

Investigation of electrostatic discharge sensitiveness of 4,6-dinitrobenzofuroxane complexes (with selected monovalent metals)

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Abstract

Previously was found that potassium 4,6-dinitrobenzofuroxane complexes have a high sensitiveness to electrostatic discharge stimuli and MIE level was measured about 30 μJ . This lead our work to focus also on the other 4,6-dinitrobenzofuroxane complexes with metal monovalent ions. From range of monovalent metal ions beside of potassium, complexes with sodium, rubidium, cesium and silver were prepared and investigated. Combinations with the selected admixtures (i.e. graphite, carbon black, copper powder, etc.) were also investigated on the influence of the ESD sensitiveness. Obtained results indicate high sensitivity of the all tested complexes. For alkali metal ions MIE levels shows the trend to rise with increasing molecular weight of metal ions. Nevertheless, obtained MIE levels are very low up to 250 μJ . These levels were not affected by using any of the selected admixtures. On the other hand compacting of samples (resp. rising bulk density) resulted in certain cases at considerable increase of minimum initiation energies. Especially in mixtures with graphite compacting resulted in values of minimal initiation energies exceeding levels of 500 μJ . In contrary with the all tested metal ions the silver complex was found to be relatively insensitive to ESD stimuli. Measured MIE of the silver analog is 10 mJ. The influence of the complex cation and used admixtures on the overall ESD sensitiveness is discussed.

Keyword: metal complexes; 4,6-dinitrobenzofuroxane; potassium; electrostatic discharge; sensitiveness

1 Introduction

Researching of new energetic materials is focused on “green” compounds today. That means minimalizing of toxicity of these compounds in production environment and to minimize the effect on the environment when they are used. In this effort usually heavy metals ions in compounds are replaced with less hazardous ones. Ions which fit these requirement are from alkali metals group (lithium, sodium, potassium), alkaline earth metals (calcium, magnesium, strontium) or some of transition metals (silver, copper, iron). The most appropriate candidate is potassium ion in these compounds. This trend resulted in possibility of using potassium ion in combination with 4,6-dinitrobenzofuroxane as possible substitute for used primary explosives. Despite the fact of the long existence of knowledge about potassium 4,6-dinitrobenzofuroxane[1] its explosive properties are still not well described. The best available source of information about 4,6-dinitrobenzofuroxane is work of Sinditskii[2]. The work summarize preparation, chemical and thermochemical properties of most of 4,6-dinitrobenzofuroxane adducts with various metal ions. Still for electrostatic discharge data only two sources are available with not enough information contained[3][4]. In many cases electrostatic discharge is the cause of accidents and still this stimuli is quite underated in its importance. It was found in previous work that electrostatic sensitivity of potassium 4,6-

dinitrobenzofuroxane is at risky levels and minimal initiation energy (MIE) could be at levels about 30 μJ . Even content of special electrically conductive graphite as admixture does not result in apparent change of risk levels[5].

This paper was focused on study of complexes with monovalent metal ions and influence of contained ion on electrostatic discharge sensitivity of 4,6-dinitrobenzofuroxane metal adducts. Cesium, rubidium and silver was chosen and prepared as promising analogs of potassium adduct. Beside testing of influence of contained metal ion was also tested how conductive admixtures will influence the electrostatic discharge sensitivity of given compounds. In this work with mentioned COND 2 995 another two graphite types were used – CR 2 995 and EG 290. Beside these admixtures carbon black, synthetic graphite and copper powder were tested. Influence of sample loading density was investigated as possible factor to influence MIE levels.

2 Experimental

All samples were prepared in laboratory with standard laboratory method using corresponding nitrate of metal ion. Chemicals for preparation were obtained from local suppliers. Conductive admixtures were supplied by Graphite Týn, Czech Republic (COND 2 995, CR 2 995, EG 290), IMERYS Graphite and Carbon, Switzerland (ENSACO 250P carbon black powder) and copper powder was used as 99 % pure with particles size <75 μm supplied by Aldrich. Important characteristic properties of used graphite were summarized in Table 1.

Table 1. Properties of used graphite admixtures

Graphite	Carbon cont. [%]	Ash [%]	Particle size [μm]		
			D10	D50	D90
COND 2 995	99,5	<0,5	-	3,5-5,5	-
CR 2 995	99,5	<0,5	-	3,5-5,5	-
EG 290	90-94	<10	<1,5	<3	<8

All samples were tested with ESD tester ESD 2008A from OZM Research, CZ. Device was set to fixed electrode mode with 1 mm spark gap and measurements were conducted in damped discharge mode. Discharge energy was evaluated by Winspark 2.5 software (OZM Research, CZ) using the V-A technique.

2.1 Preparation of 4,6-dinitrobenzofuroxane adducts

Samples of measured metallic ions were prepared with direct two step method. In case of sodium 4,6-dinitrobenzofuroxane only first step is needed.

First step is preparation of sodium 4,6-dinitrobenzofuroxane solution. In distilled water sodium bicarbonate was diluted at 50 °C. Then acetic solution of 4,6-dinitrobenzofuroxane was added dropwise and solution was mixed at constant temperature for 30 minutes.

Second step of preparation is addition of corresponding metal nitrate. To the prepared solution of sodium 4,6-dinitrobenzofuroxane was dropwise added metal nitrate (CsNO_3 , RbNO_3 or AgNO_3) in the form of aqueous solution. This took around 60 minutes and then the solution was stirred for further 30 minutes at constant temperature of 50 °C.

During adding of metal nitrate solution precipitation of product occurs. After proper stirring period solution was let to cool to ambient temperature and product was separated by filtration. Obtained precipitate was washed with diethyl ether twice to remove remaining moisture then dried freely at laboratory temperature. Product is obtained in the form of red to orange powder. Raw sodium 4,6-dinitrobenzofuroxane precipitated in the first step could be

separated by filtration the brine and washing with diethyl ether. After drying at laboratory temperature the red color powder is obtained.

2.2 Preparation of samples and ESD measurement

Raw samples of 4,6-dinitrobenzofuroxane adducts for ESD measurement were used as were obtained from preparation. Samples with conducting admixtures were prepared in the approx. 1 g batches. Conductive admixtures were added in amount of 10 wt.% and then mixed manually for approximately 10 minutes.

For the ESD testing the powder sample was placed into the measurement container without any compacting. Every sample was tested 15 times separately for GO/NO-GO result and then initiation probability was calculated.

Compacted samples were prepared by compacting of powder sample in measuring container approximately to three times higher density in comparison with loose sample.

3 Results

All values of minimal breakthrough voltages (MSV) of the spark gap and minimal initiation energies (MIE) were summarized in Table 2 and Table 3.

Table 2. Results of measurement for non-compacted samples

Sample	MSV [kV]	MIE [μ J]
KDNBF	6	54
KDNBF + 10 % COND	1,2	42
KDNBF + 10 % EG	3,2	55
KDNBF + 10 % CR	3,6	66
KDNBF + 10 % ENSACO	0,8	13 (9)
KDNBF + 10 pwd. Cu	6	38
RbDNBF	5,6	67
RbDNBF + 10 % COND	1,2	271
RbDNBF + 10 % EG	1,6	83
RbDNBF + 10 % CR	1,2	65
CsDNBF	5,6	111
CsDNBF + 10 % COND	2	90
CsDNBF + 10 % EG	1,6	32
CsDNBF + 10 % CR	1,6	27
AgDNBF	2,8	10 [mJ]

Table 3. Results of measurement for compacted samples

Sample	MSV [kV]	MIE [μ J]
KDNBF	6	45
KDNBF + 10 % EG	10	357
KDNBF + 10 % CR	10	412
KDNBF + 10 % pwd. Cu	8	-

Results shows that high sensitivity to electrostatic discharge is characteristic to adducts of 4,6-dinitrobenzofuroxane with ions of monovalent alkaline metals. In case of silver monovalent ion it is evident that sensitivity changed drastically (in range of approx. three orders) from level of approximately 13 μ J to 10 mJ. In any case of addition of conductive admixture to the studied materials causing no big change in the ESD sensitiveness.

For evaluation of influence of particle size and shape on sensitivity of adducts all prepared samples were analyzed with scanning electron microscopy (SEM). Resulting pictures compare chosen particles. Size, shape and even surface is different for every of tested adduct (Figure 1).

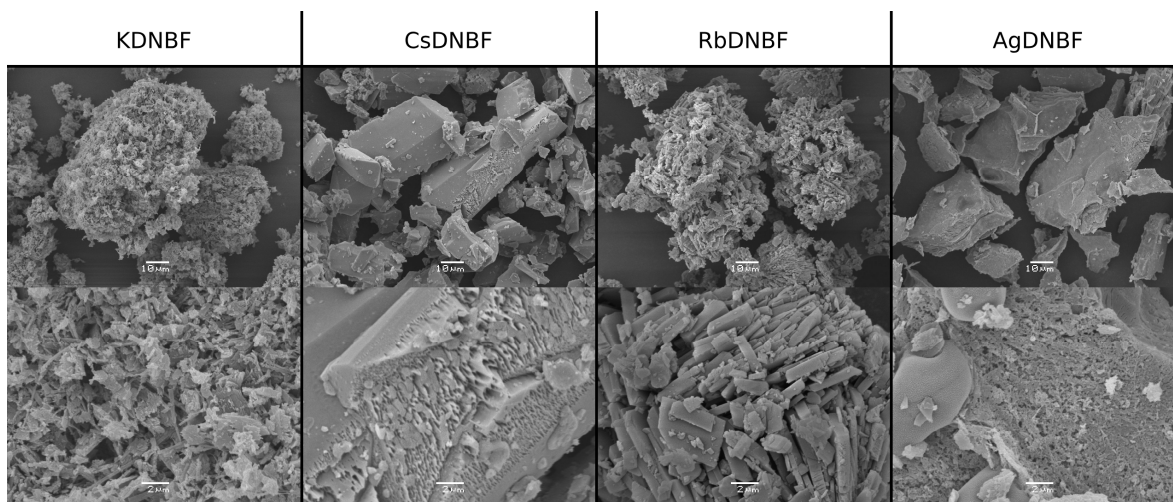


Figure 1. SEM pictures of 4,6-dinitrobenzofuroxane adducts with metal ions

4 Discussion

Difference between silver ion and alkaline metal ions may suggest that high sensitivity of adducts of 4,6-dinitrobenzofuroxane is caused by character of bond between metal ion and 4,6-dinitrobenzofuroxane.

Energy levels measured for raw samples and mixtures with conductive materials shows that in case of 4,6-dinitrobenzofuroxane adducts that are highly sensitive to electrostatic discharge it is not recommended to add conductive material. As the unwanted effect of the admixture of the conductive materials is the lowering of the value of minimum breakthrough voltage (MSV) thus make material more vulnerable to initiation with electrostatic discharge. This was observed regardless the admixture type and nature.

Acknowledgement

Funding of this work was provided from University of Pardubice grant number SGS_2019_002.

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