Letter

Influence of graphite content on ESD sensitivenes in potassium 4,6-dinitrobenzofuroxane (KDNBF)

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Received: November 7, 2017 Accepted: September 20, 2018

Abstract

In last decades there were strong efforts to replace heavy metals containing primary explosives. As one of these possible replacement potassium 4,6-dinitrobenzofuroxane (KDNBF) was considered but this compound's sensitivity was not well characterised. Effort was focused especially on electrostatic discharge (ESD) sensitivity mesurements of Meisenheimer aducts of metal ions with DNBF and primarily with potassium ion. Potassium aduct (KDNBF) has an application in explosive industry as the component of initiators and primers. In preliminary measurements of prepared KDNBF were obtained ESD minimal iniciation energy (MIE) down to levels of μJ. In comparission to practicaly used primmary explosives MIE values i.e. lead azide (dextrinated; 6–12 mJ) or lead styphnate (rehydrated; 40–100 μJ). From these number it is obvioud that electrostatic spark represents high risk in KDNBF safety. Known additive used to suppress ESD risks is graphite its effect was examinated depending on its content and quality.

Keywords: KDNBF, ESD, primary explosive, graphite

1. Introduction

Since the first use of explosives there was also demand for their safe initiation. In case of black powder the flame was sufficient but different situation was in case of secondary explosives. For this purpose heavy metal compounds were primary used. As a first wide used primary explosive mercury fulminate took a place. Today lead azide reaplaced it as a cheaper and reliable alternative. In recent years there were efforts to replace these compounds with their heavy metal-free analogs. As a replacing metals potassium, copper or silver were mainly examined. Today these metals are used in form of inorganic salts (mainly azides) or as a carbon-based compounds. Amongst these carbon-based compounds belongs various tetrazols, organic azides or metal salts of nitrocompounds (DDNP, KDNBF, KDNP)[1),2)]. For this work, combination of potassium ion with 4,6-dinitrobenzofuroxane (KDNBF) was chosen. It was due to its high burning rate the most important characteristic for possible primary explosives.

First preparation of 4,6-dinitrobenzofuroxane complexes and their explosive character were described at the end of 19th century by Drost[3)]. Described were preparations with metals of I and II.A group (Na, K, Li, Cs, Rb, Mg, Ca, Sr, Ba), with some of transition metals (Cu, Co, Ni, Fe, Cr, Cd, Pb) and with ammonia and hydrazine. Results of Sindistki's work with complexes of 4,6-dinitrobenzofuroxane and metal ions reports that potassium complex have the highest rate of fire. Compounds that reported lower burning rates than KDNBF had unsatisfing initiating abilities[4)]. This fact is very important for primary explosives due to needs of fast deflagration-to-detonation transition which is besides dependent on rate of gaseous products evolution[1)].

Preparation of 4,6-dinitrobenzofuroxane complexes are conducted in aqueous enviroment with mild heating. Usualy in two step synthesis via sodium salt. Final compounds precipitate from solution in high yield as a powder with orange to orange-brown color. Product yielded from one step synthesis doesn't meet requirements for handling and safety rules – low gravimetric density and charge accumulation. Two step synthesis product have better handling and application characteristics – finer particles, better handling

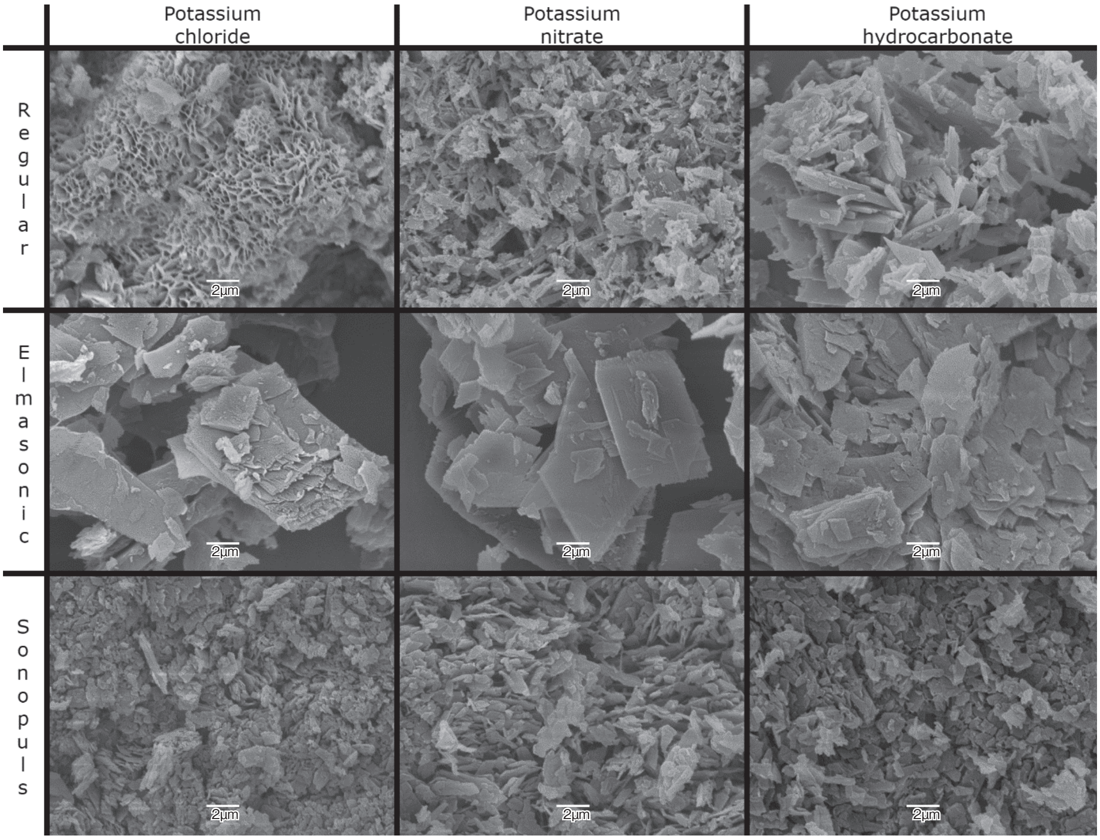

Figure 1 SEM images (6000x) of KDNBF samples.

(flowability), higher gravimentric density[4)]. As for a primary explosive KDNBF handling safety values are important:

- Impact sensitivity (H_{50})[1] – 35 cm/2 kg weight[6),7)]
- Friction sensitivity[2] – 3,8 kg[6),7)]
- ESD sensitivity – from 6[8)] to 26[7)] mJ

[1] RDX 35 cm, Tetryl 85 cm, TNT 110 cm

[2] RDX 12 kg, Tetryl and TNT 32,4 kg

2. Experimental

2.1 Potassium complex preparation

Preparation of potassium complex were conducted under various circumstances to evaluate their influence on final product. Tested samples were prepared with use of different potassium salt (KCl, KNO_3, $KHCO_3$) and with different homogenization methods. First series of samples was prepared with regular mechanical mixing. Other two series were prepared with use of ultrasound homogenizers – ELMA Elmasonic S30H and Bandelin Sonopuls HD3200 (with probe MS73 and mixing container). Samples were analyzed for mixing method influence on size and shape of particles with electron microscopy (SEM; see Figure 1). All samples were prepared as follows.

In approximately 150 ml baker was prepared solution of $NaHCO_3$ (1,86 g; 22 mmol) in 25 ml of demi-water and heated on water bath to 50–60 °C. Properly mixed and then acetonic solution of 5 g (22 mmol) of 4,6-dinitrobenzofuroxane in 50 ml of acetone was added dropwise. After 1 hour aqueous solution of potassium salt was added (22 mmol of KCl, KNO_3 or $KHCO_3$ in approx. 25 ml of demi-water). Product started to precipitate and was mixed for further 1 hour. Then was separated by filtration, slightly washed with demi-water and then dried freely in laboratory. Product was obtained as orange powder in yield from 75 to 85 %.

2.2 ESD measurements

For all ESD measurements device ESD 2008A supplied by OZM Research, CZECH REPUBLIC was used. Measuring was performed under damped mode with 1 mm spark gap.

2.2.1 Graphite mixtures

For mixture preparation graphite COND 2 995 was chosen as a one produced especialy for enhancing of ESD safety in various products. Mixtures were prepared under dry (simple mechanical mixing) and wet (a suspension of KDNBF with graphite in hexan) conditions. Dry mixtures were prepared by adding graphite content into a sample of potassium 4,6-dinitrobenzofuroxane. Wet mixture was prepared by ultrasound homogenizing sample of potassium 4,6-dinitrobenzofuroxane in hexane and then adding graphite. Mixtures of non-ultrasounded potassium 4,6-dinitrobenzofuroxane were prepared with 1, 2.5, 5, 7.5 and 12.5 % graphite content. Then mixtures of ultrasouded potassium 4,6-dinitrobenzofuroxane samples with 2.5 and 5 % of graphite were compared.

3. Results

Results shown that energies given by other authors who measured ESD sensiteveness (from 6 to 26 mJ) are not sufficient for correct safety handling with potassium 4,6-

Table 1 Influence of graphite content in KDNBF samples.

Graphite content [%]	Non-ultrasounded		Bandelin sonopuls	
	Voltage [kV]	MIE [μJ]	Voltage [kV]	MIE [μJ]
0	6	20	6	69
2.5 % (dry)	5	37	6	97
5 % (dry)	3, 5	45	10	153
2.5 % (wet)	–	–	5	61
5 % (wet)	–	–	8, 5	90

dinitrobenzofuroxane. In this work values of minimal initiation energies (MIE) were determined to levels starting at 20 μJ. So low value of MIE brings high risk of accident. To supress ESD hazards graphite as additive is usualy mixed in. For this purposes special conductive graphite (COND 2 995) was chosen and mixed into the samples. Results were summarized in Table 1.

From values summarized in Table 1 the influence of graphite content cannot be clearly verified. Only small shift in values of MIE is obvious. The addition of conductive material into the mixture resulted in the lower minimal "strike through" voltage. This voltage droped from approximately 5 kV for samples without graphite to 3 kV in case of mixture with 5 % of graphite content. Decreasing trend of minimal "strike through" voltage was verified by measurements of samples with 7.5 and 12.5 % of graphite content. Voltages for these samples were 2.5 kV respectively 1.5 kV.

4. Conclusion

- ESD characteristics of raw KDNBF may be enhanced by using ultrasound homogenizers to control particle shapes and size.
- Contents of graphite COND 2 995 lower than 2.5 % doesn't influence ESD sensitivenes of KDNBF samples. Higher content of graphite addition may lead to higher accident risk due to lowering minimal initiation voltage.
- Influence of graphite on ESD characteristics depends on mixture homogenization and preparation method. Using of wet mixing conditions resulted in worse ESD energy levels and were not investigated further than 2.5 and 5 % of grafite admixture (see Table 1).
- Graphite itself probably doesn't influence value of MIE significantly but shifts probability of initiation on given energy.

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