-rich binders or plasticizers in order to keep up performance, at the same time these improve processability and achieve the mechanical, chemical, ballistic properties of the energetic materials in the direction of the properties demanded.

Thus the Fraunhofer ICT is faced with the following tasks with regard to the development of components:

- to provide new energy-rich materials
- to manufacture known non-replaceable materials with the help of new processes to reach semi-technical standards and provide the industry with suitable technology
- to adapt the properties of already implemented materials by modifying parameters such as particle size; particle shape; density and molecule shape
- to characterize components and constituents.

6. Characterization of Products and Components

The aim of ICT's research work is to produce a product which is adapted to basic requirements whereby the production processes shall be improved, processability must be made simpler and products shall be less expensive. The product itself is produced using known or deduced components in already implemented processing techniques, or new production methods are developed which are more suited to the preliminary products as well as the requirements for the final products.

The properties of the product and its components, respectively are initially determined in routine work using

known testing methods. Examples of product qualification methods are:

- Chemical Analysis, such as
 - HCN determination
 - Wet analysis
 - AAS
 - Humidity determination
 - GC, MS
- Physical Properties, such as
 - Density
 - Structure characterization
 - Viscosity
 - Molecular weight
 - Sieve analysis
 - Surface characterization
- Thermal stability, such as
 - Deflagration
 - Weight loss
 - Vacuum stability
 - Out gassing
 - Aging
- Thermal analysis, i.e.
 - DSC, DTA, TGA, TMA, calorimetry
 - Explosion heat
 - Incineration heat
 - Thermodynamic calculations
- System characterization, including
 - Mechanical tests
 - Service life predictions
 - Component testing
 - Optical methods, such as microscopy, REM and high speed cinematography
 - Phase boundary behaviour
 - Contactless measuring techniques
- Sensitivity, determined by
 - Drop hammer
 - Friction sensitivity
 - Gap test
 - Bullet impact test.

However, in order to characterize the product better, new test procedures have to be developed. State-of-the-art technology is very useful in this case. A few methods are being listed as examples:

- Finite element (FE) analysis to determine the structure of systems containing chemical energetic materials
- Determination of specific material laws
- Model creation in the area of boundary surfaces of heterogeneous energetic materials
- Determination of the effect of environmental stress on energetic systems and derivation of simulation conditions
- Diagnostics and design of combustion processes
- Design, optimization and adaptation of measuring systems in order to be able to determine model laws such as:
 - Contact measurement of flame temperatures and mechanical properties of longitudinal stretching and transverse contraction

Particle Image Velocimetry (PIV)

Fast NIR spectroscopy

- Model considerations for the transition from deflagration to detonation
- Model considerations for pressure expansion and heat radiation of fuel air explosives.

7. New Pre-Products

The performance characteristics of energetic materials require new pre-products and production processes. This includes:

- the synthesis of energetic plasticizers such as DNDM, NENA, azido compounds
- the continuous synthesis of ADN and the production as spherical product with defined grain size
- synthesis and characterization of nitrogen-rich organic compounds
- production of explosives using supercritical fluids
- production of explosive components by crystallization out of solutions.

Initially, the syntheses worked out in the laboratory scale must be brought up to a semi-scale production in order that, if suited to their purposes, they can be produced by industry in an industrial scale.

8. Combustion of Chemical Energetic Materials as an Example of Applied Research

We are explaining an example for the combustion sector which shows how a project to set the specific properties of chemical energetic materials is structured over a period of five years. Emphasis is put on:

- ignition
- combustion
- reaction mechanisms
- internal ballistics
- detonation phenomena.

This type of research project is sub-divided into a number of smaller parts of the project and in brief, the project can be described as follows:

- evaluation and characterization of low sensitive propellants and gun propellants including ignition phenomena
- exhaust gas characterization
- incineration and pyrolysis studies, including reaction and decomposition kinetics; combustion mechanisms; laser initiation
- determination and qualifying investigations to optimize chemical energetic systems and to set their specific properties.

Typically, the following results are aimed for:

- modelling the ignition mechanism for low vulnerability ammunition (LOVA), knowledge about particle density as well as gas and particle temperatures during incineration

of ignition agent: provision of basis to develop new ignition systems

- minimization of exhaust gas signature and detectability in interaction with control systems
- clarification of incineration processes for the design of combustion processes:
 - identification and characterization of reaction patterns
 - influencing of reaction patterns
 - finding new catalysts or modifiers
- determination of LOVA properties
- characterization of internal ballistic properties and detonation behaviour.

9. Disposal of High Explosives

When designing new products, research must also include the environmentally conscious disposal possibilities. This involves two separate areas:

- disposal procedures with decomposition of binders by means of chemical processes such as:
 - solvolysis; hydrolysis; wet oxidation; recovery and re-use of energetic fillers;
 - recovery and processing of explosive components from plastic bonded explosives by extraction processes using solvents and supercritical fluids,
 - complete destruction of explosives and critical ingredients using chemical conversion such as sub- and supercritical hydrolysis or wet oxidation
- supportive work
 - safety investigations; reprocessing practicability, evolving of specific methods of analysis and special process analysis evaluation of degradation of residual products such as the removal of heavy metals using biological, thermal and electrochemical methods.

10. Conclusions

This point by point list of applied research work to achieve a qualified chemical energetic material shows the networking of different subject areas. Service life analyses without the evaluation of material properties are not possible. Amongst other things, they also affect the characteristics of stability simulations. In turn, FE calculations are also necessary for these characteristics as well as the calculations of strength, both however, depending on material properties.

Finally, products such as solid rocket propellants and gas generators, gun propellants including caseless ammunition and combustible cases, explosives and new types of chemical energetic materials can only be developed efficiently if, amongst other things, the above mentioned research work to gain their property spectrum with regard to requirements for use, service life, quality and disposal, take place simultaneously.

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