Characterization and optimalization of electrostatic discharge (ESD) sensitiveness of potassium 4,6-dinitrobenzofuroxane

Martin Zahálka†, Vojtěch Pelikán, Robert Matyáš

Institute of Energetic Materials, University of Pardubice, Pardubice, Czech Republic

†martin.zahalka@student.upce.cz

Abstract:

It was found that the electrostatic discharge sensitivity of potassium 4,6-dinitrobenzofuroxane (KDNBF) have risky value of minimal initiation energy (MIE) value. The lowest measured energy was within the range of 30 μJ. Additions of conductive graphite to KDNBF didn't changed MIE level significantly. Efforts has been made to find way how the graphite addition influence ESD sensitiveness in form of threshold initiation level and probability of sample initiation. It was found that the MIE values remains still but conductive admixtures influenced the probabilities of initiation. The highest measured energy without initiation of sample changed with the content of graphite. Influence of ultrasonic homogenizers on MIE levels was studied.

Keywords: ESD; KDNBF; potassium; 4,6-dinitrobenzofuroxane.

1 Introduction

Due to the efforts of replacing heavy metals containing primary explosives new compounds are studied. As one of the promising compounds potassium 4,6-dinitrobenzofuroxane seems to be. This explosive compound is known since the end of 19th century when Drost described its preparation for the first time[1]. Also described its explosive properties. For long time this compound was left sideways. In 1983 articles about KDNBF was published by Spear, Norris and Read[2-4]. They described preparation, structure and explosives properties for KDNBF and for some other interesting analogs (Na; Ag; Ba). Comprehensive work about KDNBF and many other complex salts of 4,6-dinitrobenzofuroxane with various cations worked Sinditskii[5]. This work contains important thermochemical values and burning rates of all prepared complex salts.

In recent years new compounds were tested as potential replacement for heavy metals containing primary explosives (i.e. lead styphnate, lead azide). For this purpose compounds containing silver, copper, potassium, sodium as a cation were tested. As new compounds appeared there was also need to characterize them well. Especially if they were categorized as a primary explosives. Basic safety characterization involves impact sensitivity (IS) and friction sensitivity (FS). These characteristics were usually well known. There was also the third not less important characteristic especially for primary explosives - sensitivity to electrostatic discharge (ESD). Values of ESD sensitivity were tested and published for secondary explosives, propellants and pyrotechnics also. But in case of primary explosives ESD characteristics there is lack of literature sources. This was one of the main reason why we chose KDNBF as a sample for testing - for this compound only two sources of ESD data were found. Mehilal[6] stated sensitivity to spark discharge at level of 26 mJ. Jones[7] stated spark sensitivity of KDNBF to 6 mJ with further information – *lowest energy available from ESD tester*.

KDNBF was presented previously as a very sensitive compound to electrostatic discharge stimuli. Also was presented response of ESD sensitivity of KDNBF according to particle size and response to addition of graphite as conductive material[8]. Graphite was chosen as commonly used conductive additive and its commercial accessibility. Alternative carbon-based conductive additives are carbon nanotubes (CNT), graphene nanoplates (GNP), polyvinyl alcohol (PVA). These additives were usually used to enhance ESD characteristics of pyrotechnic mixtures and propellants[9,10]. In case of primary explosives articles were preferably focused on studying lead styphnate and lead azide ESD sensitiveness[11-13].

2 Experimental

2.1 Preparation of KDNBF

Samples of KDNBF were prepared as it is accessible in literature sources via two step synthesis from 4,6-dinitrobenzofuroxane. First step was preparation of sodium 4,6-dinitrobenzofuroxane (NaDNBF) complex salt by using $NaHCO_3$. Sodium hydrogen carbonate was diluted in distilled water at temperature ~50 °C then 4,6-dinitrobenzofuroxane was dropwise added in form of acetonic solution. Further mixing in constant temperature was kept for approx.. 60 minutes.

In next step precipitated NaDNBF was not separated from solution and was converted to KDNBF directly in aqueous solution. Various potassium salts were used – KCl, KNO_3, $KHCO_3$. Aqueous solution of potassium salt was added dropwise at constant rate. After mixing for approx. 60 minutes solution was cooled down to ambient temperature and precipitated KDNBF was separated by filtration. Product was dried freely and collected as a orange powder. Yield up to 85 %.

Preparations of KDNBF samples were assisted by three ways of homogenization – regular laboratory magnetic stirrer, ultrasonic bath Elmasonic ELMA S 30 H and ultrasonic homogenizer Bandelin Sonopuls HD3200 with MS 73 probe.

2.2 ESD measurements of KDNBF-graphite mixtures

Measurements of ESD sensitivity were conducted at ESD2008A from OZM Research, Czech Republic. Graphite samples were supplied by GK Graphite Týn, Czech Republic. Used graphite was labelled as highly conductive graphite COND 2 995. Mixtures of KDNBF with graphite were prepared in dry circumstances by adding 2.5, 5, 7.5 and 12.5 % of graphite COND 2 995 and manually mixed for approx.. 5 minutes.

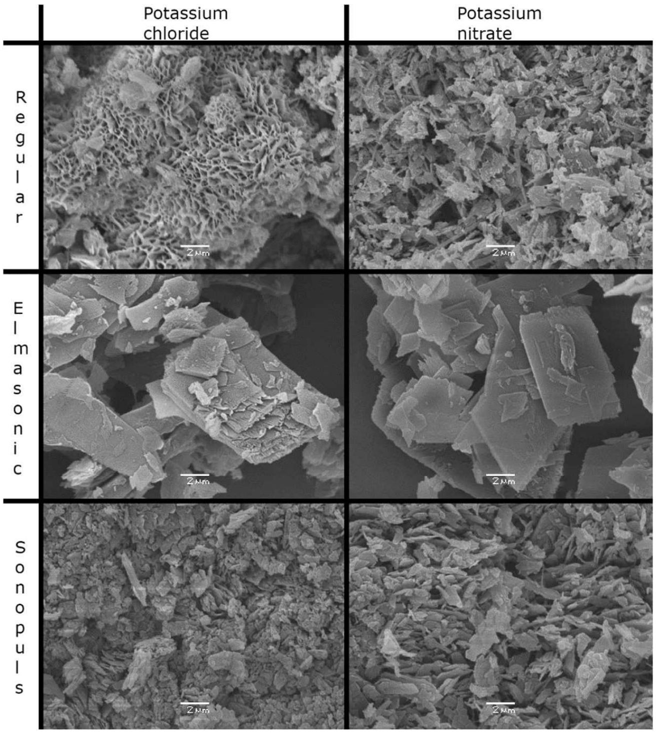

Figure 1: Scanning electron microscope picture of KDNBF samples

3 Results

Table 1: Minimal initiation energies for KDNBF samples

Mixing method	ESD sensitiveness [μJ]	
	KCl	KNO_3
Regular	176	35
Elmasonic	40	56
Bandelin	60	68

Table 2: Results of residual anions concentrations

Mixing method	Residual anion concentration [mg/l]	
	Cl^-	NO_3^-
Regular	415	9.3
Elmasonic	18	0
Bandelin	20	18.6

4 Discussion

Results of KDNBF samples analysis (Table 2) have shown that addition of non-conductive material (i.e. potassium chloride) and its concentration could influence sensitivity to ESD in the same manner as addition of conductive material (graphite). This finding could be important for understanding true response of compounds to ESD stimuli. It shows that the additions of conductive graphite didn't influence ESD sensitiveness as was thought. For better understanding of this problematic and more detailed description further experiments are necessary.

Used test method was not able to describe the samples well and it indicated difficulty to describe ESD characteristics of explosive compounds in full scale. By simple determining of MIE values and safe energy (E_{min}) we were able to only set limits of hazards. But we are still unable to describe what happens between these two values. This could open new field of view and gives us opportunity to focus our efforts on ESD characteristics and their understanding.

From data presented in graph (Fig. 2) standard deviations and coefficient of variation were calculated. Values of coefficient of variation was determined within range from 15 to 30 %. Its value did not correlated with any of variable (energy, graphite content or probability) and it was considered as a characteristic of testing method and device itself.

5 Conclusion

Electrostatic discharge stimuli response of explosive compound characterization by values of minimal initiation energy could become insufficient. In the case of KDNBF response to ESD stimuli it was stated about its high sensitiveness and even the addition of high content of conductive material did not lead to change. When measuring method was revised further experiments showed different rates in initiation probabilities of samples. Values of initiation probability was influenced significantly by graphite content around 5 % and more. In contents around 7.5 % the graphite addition also started to change values of initiation energies. It is evident that contents of graphite lower than 5 % have no influence on ESD sensitiveness of KDNBF.

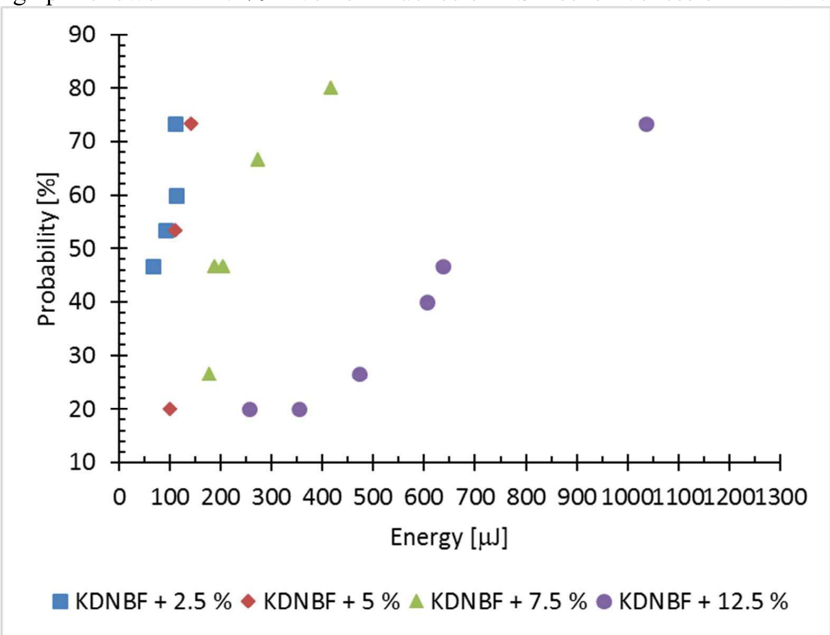

Figure 2: Graph of initiation possibility vs. energy.

References

[1] P. Drost, *Justus Liebigs Annalen der Chemie*, 307, p. 49-69, **1899.**

[2] R.W. Read, R.J. Spear, W.P. Norris, Synthesis of 4,6-Dinitrobenzofurazan, A New Electron-Deficient Aromatic, *Aust. J. Chem.*, 36, p.1227-1237, **1983.**

[3] R.J. Spear, W.P. Norris, R.W. Read, 4,6-Dinitrobenzofuroxan An Important Explosive Intermediate, DoD-MRL, technical note MRL-TN-470, Melbourne, Australia, **1983.**

[4] R.J. Spear, W.P. Norris, Structure and Properties of the Potassium Hydroxidedinitrobenzofuroxan Adduct (KDNBF) and Related Explosive Salts, *Propellants,_Explosives,_Pyrotechnics*, 8, p. 85-88, **1983.**

[5] V.P. Sinditskii, V.Yu. Egorshev, V.V. Serushkin, A.V. Mergolin, H.W. Dong, Study on Combustion of Metal-Derivates of 4,6-Dinitrobenzofuroxan, *Theory and Practice of Energetic Materials*, IV, p. 69-77, **2001.**

[6] Mehilal, A. K. Sikder, S. Pawar and N. Sikder, Synthesis, characterization, thermal and explosive properties of 4,6-dinitrobenzofuroxan salts, *J. Hazard. Mater.*, 90, p. 221–227, **2002.**

[7] D. E. G. Jones, P. D. Lightfoot, R. C. Fouchard, Q. Kwok, A.-M. Turcotte and W. Ridley, Hazard characterization of KDNBF using a variety of different techniques, *Thermochimica Acta*, 384, p. 57-69, **2002.**

[8] M. Zahálka, V. Pelikán, R. Matyáš, ESD sensitiveness of Meisenheimer complexes of 4,6-dinitrobenzofuroxane, *The 6th International Symposium on Energetic Materials and their Application ISEM2017*, Sendai, Japan, 6th-10th November, **2017.**

[9] K. H. Poper, E. S. Collins, M. L. Pantoya, M. A. Daniels, Controling the electrostatic discharge ingnition sensitivity of composite energetic materials using carbon nanotube additives, *Journal of Electrostatics*, 72, p. 428-432, **2014.**

[10] E. S. Collins, B. R. Skelton, M. L. Pantoya, F. Irin, M. J. Green, M. A. Daniels, Ignition sensitivity and electrical conductivity of an aluminum fluoropolymer reactive material with carbon nanofillers, *Combustion and flame*, 162, p. 1417-1421, **2015.**

[11] M. Zhou, Z. Li, Z. Zhou, T. Zhang, B. Wu, L. Yang, J. Zhang, Antistatic modification of lead styphnate and lead azide for surfactant applications, *Propellants, Explosives, Pyrotechnics*, 38, p. 569-576, **2013.**

[12] Z-M. Li, M-R. Zhou, T-L. Zhang, J-G. Zhang, L. Yang, Z-N. Zhou, The facile synthesis of graphene nanoplatelet-lead styphnate composites and their depressed electrostatic hazards, *Journals of Materials Chemistry A*, **2013.**

[13] S. E. Napier, G. W. C. Taylor, patent GB1093531, **1948.**