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Review of the doctoral dissertation entitled

"Achieving Balanced Cocrystals of Energetic Materials *via* Coagglomeration and Their Applications"

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Developing novel energetic materials that combine high detonation parameters with high stability and resistance to accidental detonation initiation is costly, challenging, and time-consuming. For that reason, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and its higher methylene-nitramine homolog, 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) are still the best high explosives that have been widely used in weapon systems since the World War II, even in the most technologically advanced countries. Their advantages (acceptable sensitivity to initiating stimuli, high thermal resistance, and chemical stability, as well as high density and detonation parameters) cause them to be mass-produced and used in various explosive mixtures with TNT, waxes, polymers, metal powders, as well as in gun and rocket propellants. The most critical disadvantage of RDX, HMX, and other recently developed highly energetic nitramines like HNIW (Cl-20) or bicyclo-HMX (BCHMX) is that they are too sensitive to initiating stimuli for current requirements.

Relatively recently, in 2010, a promising method of improving nitramines' functional properties was proposed: their co-crystallization, especially among themselves or with other explosive compounds, to reduce their favorable detonation parameters as little as possible. Due to the short research period, nitramines' co-crystallization methods described in the available literature have often been tested only on a laboratory scale. They can still be improved, which is why I believe that the subject matter undertaken by the author of the dissertation is up-to-date and, in addition to the scientific and cognitive aspects, has potential utilitarian significance.

The layout and structure of the dissertation

The reviewed dissertation has 255 pages and is divided into 5 chapters. The author refers to 158 articles, studies, reports, and textbooks in the introductory part. The structure of the dissertation is classic, i.e., it contains the purpose and scope of the work, a literature overview (Chapter 1), a description of the used materials and test methods (Chapter 2), followed by an extensive presentation (139 pages) of own research with an insightful discussion of the obtained results (Chapter 3), and a description of undertaken attempts to applicate the developed energetic materials as ingredients of gun powders and solid rocket propellants (Chapter 4). In Chapter 5, the author summarized his research on the co-crystallization and co-agglomeration of explosive compounds and formulated essential conclusions regarding their properties and possible applications in modern and high-energy compositions.

Substantive assessment of the dissertation

The Introduction includes a research background, an overview of energetic materials' cocrystal preparation methods, and a characterization of their structures and physicochemical and explosive properties. This part ends with a discussion of the most significant technological challenges in preparing energetic materials' cocrystals and a preliminary selection of research allowing the development of a universal strategy for their preparation. I assess that this is a complete and in-depth analysis of literature data, taken mainly from research papers published after 2010. Still, it contains many linguistic errors, making it difficult to understand.

The author begins the dissertation section on research methodology by describing the equipment used to determine the structure, morphology, purity, and characterization of the produced cocrystals and co-agglomerates, i.e., powder X-ray diffraction, high-performance liquid chromatography, field emission scanning electron spectroscopy, Raman and FTIR spectroscopy, thermal analyses, elemental analysis, bomb calorimetry, test methods for determining sensitivity to external stimuli as well as computer programs for calculating detonation parameters. The multitude of measurement techniques proves the PhD student's versatile skills in selecting appropriate tools and the ability to use them. However, the author should devote more space to discussing the measurement uncertainties with which the results were obtained. I did not find any information in the text about (i) the methods of determining measurement uncertainties, (ii) the procedure for verifying the correct operation of the measuring devices used, and (iii) the number of averaged test results and the repeatability of the results.

The main part of the dissertation (Chapter 3) is divided into five subchapters, the layout of which is identical. The first one is devoted to the study of co-agglomerated crystals of nitramines (RDX, HMX, CL-20, BCHMX) with 1,3-di- and 1,3,5-triamino-2,4,6,-trinitrobenzene. The second one presents the results of testing co-agglomerated crystals of CL-20 and BCHMX. The third one describes the results of tests on co-agglomerated crystals of hexanitrostilbene (HNS) and hexanitroazobenzene (HNAB) with the tested nitramines. In the fourth subchapter, the author presents the research results on the structure and properties of composites containing polyaniline and nitramine crystals obtained via the co-agglomeration method. In contrast, the last subchapter describes research on co-agglomerated crystals of cyclic nitramines with bis(tetrazoloamino)tetrazine (BTATz). Each subsection contains detailed research results on the structure and morphology, physicochemical and explosive properties of the obtained materials, and an exhaustive discussion of the obtained results. The only thing missing is descriptions of how the tested cocrystals and co-agglomerated crystals were prepared, isolated from reaction mixtures, and purified. The conclusions are correct and sufficiently justified by experimental research results. The influence of intermolecular interactions in the crystal lattice of the cocrystals and co-agglomerated crystals on thermochemical properties, sensitivity, and detonation parameters is presented in great detail. In each case, the author explains the mechanism (structural conditions, intermolecular forces, binding energy) behind the observed relationship to generalize the findings to a broader group of materials and phenomena. Comprehensive analysis, generalizability, and the resulting predictive nature of research are the essence of the scientific method and thus constitute a high value of this part of the dissertation. It is worth emphasizing that each part of Chapter 3 has been previously published or is in the process of publication in five renowned scientific journals with a chemical and materials engineering profile. M.Sc. V. B. Patil is the first co-author of these papers. Thus, demanding editors and reviewers appreciated the innovative nature of his research and the high quality of their presentation.

In Chapter 4, the author presents the research results of HMX/BCHMX and CL20/BCMX co-agglomerated crystals (CACs) as potential ingredients of composite rocket propellants and components of non-primary explosive detonators, respectively. Additionally, he attempted to use RDX/BCMX CACs in gun powders. The obtained test results were correctly interpreted and confirmed that the tested co-agglomerates BCMX with HMX and BCMX with RDX could slightly improve some operational properties of rocket and gun propellants. Unfortunately, the English language used in this chapter contains many mistakes, making it impossible to understand the full extent of the work the author wished to describe unambiguously.

My most significant complaints are the omission in Chapter 3 of the description of methods for preparing co-agglomerated crystals and a blatant lack of care in editing Chapters 1, 4, and 5, which manifests in numerous linguistic and substantive errors and unnecessary repetitions. Here are the most striking examples:

Page 25 "*In C-NO_2 linkages needs more energy to decompose and detonate than the N-NO2 linkages [154], it needs taken care while selecting coformers all these facts to obtain better performing EECCs for military weapons as well as civil applications.*"

Page 26 "*So, overall, it directs our interest cocrystallization is attractive strategy to produce decreased sensitivities which helps to avoid accidental detonation with maintaining the detonation properties.*"

Page 198 "*In the past, HMX was employed in double base propellant window bombs with different percentages of 20 to 60%.*" and "*However, because of polymorphic transition, impacts from the combustion surface, and weakens agglomeration during the process, it occasionally appears to be incompatible with coagglomeration with AP.*"

Page 199 "*Both coformers shown the polymorphic stability after undergoing coagglomeration, with HMX tranfered into α to β polymorphic state after interaction with the BCHMX whereas in physical mixture it remains same. It indicates there will interaction between he both coformers in the form of weak hydrogen and von der waals kinds of interactions, which further caused changes in the polymoprhic changes in HMX*"

Page 202 "*This enhancement in specific surface area plays a very important role in propellant coarse*"; "*There is Slight surface damage is visible in images due to cutting of samples into cubes took extra care done with sharp cutting table knife, still it's obvious in micro level they can be seen.*"

Page 206 "*The ignition temperatures of all samples measured by peters apparatus at room temperature (20.1 C) observed results shown in Table 4.1.6.*"

Page 226 "*Internal ballistics deals with the movement of the projectile in the gun barrel due to the pressure of the powder gases produced by the combustion of the ammunition.*"

Page 228 "*The measurements in the ballistic bomb determined the specific energy of the powder f and the metalum of the powder α, which are important input values for the intra-ballistic calculation.*"

Concluding the review, I would like to ask the author why he expected to find a relationship between the logarithm of the linear burning rate and the hardness of the rocket propellant samples (Fig. 4.1.14). Is there any theoretical/physical justification for such a relationship?

Summary and conclusion

The doctoral dissertation proves that M.Sc. Veerabhadragouda B. Patil has acquired the ability to conduct a multi-threaded research process. He confirmed his research hypotheses and demonstrated that obtaining cocrystals and co-agglomerated crystals of explosive compounds with a lower sensitivity to initiating stimuli than neat high-energy ingredients, which can be applied in gun powders and solid rocket propellants, is possible. His work has aspects of scientific novelty and meets other formal and – in the main part of the dissertation – also linguistic requirements for a doctoral thesis. Moreover, V. B. Patil's scientific achievements are documented by co-authorship of as many as 8 scientific articles in excellent journals with a very high impact factor and presentations at eight international conferences. The linguistic shortcomings I have pointed out lower the overall assessment of the dissertation, but they do not have a decisive impact on the conclusion: I recommend the dissertation for public defence.

Stanisław Cudziło