Full Paper

Alkali-Dinitramide Salts Part 2: Oxidizers for Special Pyrotechnic Applications

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Abstract

Ammonium dinitramide is planned to be a substitute for commonly used oxidizers in rocket motor compositions. Different teams worldwide have already synthesized alkali salts of dinitramide and several times it was used as an oxidizer for pyrotechnic compositions containing boron as a reducing agent. In this paper the results of a systematic investigation to characterize the pyrotechnic redox systems titanium/potassium dinitramide and titanium/cesium dinitramide are presented and the data are compared. The heats of reaction as well as the burning rates of the redox system titanium/potassium dinitramide. Both systems show a moderate sensitivity to friction and electrostatic discharges. However the sensitivity of mixtures of both redox systems shows a very high sensitivity to impact. These sensitivities are in the range of pure HMX or pentaerythritol tetranitrate.

Keywords: Potassium Dinitramide, Cesium Dinitramide, Pyrotechnics, Oxidizer

1 Introduction

In the framework of research activities with energetic molecules based on a cubane structure, Botarro was the first who synthesized cubane dinitramide, a forerunner molecule of ammonium dinitramide (ADN). Botarro and Schmitt protected the synthesis of ADN during the time from 1993 till 1994 by three patents [1, 2, 3]. After the publication of these patents, it was discovered that in the former Soviet Union, different energetic systems based on ADN were already in service for a long time. Ammonium dinitramide is known as an interesting new oxidizer in rocket propellants and a revolutionary substitute for the oxidizer ammonium perchlorate. As main advantages a high combustion rate, a high specific impulse, less smoke production and low price are mentioned [4]. At the moment, only the corresponding ammonium salt is commercially available. But it was also realized long ago, that there are some other dinitramide salts that show a remarkable potential as oxidizer. For example alkali dinitramides were used as additional oxidizers in propellants and pyrotechnics. In 1998 V. A. Tartakosky et al. were publishing a work on the subject Synthesis of Dinitramide Salts [5]. Therein, some physicochemical data of different dinitramide salts including potassium dinitramide and cesium dinitramide were listed.

In the same year, the results of an investigation on the subject of metal dinitramides with the title New Novel Oxidants for the Preparation of Boron Based Flare Compositions were published by J. R. Dawe et al. [6]. For their investigation they used sodium and potassium dinitramide as oxidizers. After the synthesis the handling safety data of both oxidizers were determined. Additionally, the thermal behavior of these oxidizers was investigated using Differential Scanning Calorimetry (DSC) und Thermal Gravimetric Analysis (TGA). The pyrotechnic mixtures produced for this investigation contained in one part no binder and in the other part HTPB was used as binder. The reaction velocities and the resulting emission spectra were measured. In a first step the aim of our investigation was to acquire the needed know-how for the synthesis of dinitramide salts. Secondly, we would produce pyrotechnic compositions containing one of various alkali dinitramide salts as an oxidizer and titanium as reducing agent. These compositions should be characterized with respect to their combustion properties and their handling safety behavior.

2 Substances

2.1 Titanium Metal Powder Type E (Ti_E)

2.1.1 Technical Specifications

Table 1 shows the specification of the used titanium powder.

2.1.2 Particle Size Distribution/Active Surface

Particle size distribution (Figure 1) and mean particle size were measured using the Malvern method. Based on this data, the specific surface could be calculated.



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Table 1. Specification of the used titanium powder.

Auto Ignition Temperature	>315 °C
Combustion Rate	$40 \pm 10 \text{ s/}50 \text{ cm}$
Particle Size	99.9% < 45 μm
Average Particle Size	$3\pm1\mu m$
Apparent Density	Approx. 1.4 g/cm
Gain on Ignition	$56.0 \pm 1.5\%$
Ti total	$93.5\pm1.0\%$
Ti active	$84 \pm 2.5\%$
Ca	max. 1%
Ν	max. 1%
Si	max. 2.5%



Particle Diameter [µm]

Figure 1. Particle size distribution of titanium metal powder.

The reducing agent shows the following particle properties:

Mean particle size (measured according to the method of Blaine): $3.0 \ \mu m$

Mean particle size (measured according to the Malvern method): $19.0 \ \mu m$

Specific surface according to the BET method: $3.2 \text{ m}^2/\text{g}$ Specific surface according to the Malvern method: $1.2 \text{ m}^2/\text{g}$

2.1.3 Particle Shape of the Titanium Powder

The major part of the particles in Figure 2 shows a small diameter, there are only a few particles with a diameter of 15 to 20 μ m. The preferred spherical shape of particles nearly does not occur.

2.1.4 Thermal Behavior

The Thermo Gravimetric Analysis (TGA) of titanium E (Figure 3) shows an increase of weight beginning at 400 °C



Figure 2. Picture of the used titanium metal powder, recorded with SEM.



Figure 3. DTA/TGA plot of titanium powder type E.

and ending at approx. 959 °C. This effect is caused on the exothermal oxidation of titanium to titanium oxide. The reaction is confirmed with the DTA curve which shows an exothermal peak at a temperature maximum of 750 °C.

2.2 Potassium Dinitramide (KDN)

2.2.1 Synthesis

Potassium dinitramide (KDN) was synthesized using an acid/base reaction in water with equimolar quantities of potassium hydroxide and ammonium dinitramide. After the end of the formation of ammonia gas the solution was cooled down. Thereby, the crystallization of KDN took place. Afterwards the KDN was purified by re-crystallization in methanol.

$$\begin{array}{l} \mathrm{NH}_{4}^{+-}\mathrm{N}(\mathrm{NO}_{2})_{2} \xrightarrow{\mathrm{KOH}/\mathrm{H}_{2}\mathrm{O}} \mathrm{K}^{+-}\mathrm{N}(\mathrm{NO}_{2})_{2} \\ + \mathrm{NH}_{3}(\uparrow) + \mathrm{H}_{2}\mathrm{O} \end{array}$$
(1)

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2.2.2 Particle Size Distribution

Particle size was measured according to the method of Malvern. The mean particle diameter of the used KDN was 256 μ m and the particle size distribution shows approximately a Gaussian shape (Figure 4).



Figure 4. Particle size distribution of potassium dinitramide.

2.2.3 Thermal Behavior

The DSC and TGA plot (Figure 5) show an exothermal reaction at a temperature of about 100 °C coupled with a weight loss. XRD measurements show no solid-solid phase transition of KDN (Figure 6). At approximately 130 °C this reaction is evolving in a strong endothermal reaction. This process must be the melting of KDN. The foregoing weak exothermal process cannot be explained at the moment. The strong exothermal reaction in the range of 220-230 °C is to be assigned to the decomposition of KDN and the endothermal reaction at 335 °C to the melting of the accrued KNO₃ (literature value: 339 °C).



Figure 5. DSC/TG plot of potassium dinitramide.



Muster KDN Original und nach TG

Figure 6. XRD plot of not thermal treated KDN and of KDN heated up to 393 K.

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2.2.4 Handling Safety

The handling safety data in Table 2 were acquired according to the methods described in the Swiss AOP-7 specifications.

2.3 Cesium Dinitramide (CsDN)

2.3.1 Synthesis

The synthesis was performed analogously to the procedure described in 2.2.1.

$$NH_{4}^{+-}N(NO_{2})_{2} \xrightarrow{CSOH/H_{2}O} Cs^{+-}N(NO_{2})_{2} + NH_{3}(\uparrow) + H_{2}O$$
(2)

2.3.2 Particle Size Distribution

Particle size was also measured according to the method of Malvern. Mean particle diameter of the used CsDN was 79 μ m; the particle size distribution shows approximately a Gaussian shape (Figure 7).

2.3.3 Thermal Behavior

The thermal behavior of cesium dinitramide was investigated by Differential Scanning Calorimetry (DSC) (Figure 8). In contrast to the DSC and TGA plots of KDN, the plots of CsDN show no exothermal process in the temperature range around 100 °C. However an endothermal process takes place at a temperature of 90 °C (peak maximum) which indicates the melting of CsDN. The strong exothermal reaction in the temperature range from 220 to 225 °C is to be assigned to the decomposition of CsDN and the endothermal reaction at 330 °C to the melting of the accrued CsNO₃ (data published in literature: 414 °C).



Particle Diameter [µm]

Figure 7. Particle size distribution of the synthesized cesium dinitramide.



Figure 8. DSC/TG plot of cesium dinitramide.

2.3.4 Handling Safety

Also for CsDN the handling safety data (Table 3) were acquired according to the methods described in the Swiss AOP-7 specifications.

Table 2.	Handling	safety	data	of	potassium	dinitra	mide
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Substance	Sensitivity to Impact [J]	Sensitivity to Friction [N]	Sensitivity to electrostatic discharge [mJ]
Potassium dinitramide	>20	>360	>5.6

Table 3.	Handling	safety	data	of	cesium	dinitr	amide.
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Substance	Sensitivity to Impact [J]	Sensitivity to Friction [N]	Sensitivity to electrostatic discharge [mJ]
Cesium dinitramide	>20	>360	>5.6

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3 Investigated Compositions

3.1 Titanium/Potassium Dinitramide

The mixing of the titanium powder and the potassium dinitramide was done in a Turbula mixing apparatus. Afterwards the nitrocellulose (NC), dissolved in an acetone/ether mixture was added and the dough containing still a small amount of solvent was granulated using a sieve. Compositions of these mixtures are given in Table 4.

Table 4. Compositions of the redox system Ti/KDN.

Substance	Co	Composition [weight %]										
Ti	10	20	30	35	36.5*	40	45	50	60	70	80	90
KDN	89	79	69	64	62.5	59	54	49	39	29	19	9
NC	1	1	1	1	1	1	1	1	1	1	1	1

Possible reaction equations for this redox reaction:

$$7 \text{ Ti} + 4 \text{ KN}_3\text{O} \rightarrow 7 \text{ TiO}_2 + 2 \text{ K}_2\text{O} + 6 \text{ N}_2$$
 (1)*

 $4 \text{ Ti} + 2 \text{ KN}_3\text{O}_4 \rightarrow 4 \text{ TiO}_2 + 2 \text{ K} + 3 \text{ N}_2$ (2)**

 $Ti + 4 KN_3O_4 \rightarrow TiO_2 + 2 K_2O + 12 NO_x$ (3)***

- * According to reaction equation (1) the mixture with balanced oxygen content contains 36.5% titanium.
- ** According to this reaction equation the mixture with balanced oxygen content contains 39.8% titanium.
- *** According to this reaction equation the mixture with balanced oxygen content contains 7.6% titanium.

In this investigation it was assumed that the pyrotechnic reaction runs according to reaction Equation (1). X-Ray Diffraction Analysis (XDR) of the accrued reaction products could verify this assumption.

3.2 Titanium/Cesium Dinitramide

Compositions of this redox system (Table 5) with a positive and a negative oxygen balance as well as the composition with a neutral oxygen balance were prepared the same way as described in Section 3.1.

Possible reaction equations for this redox reaction:

$$7 \text{ Ti} + 4 \text{ CsN}_3\text{O}_4 \rightarrow 2 \text{ TiO}_2 + 2 \text{ Cs}_2\text{O} + 6 \text{ N}_2$$
 (4)*

 $4 \text{ Ti} + 2 \text{ CsN}_3\text{O}_4 \rightarrow 4 \text{ TiO}_2 + 2 \text{ Cs} + 3 \text{ N}_2$ (5)**

$$Ti + 4 CsN_3O_4 \rightarrow TiO_2 + 2 Cs_2O + 12 NO_x$$
 (6)***

Table 6. Combustion velocity of the redox systems Ti/KDN.

Table 5. Mixtures of the redox system Ti/CsDN.

Substance	Comp	Composition [weight %]										
Ti	20	26*	30	40	60	80						
CsDN	79	73	69	59	39	19						
NC	1	1	1	1	1	1						

- * According to reaction equation (4) the mixture with balanced oxygen content contains 26% Titanium.
- ** According to this reaction equation the mixture with balanced oxygen content contains 28.6% Titanium.
- *** According to this reaction equation the mixture with balanced oxygen content contains 4.8% Titanium.

Again it was assumed that the pyrotechnic reaction runs according to reaction Equation (4). X-Ray Diffraction Analysis (XDR) of the accrued reaction products confirms this assumption.

4 Performance and Handling Safety Data

4.1 Combustion Velocity

4.1.1 Redox System Ti/KDN

Table 6 shows the measured combustion velocities of the redox system titanium/potassium dinitramide as a function of a changing oxygen balance.

The measured combustion velocities correspond to a median range of pyrotechnic mixtures.

The combustion velocities were measured with the experimental set up sketched in Figure 9.

4.1.2 Redox System Ti/CsDN

Table 7 shows the measured combustion velocities of the redox system titanium/cesium dinitramide as a function of the changing oxygen balance.

Also for this system, the measured combustion velocities correspond to a median range of pyrotechnic mixtures.

Table 7. Combustion velocity of the redox systems Ti/CsDN.

Substance	Composition [weight %]									
Tì	20	26	30	40	60	80				
CsDN	79	73	69	59	39	19				
NC	1	1	1	1	1	1				
Combustion velocity $[m s^{-1}]$	0.30	0.55	0.66	0.94	0.71	0.34				
σ	0.02	0.03	0.03	0.03	0.02	0.01				

Substance	Composition [weight %]										
Ti	20	30	35	36.5	40	45	50	60	70	80	90
KDN	79	69	64	62.5	59	54	49	39	29	19	9
NC	1	1	1	1	1	1	1	1	1	1	1
Combustion velocity [m s ⁻¹]	0.08	0.44	0.67	0.78	0.82	1.08	1.36	1.28	1.03	0.75	0.35
σ	0.00	0.01	0.04	0.05	0.03	0.10	0.20	0.20	0.17	0.05	0.05

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Counter

Figure 9. Experimental set up to measure the combustion velocity.

4.2 Heat of Reaction

4.2.1 Redox System Ti/KDN

In Table 8 the heats of reaction are listed. They were measured with an adiabatic calorimeter (IKA, Type C-4000) in an inert helium atmosphere of 3.0 MPa pressure.

The mixture with a titanium content of 50 wt.-% creates the highest heat of reaction. The measured value is 5400 J g^{-1} . The values for the different mixtures with positive or negative oxygen balances can be found in the range of 3700 to 2400 J g^{-1} .

The relationship between the ratio of burning rate/ exothermicity and the titanium content is found to be complex, but a linear trend is apparent for the compositions containing 20% to 50% titanium (Figure 10).

4.2.2 Redox System Ti/CsDN

Table 9 shows the heats of reaction. They were measured with an adiabatic calorimeter (IKA, Type C-4000) in an inert Helium atmosphere of 3.0 MPa.

Table 9. Heats of reaction of compositions of the redox system Ti/CsDN.

Substance	Composition [weight %]									
Ti	20	26	30	40	60	80				
CsDN	79	73	69	59	39	19				
NC	1	1	1	1	1	1				
Heat of reaction [kJ g ⁻¹]	3.28	3.70	3.66	3.94	3.57	2.58				

The composition with a content of 40 wt.-% of titanium creates a heat of reaction of 3940 J g⁻¹. It is the highest measured value of this redox system. The different compositions with positive and negative oxygen balances show heats of reaction in the range from 3280 to 2580 J g⁻¹. The measured values are relatively close together.

The relationship between the ratio of burning rate/ exothermicity and the titanium content is found to be complex, but a linear trend is apparent for the compositions containing 20% to 40% titanium (Figure 11).

4.3 Handling Safety

4.3.1 Redox System Ti/KDN

The handling safety data (Table 10) were determined according to the methods described in the Swiss AOP-7 specifications.

Table 8. Heats of reaction for the compositions of the redox system Ti/KDN.

Substance	Compo	Composition [weight %]											
Ti	20	30	35	36.5	40	45	50	60	70	80	90		
KDN	79	69	64	62.5	59	54	49	39	29	19	9		
NC	1	1	1	1	1	1	1	1	1	1	1		
Heat of reaction [kJ g ⁻¹]	3.7	4.8	5.1	5.3	5.2	5.3	5.4	4.9	4.6	3.9	2.4		



Figure 10. Ratio of combustion velocity and heat of reaction as a function of the titanium content.

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Figure 11. Ratio of combustion velocity and heat of reaction as a function of the titanium content.

Table 10. Handling safety data of compositions of the pyrotechnic redox system titanium/potassium dinitramide.

Substance Composition [weight %]											
Ti	20	30	35	36.5	40	45	50	60	70	80	90
KDN	79	69	64	62.5	59	54	49	39	29	19	9
NC	1	1	1	1	1	1	1	1	1	1	1
Impact Sensitivity [J]	2	2	2	4	3	4	3	5	5	3	3
Friction Sensitivity [N]	360	288	180	192	216	252	252	240	216	360	360
Sensitivity to electrostatic discharge [mJ]	320	0.56	0.56	0.18	0.32	1.0	0.10	1.0	1.0	1.0	1.0

Table 11. Handling safety data of mixtures of the pyrotechnic redox system titanium/cesium dinitramide.

Substance	Composition [weight %]					
Ti	20	26	30	40	60	80
CsDN	79	73	69	59	39	19
NC	1	1	1	1	1	1
Impact Sensitivity [J]	1	1	1	1	1	1
Friction Sensitivity [N]	240	252	192	240	252	360
Sensitivity to electrostatic discharge [mJ]	0.32	0.56	3.2	0.56	1.0	1.8

4.3.2 Redox System Ti/CsDN

Also for Ti/CsDN compositions the handling safety data (Table 11) were determined according to the methods described in the Swiss AOP-7 specifications.

Due to the high impact sensitivity of the tested compositions an additional investigation using a more sophisticated test method was executed. This investigation was also performed with a BAM-Impact apparatus but in place of the 2 kg drop weight, a 0.25 kg drop weight was used. Results are given in Table 12.

The occurring reactions during this test could often be assigned as a deflagration or even as a detonation reaction.

Table 12. Sophisticated test of the impact sensitivity.

Substance	Composition [weight %]			
Ti	20	26	30	
CsDN	79	73	69	
NC	1	1	1	
Impact Sensitivity [J]	0.875	1	1.5	

These reactions were associated with a strong ejection of sparks in each case (Figure 12).

Because of this behavior, which is unusual for pyrotechnic compositions, all three mixtures were pressed in a metal



Figure 12. Spark ejection during the impact test.

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Figure 13. Test arrangement DDT-test.

tube which is closed by an electrical HU-firing device (Figure 13).

4.4 Explosive Properties of the Redox Systems Ti/CsDN

Due to the distinctive impact sensitivity of the redox system Ti/CsDN such compositions could eventually be used as part of ignition mixtures for the enhancement of the impact sensitivity. In view of this application, the DDT (Deflagration to Detonation Transition) potential for the ignition of secondary explosives was tested with a modified standard blasting cap. Figure 13 shows a drawing of the test cap. The flash of the firing device passes the firing nozzle and initiates the following confined Ti/CsDN mixture. The lower end of the metal tube is open so that it enables an unrestricted transition of the reaction energy to the secondary explosive. Each test was performed twice. In Table 13 the results of the different tests are listed.

Although the reactions were partially strong the PBXN-5 could not be initiated with the Ti/CsDN mixtures. The weakest reaction resulted from the composition with the highest reducing agent content. With this mixture, the steel tube persisted intact (compare Figure 14, left side, down).

The results show that the tested Ti/CsDN redox system has not the potential for a primary explosive. However, because of its distinctive impact sensitivity and massive spark ejection, it could be possible to use these mixtures as part of ignition mixtures to replace toxic primary explosives, which are used to increase the impact sensitivity.

5 Summary and Conclusion

The oxidizers potassium- and cesium dinitramide were synthesized by an acid/base reaction based on an equimolare amount of the corresponding alkali hydroxide and ammonia dinitramide (ADN) in water. Their handling safety data were measured and compared to values published in literature. Based on the reducing agent titanium

Table 13. DDT-behavior of Ti/CsDN mixtures compared to pentaerythritol tetranitrate.

Mixture	Ti/CsDN/NC 20/79/1	Ti/CsDN/NC 26/73/1	Ti/CsDN/NC 30/69/1	Nitropenta (reference)
Initiation PBXN-5 Fragmentation of the steel tube (compare Figure 11) Witness plate	2 × no Yes; ripped alongside Little dent	2 × no Yes; ripped alongside Little dent	2 × no No; only Al-tube fragmented Little dent	2 × yes Yes; fragmentation in small fragments Hole with crater



Figure 14. Lead witness plate and remains of the modified blasting cap after the DDT-test.

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and the particular oxidizer, compositions with positive and negative oxygen balances as well as the composition with neutral oxygen balance were manufactured. From all these mixtures, the heat of reaction, the combustion velocity and the handling safety data of the produced compositions were determined. It was found that compositions based on titanium and potassium dinitramide as well as those based on titanium and cesium dinitramide are extremely sensitive to impact. The sensitivity is in the range of pure HMX and pentaerythritol tetranitrate. On the other hand, the produced compositions of both systems show a moderate sensibility to friction and electrostatic discharges. A detailed investigation of the impact sensitivity has shown that mixtures consisting of titanium and cesium dinitramide are more sensitive to impact than those of titanium and potassium dinitramide. Their impact sensitivity is in the range of standard ignition mixtures. Although the booster explosive PBXN-5 could not be initiated in the DDT-test, such compositions ripped off the massive steel tube length wise. It seems to be of interest, to test compositions of both redox systems as components in ignition compositions. This could be a way to substitute some of the toxic heavy metal primary explosives in these compositions. This conception will be part of further investigations.

6 References

[1] J. C. Bottaro, R. J. Schmitt, D. S. Ross, P. E. Penwell, *Dinitramide Salts and Method of Making Same*, U.S. Patent No. 5,254,324, **1993**, USA.

- [2] J. C. Bottaro, R. J. Schmitt, D. S. Ross, P. E. Penwell, *Method of Forming Dinitramide Salts*, U.S. Patent No. 5,198,204, **1993**, USA.
- [3] R. J. Schmitt, J. C. Bottaro, P. E. Penwell, D. Bomberger, Process for Forming Ammonium Dinitramide Salts by Reaction between Ammonia and a Nitronium-Containing Compound, U.S. Patent No. 5,316,749, 1994, USA.
- [4] H. Östmark, N. Wingborg, A. Langlet, A New High Performance Oxidizer for Solid Propellants, *16th International Symposium on Ballistics*, San Francisco, CA, USA, September 23–27 **1996**, Vol. 1, p. 285.
- [5] V. A. Tartakovsky, O. A. Luk'yanov, Synthesis of Dinitramide Salts, 25th Int. Annual Conference of ICT, Karlsruhe, Germany, June 28–July 1, 1994, p. 13/1.
- [6] J. R. Dawe, M. D. Cliff, Metal Dinitramides; Novel Oxidants for the Preparation of Boron Based Flare Compositions, 24th International Pyrotechnics Seminar, Monterey, California, USA, 27–31 July 1998, p. 789.

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