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Subject: The opponent report on the dissertation work by **Ing. Qi-Long Yan**

"Thermal Analysis of Polymer Bonded Explosives Based on Cyclic Nitramines".

The dissertation consists of enormous 190 pages sectioned in seven chapters each of which having its own reference parts (1 – 190, 2 – 64, 3 – 48, 4 - 103, 5 - 32, 6 – 132, 7 – 80; total over 500 references ! extraordinary !) missing, however, dissertant own publications shown separately in the extra leaflet 'summary'. The text is written clearly and the author shows a good overview of the concept of the current state of solution problematic, which in the recent years acquired a considerable amount of theoretical work and moreover experimental results revealing the leading position of the Pardubice University.

The work is written in English (which gives it the necessary internationalist character, which I do welcome in general), is suitably designed and straightforward readable though the text is somehow demandable to be fully understood in details as well as too all-embracing for a standard dissertation reading. Besides the conclusion and suggestions I am missing at the dissertation a Czech and English written end-

summary as well as discussion needed on the definition of dissertant personal opinion for the processes optimization, including estimates of the prospects for further development, which is not enough in the paragraph of suggestions. The list of symbols, abbreviations and figures is usually reserved at the ending position.

At my review opening I have to admit that I am not an expert in the entire field of explosives but I found some resemblance with my experience in the study of thermal properties of some extreme materials such polymeric composites and inherent micro- and nano- specificity of heat behavior and structural analysis. Theoretical basis of material's micro-behavior as the area of expertise stays thus factually analogous to various macroscopic resources. Thermal properties lays on the boundary between macro- and micro- perform thus the inherent heat behavior and transfer in micro-scale (i.e.: Volz S, Micro-scale and Nano-scale Heat Transfer. Springer, Heidelberg 2007) can vary from that in a classically assumed macro-scale (i.e.: H.S. Carslaw, J.C. Jeager. Heat Conduction in Solids. Cleradon, London 1959 or R. Černý, P. Rovaníková. Transport Processes. SponPress, London 2002) which is becoming dependent on other unique phenomena such as ballistic effects, etc., which may be of the further theoretical and numerical interest not yet appreciated in the sphere of behavioral understanding of explosives...

Measurement of thermal properties of explosives bears it specificity and tradition. Whatsoever, investigated materials habitually involve non-equilibrated states where the inherent heat treatment may affect the minute material properties. Most wanted procedure would be a joint determination of threefold data such as specific heat, c_p, thermal diffusivity, a, and thermal conductivity, λ, but mostly a single parameter is resolved and then the crucial problem of consequent data consistency from different sources must be solved. A thermometric procedure based on the convenient relaxation calorimetric method for measuring heat capacities is thus the pulse-heating technique which has not been included and is the question if beneficial at all. Heat pulse or laser flush method for the determination of diffusivity was well inspected by Slovak Kubičár (L. Kubičár. Pulse Methods of Measuring Basic Thermophysical Parameters. Elsevier, Amsterdam 1990) and commercially produced apparatuses by the German Netzsch instruments are available at different laser flush modes (LFA 427, 437 or 447) using various measuring set ups and sample

arrangements. This contact-less and non-destructive method is of a simple geometry, with easy sample preparation and wide range of temperature applicability, employing different (even very small) sample size of a range of conductivity (from isolators to conductors), certainly not yet accustomed to a sensitive case of explosives.

It is clear that the inherent field of reaction dynamics has many facets which may be dealt with from various angles by a range of authors and even under a differently biased gaze so that this dissertation is one of them: in a way exhaustive regarding kinetics on the other hand non-adequate but acceptable to recent trends. First I disagree with the dissertant term 'DSC' (Netzsch 200F3) which is just an adapted DTA. In contradiction to the true DSC, where differences between the two compensating heat fluxes are measured directly and unequivocally, in any pseudo-DSC, it is just technically assured that the magnitude of initial DTA-signal, ΔT, is calibrated to become a straight indication the of the process energetics. Than the standardized heat flow difference between the samples, dq is build on the averaged temperature difference ΔT, under a suitable normalization, i.e., $K\,\Delta T \approx \Delta(\mathrm{d}q/\mathrm{d}t)$, providing thus a better depiction for an instrument advertising and selling. Such a calibrating approach factually obscures the inherent nature of the 'as-received' heat-flow DSC (~ DTA) signal which, in contradiction to the true compensating DSC, requires *heat inertia* correction (often called rectification). It is in the same manner as in the case of an authentic DTA involving thus an extra relation $K\,\Delta T \approx C_s\,(\mathrm{d}\,\Delta T/\mathrm{d}t)$ dependent on sample heat capacity inertia C_s. This reflects to the derived kinetic analysis and if assumed neglectable thus should be proved and not mere ignored.

In dissertation it is convenient to cite the original papers and not just their secondary usage as well as I am missing reference on some basic books, which are traditionally included.

Let me present some further remarks and inquiries.

What is your interpretation and personal sense of thermal inertia which is shockingly known since the time of legendary Newton cooling law?

Would be a commercially available pulse technique (see above) applicable in the business of explosives?

Would be the micro-scale properties (see above) of your interest in the domain of explosives?

In conclusion I am satisfied with the presented text and its scientific and expert contents ranking the dissertation in the upper standard of comparable presentations within similar material specializations.

The work meets the requirements for a doctoral thesis specified both by the Ministry of Education, Sport and Young (MSMT) and the Pardubice University, and therefore recommending the work for an appropriate support and positive defense realization as well as the dissertant to be granted by PhD degree.

Best regards,

Yours

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The review of doctoral dissertation of ing. Qi-Long Yan
"Thermal Analysis of Polymer Bonded Explosives on Cyclic Nitramines "

The review subject is ing. Qi-Long Yan's doctoral dissertation entitled "Thermal Analysis of Polymer Bonded Explosives on Cyclic Nitramines" performed under prof. ing. Svatopluk Zeman's Dr Sc. guidance. The essential dissertation contains 187 pages of typescript, 38 tables, 5 diagrams and 97 figures included and is complemented with four appendices. It contains eight chapters with the following titles: Introduction, Literature Review, Materials, Experiments and Fundamental Theories, Thermophysical Propeties of Nitraamine Based PBXs, Decomposition Kinetics and Physical Models, Thermal Safety Predictions Based on Kinetic Triplets, Mitigation Effect of Polymers on Reactivity of Nitramines, Mutual Corrections among Sensitivities, Detonation and Kinetics Parameters, Conclusions and Sugestions. Bibliography, attached separately to each chapter (except the last one), contains in total 649 literature items (a few with author's participation), some items are cited in many chapters, put in cited order.

1. Assessment of topicality of the dissertation subject matter

Currently, research on composition modyfication of explosives used in military technology are oriented to receive the substance of the maximum detonation parameters and at the same time characterized by decreased sensitivity to mechanical stimulation. In addition to the sensitivity to friction and impact, taking into account the use of military explosives in combat, should also be consider the sensitivity to missile overshoot. One of the way to reduce the sensitivity to the aforementioned stimulus is using polymeric binders in explosive mixtures. These binders at the same time have technological significance since they allow to obtain high density. This approach was the basis for James and Smith to develop the first type of PBX explosives, which hundreds of this kind are currently known. As far as the amount of high explosives used in a PBX is limited mostly to the cyclic nitramines

(hexogen, octogen, CL -20), insomuch possible to use various types of polymers with differential physico-chemical properties. However, at the selection of polymers should also be taken into account the impact on the final product thermal stability, which, inter alia, could be determine by thermal analysis methods.

That is why the subject matter undertaken by this dissertation author is really up-to-date.

2. Characteristic and positive aspects of the dissertation

Reviewed work possessed experimental character. Chapter 1 contains five subsections. First by the author presented the insensitive high explosives characteristic, including a development of PBS. Next he described PBX based nitramines (RDX, HMX, BCHMX, CL-20, TNAZ and TATB), the first four of which are used in experiments. In the next section he presented general introduction to the thermal analysis and the thermal degradation of fluoropolymers (Viton A and Fluorel), polyisobutylene (PIB), styrene butadiene rubber (SBR) and nitryle-butadiene rubber (NBR). He described the thermal analysis of nitramines and their PBXs, *inter alia*, paying attention to the problem on polymers impact to activation energy distributions for nitramines decompositions. The logical structure of research topic was based on the literature review.

In chapter 2 author of the dissertation quite exactly characterized nitramines used in researches – RDX, HMX, BCHMX, CL-20 and BCHMX/CL-20 co-crystals as well as polymer matrices (marked as: Formex P1, Semtex 10, Viton A and Fluorel), which, in various amounts (9 to 15) were used in the tested PBXs.

Then he described applied research experimental methods: Differential Scanning Microscopy, Thermogravimetric Analysis, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, X-ray Difraction and Bomb Calorymetry. He described methods of activation energy determination: Kissinger method and isoconversional method. The last subsection concerns issues associated with molecular dynamic simulations and contains decomposition mechanisms by ReaxFF and gasses diffusion coefficients.

In the next chapter ing. Qi-Long Yan investigated by non-isothermal TG and DSC techniques the mass loss and heat flow properties of PBXs. Additionally he made TG experiments for BCHMX and BCHMX/CL-20 co-crystal and he described their impact sensitivity. Based on the results, inter alia, he found the heat of decomposition of the

nitramine based PBXs was significantly lower than that of pure nitramine except RDX based explosives. The fluoropolymers with different chain structure had almost the same impact on the planar molecules RDX and HMX, but they have different impact on crowded molecules BCHMX and ε-CL-20. The thermal decomposition of α-CL-20 and PBXs ε-CL-20-C4 and rs-ε-CL-20-C4 has a two-step mechanism.

In the next chapter the thermal decomposition kinetics and physical models of nitramine based PBXs were determinate by non iso-thermal TG data. The results of the experiments allowed to conclude that PBXs including β-HMX, ε-CL-20 and BCHMX was very sensitive to temperature gradient. The PBXs including Viton A underwent one-step decomposition. However BCHMX, α-CL-20 and PBXs on this base, including other binder than Viton underwent two- or three-step decomposition. The binders contain plasticizers (Formex, C4, Semtex) had significant impact on the activation energy distribution of nitramines, and the initial autocatalysis impact was inhibited or weakened. It appears that the isokinetic temperature of nitramine based PBXs were higher than that of nitric esters and azido compounds, but lower than that of aromatic nitrocompounds.

In the next section ing. Qi-Long Yan was using established kinetics triplets to predict the constant decomposition rate, temperature profiles, the critical radius for thermal explosion and isotherms under a low temperature. On the basis of obtain results he compared the impact of polymer matrices on the thermal hazard properties BCHMX, RDX and CL-20. He concluded that threshold cookoff time until loss functionality at 82 °C for hexogen PBXs containing matrices FM and C4 was much shorter (<500 days) than for PBXs including CL-20 and BCHMX. Unlike simulated isothermal curves RDX-FM and RDX-C4 were better than RDX-SE in storage safety at a certain temperature. He also considered, that the impact energy depends not only on kinetic parameter, but also on the probality of hot-spots generation and also on the temperature of hot spots, which plays dominant role for explosives (CL-20 and BCHMX) which decompose in solid stage.

In chapter 6 the molecular simulations of RDX, BCHMX and CL-20 and their containing PBXs were performed in terms of their gas production under fast heating and gas diffusion in a temperature of 508 K. Ing. Qi-Long Yan compared simulation results with the thermal decomposition physical model.

He stated, inter alia, that there were three possible mechanisms of decomposition cyclic nitramines: homolitic cleavage of an N-N bond accompanied by the elimination

of the -NO_2 group, HONO elimination and ring-opening reaction. Under fast heating of 300 $K.ps^{-1}$, the disintegration of N-NO_2 is the initial step for BCHMX pyrolysis, which is followed by the HONO/HNO eliminations and the HNO elimination is due to nitro-nitrite rearrangement. However, for hydrocarbon polymer based materials, the HONO/HNO elimination and collapse of ring structure occured earlier while there was a little impact on the decay time of N-NO_2.

In the penultimate chapter the author has studied the correlation among sensitivity (impact and friction), detonation velocity and thermodynamic parameters.

He reached out particularly interesting conclusions for correlation searches between the velocity of detonation and other PBXs tesed parameters. The higher detonation velocities corresponds to lower heat bealt-up time and lower critical temperature, although those last correlation is not applicable for RDX based materials. For explosives that decompose in liquid states, the detonation velocity increase with the activation energy,

The work ends a chapter containing conclusions and suggestions. Collected conclusions have been presented in the previous chapters. Whereas suggestions concern the proposal for the future works, which should have both theoretical and utilitarian importance.

Reviewed dissertation is an original work concerning thermal analysis of PBX based on cyclic nitramines issues. Submitted dissertation proved the author's big knowledge in the field of problems connected with explosives thermal analysis. The author performed a very large number of experiments. All presented considerations and conclusions show a careful and multilateral approach to investigated issues. The author indicated that he was able to choose some proper research methods and in the right way interpreted the experiments results. The experiments results presented in this work have been positively verified in the form of articles published in journals with high Impact Factors.

3. Critical remarks

The author could not avoid some errors, although the dissertation was carefully prepared in editorial respect and characterized by a high level of the content.

- In my opinion in table 1-1, relative to some typical formulations of RDX based PBX-s, the presentation of Compositions B is not needed. In the same table explosives C -4 appears twice.

- In chapter 2 two figures have the same number 2.3 (pg. 30 and 36), whereas in section 4 there are missing figures 4.8 and 4.9.
- Most editorial objections I have to cited references. Some references are repeated (for example 14 and 16, 68 and 72, 75 and 76, 77 and 160 – Chapter 1). List of publications authors is not unified – initials are placed before or after the names. Tittles of articles are written in lowercase or uppercase. Abbreviations for journal titles are repeatedly recorded incorrectly - for examples lack of full stops. Writing order of a year's issue and a year for the journals is not maintained.

All mentioned above remarks, have editorial character, do not lower the value of dissertation content and do not diminish the author's scientific achievements.

4. Conclusion

In this connection I put forward a proposal of ing. Qi-Long Yans admission to a public defense of doctoral thesis.

Review on Ph.D. thesis entitled

"Thermal Analysis of Polymer Bonded Explosives Based on Cyclic Nitramines"

Written by Eng. Qi-Long Yan
from Institute of Energetic Materials, Faculty of Chemical Technology,
in University of Pardubice,

General Comments

Presented Ph.D. thesis mainly deals with thermal analysis of cyclic nitramine based PBXs. It contains 212 pages (including list of references and appendix). The dissertation work is composed of the following parts: declaration, acknowledgement, nomenclature, summary, contents, introduction, 8 chapters with references and appendix. In this project, the thermal behaviors of cyclic nitramines based PBXs were investigated by means of TG and DSC, XRD, FTIR and SEM techniques, as well as molecular dynamic (MD) simulations. The kinetic parameters and physical models were determined based on TGA data using master plots and combined kinetic analysis methods, where the overlapped peaks were properly separated before kinetic evaluations. The obtained kinetic triplets were used to predict the storage lives and constant rate decomposition temperature profiles of involved PBXs. Based on comparative investigations and correlations, the inherent mechanisms for the effects of the polymer binders on decomposition kinetics and mechanical sensitivities were determined and supported by the molecular dynamic simulations. The thesis in general is well organized and the English expression is very clear. The followings are the specified comments on the chapters:

1) In the introduction part, the author introduced the history of the nitramine based PBXs and the current advances in the thermal analysis of these materials. It shows that a number of explosive fillers and polymers have been used to form a variety of PBXs, where only a part of them (e.g. TNT, RDX, HMX and TATB based PBXs) have been widely investigated and have practical applications. However, the data for thermal decomposition kinetics of CL-20 and BCHMX are not available in the literature, and hence it is essential to carry out this work. There seems no obvious error in this chapter.

2) In the experimental and theoretical part, the authors stated the state-to-art techniques that used for kinetic evaluation. The materials and the preparation methods are well described. The testing techniques such as SEM, DSC, TGA and XRD are simply introduced, which is great for readers with different level of knowledge. The molecular dynamic simulation method especially the principles of ReaxFF code are introduced in detail.

3) In the following Chapter, the mass loss and heat flow properties of involved nitramine based PBXs were investigated by non-isothermal TG-DTG and DSC techniques. Some sound conclusions are made. It would be great if the author continue to work on the gaseous products of the involved materials by MS or FTIR techniques.

4) On the basis of TGA data, the thermal decomposition kinetics and physical models of nitramine based PBXs were determined by both Combined Kinetic Analysis and Master Plot methods. These two methods yield very close kinetic parameters and almost equivalent results of physical models. The comparisons of the physical models with the ideal models are impressive, which provides physical insights on how the polymers affect the decomposition processes of cyclic nitramines.

5) Upon determination of kinetic triplets, the constant rate decomposition temperature profiles, the critical radius for thermal explosion and isotherms under a low temperature were predicted. Then, the effect of polymer matrices on the thermal hazard properties of RDX, BCHMX and CL-20 are compared and clarified.

6) The molecular dynamic simulations of RDX, BCHMX and CL-20 and their PBXs were performed in terms of their gas production under fast heating and gas diffusion under a temperature of 508 K. The simulation results are compared with the thermal decomposition physical models and the impact sensitivity. The connections among the initial decomposition pathways under fast heating, impact sensitivity, physical models of decomposition, and diffusion coefficients of gaseous products in polymers bases have been established. The main problem might be there too many correlations among those materials, which may confuse the readers. It may be better to only present the correlations that are quite reliable and meaningful such as the critical temperature with the sensitivities.

7) In conclusion and suggestion part, the authors summarized the results of the whole thesis, including the heat flow properties, kinetic parameters, reaction models, thermal stability as well as decomposition pathways under fast heating for the involved materials. PBXs based on CL-20 and Fluoropolymer matrices seem to be interesting for future practical applications. Opinion of the author on how the polymers desensitize the nitramines seems applausive with quite promising proofs from the molecular dynamic simulations.

Question to be answered:

1) Which kind of PBXs is probably the used in military application in the near future? What preconditions should be fulfilled?

2) Have you got any information about the mechanical properties of involved materials, which is considered very important for their practical application?

Conclusion Remarks

Eng. Qi-Long Yan proved his scientific capacity to elaborate Ph.D. thesis. Based on extensive literature survey, he has applied adequate experimental techniques and theoretical methods to solve target problems. Meanwhile, the conclusions made through relevant experiments and calculations are comprehensive and impressive. Therefore, it can be a fundamental scientific contribution in the field of thermal analysis and safety of energetic materials. The reviewer is sure to conclude that Eng. Qi-Long Yan is eligible to make his final PhD defense.

On the 8th of April, 2015, in Beijing

Signature:

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