Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater., 2016, *13*(4), 978-988; DOI: 10.22211/cejem/67312

Compatibility Study of 2,6-Diamino-3,5-dinitropyridine-1-oxide with Some Energetic Materials

Xi LI, Bo-liang WANG*, Qiu-han LIN**

School of Chemical Engineering,
Nanjing University of Science and Technology,
Nanjing, Jiangsu, 210094, China
*E-mail: *boliangwang@163.com, ** linqh@njust.edu.cn*

Abstract: For the application of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) in composite explosives, the compatibility of ANPyO with some energetic materials was studied by the use of differential scanning calorimetry (DSC), where the energetic materials were cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), 3,4-dinitrofurazanfuroxan (DNTF), hexanitrohexazaisowurtzitane (CL-20), 2,4,6-trinitrotoluene (TNT), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), 3-nitro-1,2,4-triazol-5-one (NTO), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), 5-amino-1H-tetrazole nitrate (5-ATEZN), ammonium perchlorate (AP), potassium perchlorate (KP), aluminum powder (Al), boron powder (B), magnesium hydride (MgH_2) and magnesium borohydride ($Mg(BH_4)_2$). The results showed that the binary systems of ANPyO/CL-20, ANPyO/NTO, ANPyO/5-ATEZN, ANPyO/Al, ANPyO/B, ANPyO/MgH_2 and ANPyO/$Mg(BH_4)_2$ are compatible, and that the systems of ANPyO with RDX, LLM-105, HMX, AP and KP are sensitive, and with DNTF, TNT and TATB are incompatible.

Keywords: compatibility, energetic materials, ANPyO

1 Introduction

Highly energetic compounds with low sensitivity and good explosive performance are the focus of advanced energetic materials research aimed at the future needs in modern ordnance. Recently, nitrogen heterocyclic rings have become of considerable interest as ligands to construct energetic coordination compounds, due to a positive heat of formation and good thermal stability [1-4]. ANPyO is

a novel high energy explosive, thermally stable and less sensitive than commonly used explosives such as RDX and 2,6-dipicrylamino-3,5-dinitropyridine (PYX) [5, 6]. It has been established that the comprehensive performance of ANPyO is close to that of TATB, apart from the higher cost of the latter [7].

As a low sensitivity energetic additive, the incorporation of ANPyO into a propellant or explosive may be a very promising route for enhancing the thermal stability and for decreasing the sensitivity. Actually, the properties of the final mixture formed are, for the most part, highly dependent on the components chosen, their content and interaction with both the ANPyO and the other components. Potential physical and chemical interactions between energetic materials and other components can affect the chemical nature, stability and, consequently, safety [8]. Compatibility studies of a new energetic material and other components in propellants or explosives represents an important phase in the pre-formulation stage for the development of all new explosive forms.

Thermoanalytical techniques, especially DSC, are frequently used in compatibility tests for energetic materials before practical application [9-11]. The main advantages of thermal analysis techniques aimed at compatibility tests in energetic materials are the use of small amounts of material and rapid measurements [12].

Two criteria have been developed mainly to test the compatibility of individual energetic compounds and their mechanical mixtures with contacting materials, as determined by means of the DSC technique. A part of this effort involves compatibility research according to STANAG 4147 [13-15]. Others [16-18] are engaged in the evaluation of compatibility according to the basis released in Ref. [19]. From the point of view of Ilyushin [20], the criteria for compatibility reported in Ref. [16-18] are more strict than those in STANAG 4147.

Compared with the structure and synthesis of ANPyO studies [21-24], few compatibility researches on ANPyO have been performed. Therefore, the aim of the present work was to experimentally estimate the compatibility of ANPyO with some energetic materials using DSC.

2 Materials and Equipment

2.1 Materials

ANPyO was prepared according to the reported literature method [25], as shown in Figure 1. The purity of the ANPyO was greater than 99% and the sample was stored in a vacuum desiccator before use. Its calculated detonation velocity and detonation pressure were 7840 m/s and 27.5 GPa, respectively.

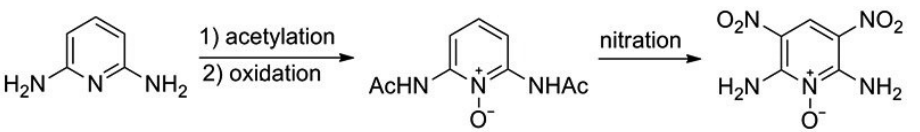


Figure 1. Synthetic route for ANPyO.

Cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), 3,4-dinitrofurazanfuroxan (DNTF), hexanitrohexazaisowurtzitane (CL-20), 2,4,6-trinitrotoluene (TNT), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), 3-nitro-1,2,4-triazol-5-one (NTO), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), 5-amino-1H-tetrazole nitrate (5-ATEZN), ammonium perchlorate (AP), potassium perchlorate (KP), aluminum powder (Al, 24.31 μm), boron powder (B, 10-20 μm), magnesium hydride (MgH_2), and magnesium borohydride ($Mg(BH_4)_2$) were used as energetic materials.

2.2 Equipment and experimentation

Binary mixtures (BMs) of ANPyO with each selected energetic material were prepared in 1:1 (m/m) ratios by simple physical mixing of the components with a pestle in an agate mortar for several minutes. The 1:1 (m/m) ratio was chosen in order to maximize the probability of observing any interactions [8].

All DSC curves were obtained in a SETARM DSC 131 differential scanning calorimeter, using a stainless steel crucible with a sample mass of approximately 1 mg in 1:1 ratios of premixed mixtures, under a dynamic atmosphere of N_2 (flow rate 50 mL/min), heating rate 10 °C/min, and pressure 0.1 MPa.

3 Results and Discussion

The DSC curves of the single components and mixtures, measured at a heating rate of 10 °C/min, are shown in Figure 2. For the single system of ANPyO, there exists only one exothermic peak at 360.6 °C due to the rapid decomposition of the compound. This exothermic peak of ANPyO was chosen for calculating the differences in temperature between a single system and a BM when the latter temperature was lower than the lowest decomposition peak temperature of the other single system, according to Equation 1.

$$\Delta T_P = T_{P1} - T_{P2} \tag{1}$$

where: T_{P1} is the maximum exothermic peak temperature of the single system

and T_{P2} is the maximum exothermic peak temperature of the mixture. The first exothermic peak temperature and the calculated difference between the single system with a lower decomposition peak temperature and the mixture are shown in Table 1, and the evaluated standards of compatibility for the explosive and the contacted materials [19] are listed in Table 2. From Figure 2 and Table 1, the following observations can be obtained.

Table 1. Decomposition temperatures of BMs obtained by DSC

System		Peak temperature			
Mixture [a]	Single system [b]	T_{P1} [°C]	T_{P2} [°C]	ΔT_P [°C]	Rating
ANPyO/RDX	RDX	240.2	232.9	7.3	C
ANPyO/HMX	HMX	281.7	273.5	8.1	C
ANPyO/DNTF	DNTF	286.2	228.5	57.7	D
ANPyO/CL-20	CL-20	246.5	245.8	0.7	A
ANPyO/TNT	TNT	295.5	252.0	43.6	D
ANPyO/TATB	ANPyO	360.6	342.1	18.5	D
ANPyO/NTO	ANPyO	360.6	363.2	-2.6	A
ANPyO/LLM-105	LLM-105	320.5	310.7	9.7	C
ANPyO/5-ATEZN	5-ATEZN	177.6	178.1	-0.5	A
ANPyO/AP	AP	326.7	318.1	8.6	C
ANPyO/KP	ANPyO	360.6	354.1	6.4	C
ANPyO/Al	ANPyO	360.6	364.9	-4.3	A
ANPyO/B	ANPyO	360.6	365.0	-4.4	A
ANPyO/MgH_2	ANPyO	360.6	364.9	-4.3	A
ANPyO/$Mg(BH_4)_2$	ANPyO	360.6	361.4	-0.8	A

[a] Mixture, 50/50 ANPyO/additive component binary system.
[b] Single system, the component with its exothermic peak temperature lower than the other one in a two-component system.

The DSC curve of the ANPyO/RDX mixture consisted of one endothermic peak and two exothermic peaks. The melting point of ANPyO/RDX is 2.9 °C lower than that of RDX, and both of the endothermic peaks of RDX and ANPyO/RDX are caused by the phase change of RDX from solid to liquid. The exothermic peak at 232.9 °C is caused by the rapid decomposition reaction of RDX, and the exothermic peak at 351.5 °C is attributed to that of ANPyO. The first exothermic peak of ANPyO/RDX is 7.3 °C lower than that of RDX. According to Table 2, the rating for the BM ANPyO/RDX is therefore C.

Table 2. Evaluation standards for the compatibility of explosives and the contacted materials [19]

Criteria ΔT_P [°C]	Rating	Note
≤ 2	**A**: Compatible or good compatibility	Safe for use in any explosive design
3-5	**B**: Slightly sensitized or fair compatibility	Safe for use in testing, when the device will be used within a very short period of time; not to be used as a binder material, or when long-term storage is desired
6-15	**C**: Sensitized or poor compatibility	Not recommended for use with explosive items
>15	**D**: Hazardous or bad compatibility	Hazardous. Do not use under any conditions

The values of ΔT_P between ANPyO and CL-20, NTO, 5-ATEZN, Al, B, $Mg(BH_4)_2$ as well as MgH_2 were 0.7, −2.6, −0.5, −4.3, −4.4, −0.8 and −4.3 °C, respectively. The BM ANPyO/CL-20 possesses good compatibility according to Table 2 because the ΔT_P was less than 2 °C. 5-ATEZN is also considered as compatible with ANPyO according to STANAG 4147 because the shifts in peak temperature between ANPyO/5-ATEZN and 5-ATEZN was not more than 4 °C. For the mixtures ANPyO/NTO, ANPyO/Al, ANPyO/B, ANPyO/MgH_2 and ANPyO/$Mg(BH_4)_2$, the addition of NTO, Al, B, MgH_2 and $Mg(BH_4)_2$ enhanced the thermal stability of ANPyO. Therefore, ANPyO is compatible with NTO, Al, B, MgH_2 and $Mg(BH_4)_2$ in the sense of STANAG 4147.

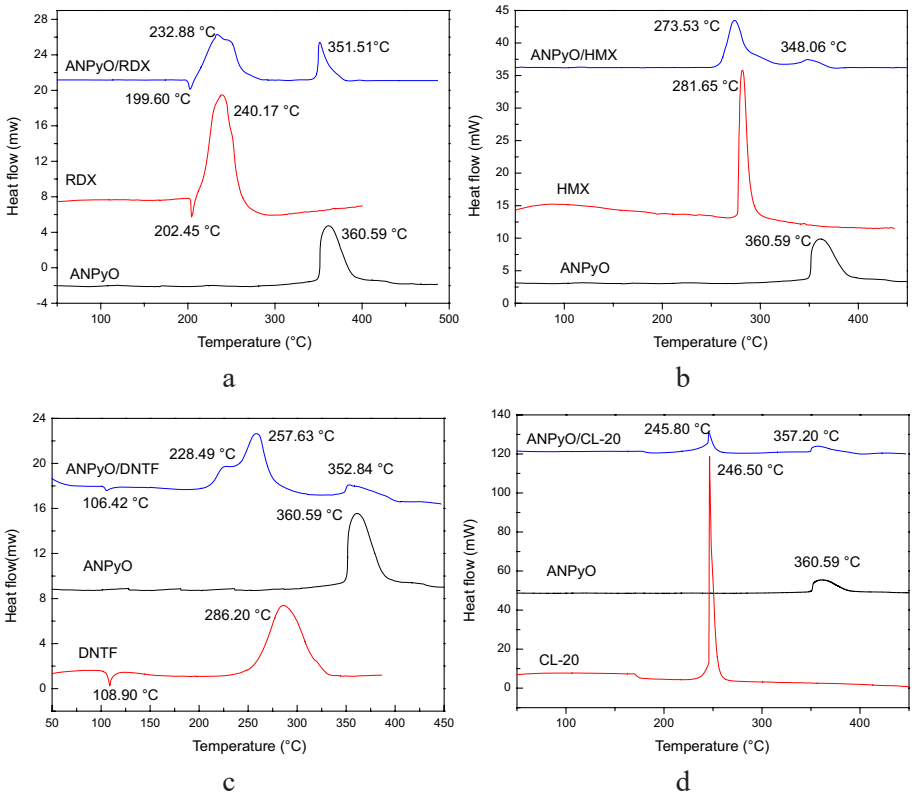
As in the BM ANPyO/RDX, there is an endothermic peak before the main exothermic peak for both ANPyO/KP and ANPyO/AP BMs (see Figures 2h and 2i). The maximum exothermic peak temperature difference between ANPyO and the ANPyO/KP mixture (ΔT_P) was 6.4 °C. The ΔT_P value between the ANPyO/AP mixture and AP was 8.6 °C. Therefore according to the standards of compatibility given in Table 2, both ANPyO/KP and ANPyO/AP BMs have poor compatibility.

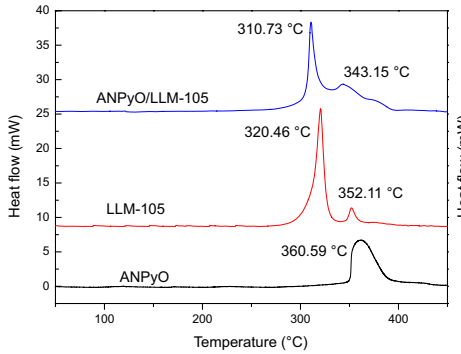
The values of ΔT_P between ANPyO and its mixture with HMX, LLM-105 and TATB were 8.1 °C, 9.7 °C and 18.5 °C, respectively, which is similar to the destabilization of ANPyO by the presence of AP. The information obtained by DSC confirmed the occurrence of possible chemical reaction between the components of these mixtures, and the mixtures therefore have poor compatibility.

As shown in Figures 2c and 2g, there exists one endothermic peak and two major exothermic peaks on the DSC curves of ANPyO/DNTF and ANPyO/TNT.

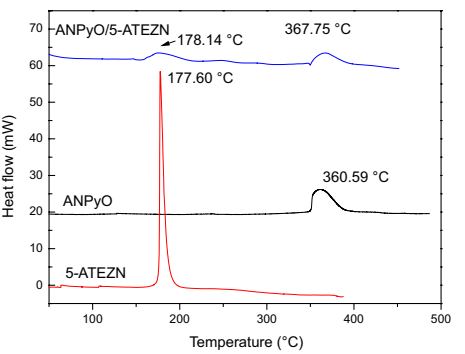
Notably, a slight "shoulder" emerges before the first exothermic peak of the ANPyO/DNTF, which suggests possible chemical interaction between ANPyO and DNTF. The values of ΔT_P between ANPyO/DNTF and DNTF, ANPyO/TNT and TNT were 57.7 and 43.6 °C, respectively. Evaluation of the DSC curves of the BMs ANPyO/DNTF and ANPyO/TNT confirmed that there was an increase in reactive ability and a decrease in the thermal stability of the mixtures. The two BMs have poor compatibility with a rating of D according to Table 2.

The relative thermal stability of the BMs ANPyO /energetic component decreases in the order: ANPyO/B > ANPyO/MgH_2 > ANPyO/Al > ANPyO/NTO > ANPyO/$Mg(BH_4)_2$ > ANPyO/KP > ANPyO/TATB > ANPyO/AP > ANPyO/LLM-105 > ANPyO/HMX > ANPyO/TNT > ANPyO/CL-20 > ANPyO/RDX > ANPyO/5-ATEZN.

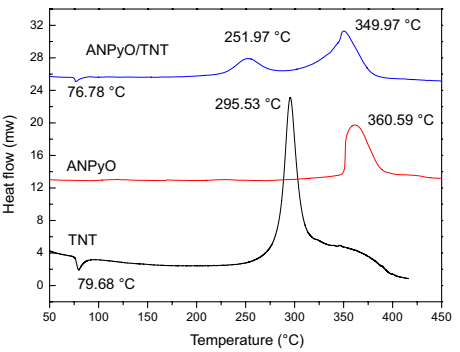




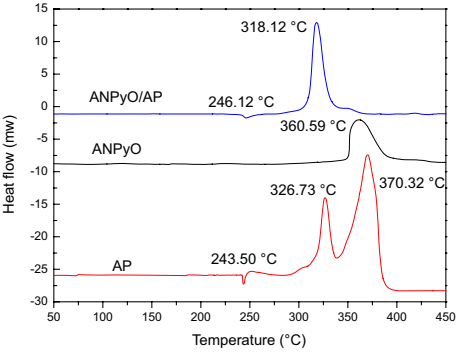
e



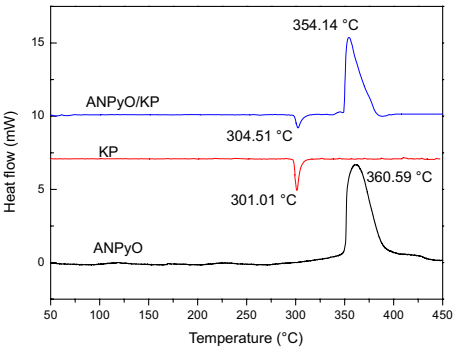
f



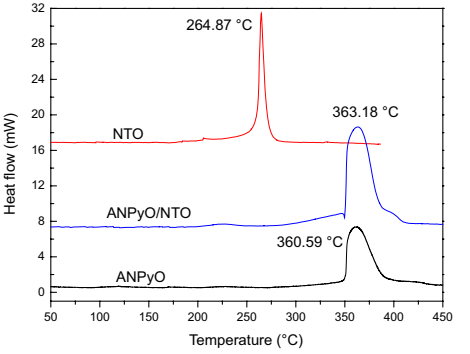
g



h



i



j

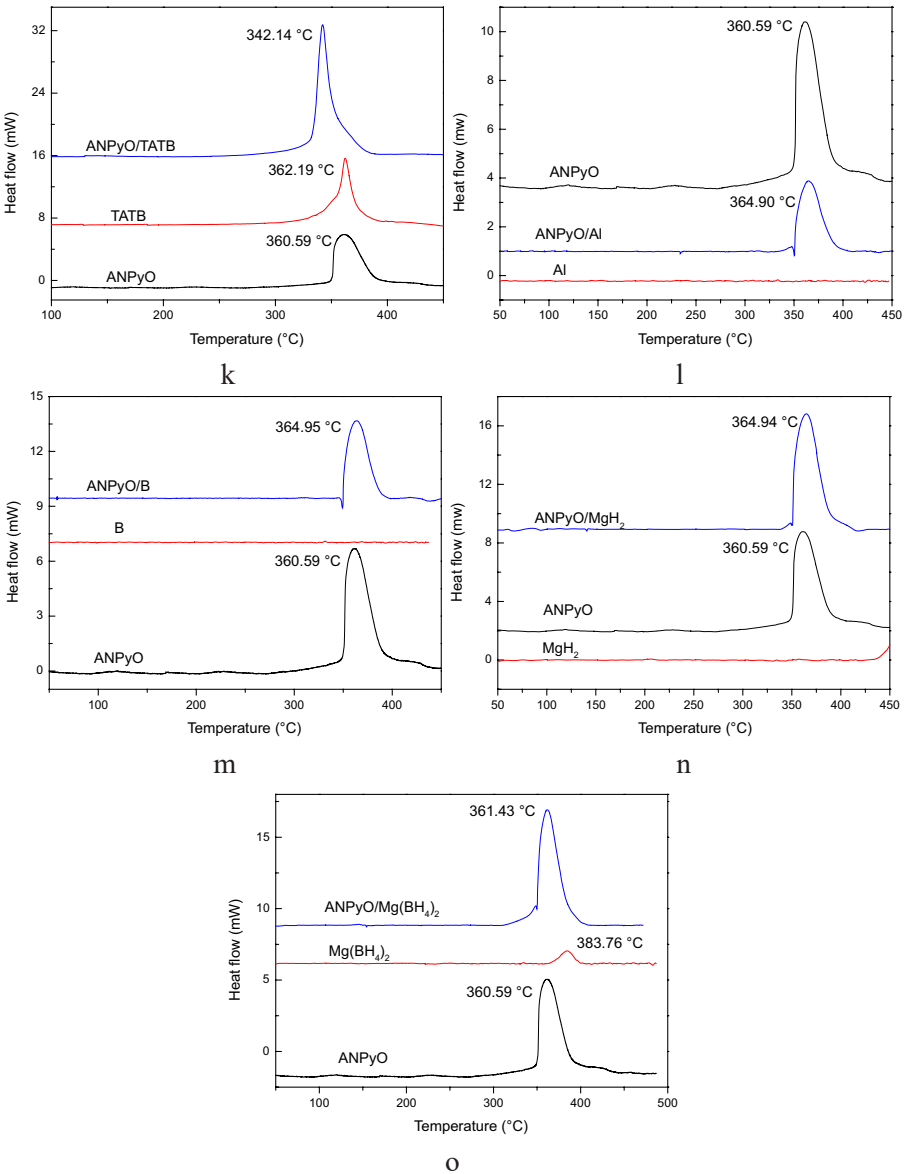


Figure 2. DSC curves with maximum peak temperatures for all of the BMs.

4 Conclusions

The present study explored the compatibility of ANPyO with some energetic materials using DSC. Based on the DSC results it was concluded that the BMs ANPyO/CL-20, ANPyO/NTO, ANPyO/5-ATEZN, ANPyO/Al, ANPyO/B, ANPyO/MgH_2 and ANPyO/$Mg(BH_4)_2$ possess good compatibility, the compatibilities of the ANPyO/RDX, ANPyO/LLM-105, ANPyO/HMX, ANPyO/KP and ANPyO/AP binary systems are poor, and the BMs ANPyO/DNTF, ANPyO/TNT and ANPyO/TATB are incompatible.

Acknowledgments

This research was supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions, the Natural Science Foundation of Jiangsu Province (BK20150780) and the opening project of State Key Laboratory of Explosion Science and Technology (Beijing Institute of Technology, the opening project number is KFJJ16-09M).

References

[1] Singh G., Prem Felix S., Studies on Energetic Compounds: 25. An Overview of Preparation, Thermolysis and Applications of the Salts of 5-Nitro-2, 4-dihydro-3H-1, 2, 4-triazol-3-one (NTO), *J. Hazard. Mater.*, **2002**, *90*(4), 1-17.

[2] Klapötke T.M., Stierstorfer J., Weber B., New Energetic Materials: Synthesis and Characterization of Copper 5-Nitriminotetrazolates, *Inorg. Chim. Acta*, **2009**, *362*(7), 2311-2320.

[3] Damavarapu R., Klapötke T.M., Stierstorfer J., Tarantik K., Barium Salts of Tetrazole Derivatives – Synthesis and Characterization, *Propellants Explos. Pyrotech.*, **2010**, *35*(4), 395-406.

[4] Xia Z.Q., Chen S.P., Wei Q., Qiao C.F., Syntheses and Characterization of Energetic Compounds Constructed from Alkaline Earth Metal Cations (Sr and Ba) and 1,2-Bis(tetrazol-5-yl)ethane, *J. Solid State Chem.*, **2011**, *184*(7), 1777-1783.

[5] Ritter H., Licht H., Review of Energetic Materials Synthesis, *J. Heterocycl. Chem.*, **1995**, *32*, 585-590.

[6] Liu J.J., Liu Z.L., Cheng J., Fang D., Synthesis, Crystal Structure and Catalytic Effect on Thermal Decomposition of RDX and AP: An Energetic Coordination Polymer $[Pb_2(C_5H_3N_5O_5)_2(NMP)\cdot NMP]n$, *J. Solid State Chem.*, **2013**, *200* ,43-48.

[7] Cheng J., Yao Q.Z., Zhou X.L., Du Y., Fang D., Liu Z.L., Synthesis and Properties of 2,6-Diamino-3,5-dinitropyridine-1-oxide, *Chin. J. Energ. Mater.*, **2008**, *16*(6), 672-675.

[8] de Barros Lima Í.P., Lima N.G.P.B., Barros D.M.C., Oliveira T.S., Mendonça C.M.S.,

Barbosa E.G., Raffin F.N., de Lima e Moura T.F.A., Gomes A.P.B., Ferrari M., Compatibility Study between Hydroquinone and the Excipients Used in Semi-solid Pharmaceutical Forms by Thermal and Non-thermal Techniques, *J. Therm. Anal. Calorim.*, **2015**, *120*(1), 719-732.

[9] Lee J.S., Jaw K.S., Thermal Decomposition Properties and Compatibility of CL-20, NTO with Silicone Rubber, *J. Therm. Anal. Calorim.*, **2006**, *85*(2), 463-467.

[10] Hong D., Li Y., Zhu S.G., Zhang L., Pang C.C., Three Insensitive Energetic Co-crystals of 1-Nitronaphthalene, with 2,4,6-Trinitrotoluene (TNT), 2,4,6-Trinitrophenol (Picric Acid) and D-Mannitol Hexanitrate (MHN), *Cent. Eur. J. Energ. Mater.*, **2015**, *12*, 47-62.

[11] Bhowmik D., Sadavarte V.S., Pande S.M., Saraswat B.S., An Energetic Binder for the Formulation of Advanced Solid Rocket Propellants. *Cent. Eur. J. Energ. Mater.*, **2015**, *12*, 145-158.

[12] de Klerk W. P. C., Schrader M. A., van der Steen A. C., Compatibility Testing of Energetic Materials, Which Technique? *J. Therm. Anal. Calorim.*, **1999**, *56*(3), 1123-1131.

[13] Gołofit T., Zyśk K., Thermal Decomposition Properties and Compatibility of CL-20 with Binders HTPB, PBAN, GAP and polyNIMMO, *J. Therm. Anal. Calorim.*, **2015**, *119*, 1931-1939.

[14] Krabbendam-La Haye E., de Klerk W., Miszczak M., Szymanowski J., Compatibility Testing of Energetic Materials at TNO-PML and MIAT, *J. Therm. Anal. Calorim*., **2003**, *72*, 931-42.

[15] Santhosh G., Ang H.G., Compatibility of Ammonium Dinitramide with Polymeric Binders Studied by Thermoanalytical Methods, *Int. J. Energ. Mater. Chem. Prop.*, **2010**, *9*(1), 17-41.

[16] Yan Q.L., Li X.J., Zhang L.Y., Li J.Z., Li H.L., Liu Z.R., Compatibility Study of *trans*-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin (TNAD) with Some Energetic Components and Inert Materials, *J. Hazard. Mater*., **2008**, *160*, 529-34.

[17] Pang W.Q., Fan X.Z., Xue Y.N., Xu H.X., Zhang W., Zhang X.H., Li Y.H., Li Y., Shi X.B., Study on the Compatibility of Tetraethylammonium Decahydrodecaborate (BHN) with Some Energetic Components and Inert Materials, *Propellants Explos. Pyrotech.*, **2013**, *38*(2), 278-285.

[18] Huang H., Shi Y., Yang J., Li B., Compatibility Study of Dihydroxylammonium 5,5′-Bistetrazole-1,1′-diolate (TKX-50) with Some Energetic Materials and Inert Materials, *J. Energ. Mater.*, **2015**, *33*(1), 66-72.

[19] Beach N.E., Canfield V.K., Compatibility of Explosives with Polymers (III), *Plastic Rep*., **1971**, 40-73.

[20] Ilyushin M.A., Bachurina I.V., Smirnov A.V., Tselinsky I.V., Shugalei I.V., Study of the Interaction of Polynitro Compounds with Transition Metals Coordination Complexes with 1,5-Pentamethylenetetrazole as a Ligand, *Cent. Eur. J. Energ. Mater.*, **2010**, *7*(1), 33-46.

[21] Shi W., Xia M., Lei W., Wang F., Solvent Effect on the Crystal Morphology of 2,6-Diamino-3,5-dinitropyridine-1-oxide: a Molecular Dynamics Simulation Study,

J. Mol. Graph. Model., **2014**, *50*, 71-77.
[22] Liu J.J., Liu Z.L., Cheng J., Fang D., Synthesis, Crystal Structure and Properties of Energetic Complexes Constructed from Transition Metal Cations (Fe and Co) and ANPyO, *RSC Advances*, **2013**, *3*(9), 2917-2923.
[23] Liu J.J., Liu Z.L., Cheng J., Synthesis, Crystal Structure and Properties of a Novel Tetra-nuclear Cu Complex of ANPyO, *J. Solid State Chem*., **2013**, *197*, 198-203.
[24] Xie L.F., Ye C.C., Ju X.H., Zhao F.Q., Theoretical Study on Dimers of 2,6-Diamino-3,5-dinitropyridine and its N-oxide, *J. Struct. Chem.*, **2012**, *53*, 659-664.
[25] Cheng J., Yao Q.Z., Zhou X.L., Du Y., Fang D., Liu Z.L., Novel Synthesis of 2,6-Diamino-3,5-dinitropyridine-1-oxide, *Chin. J. Org. Chem. (Youji Huaxue)*, **2008**, *17*(2), 166-168.