

DAPO-LLM-105: improving the particle morphology and thermal stability

Eric Pasquinet, Nicolas Pin, Alexandre Forzy, Pascal Palmas, Joël Rideau, Arnaud Beaucamp, Eric Lalière, Marie-Lou Perdrigeat, Stéphane Quéré, Christelle Barthet, Anne Guillaume.

CEA-DAM Le Ripault, BP 16, 37260 Monts (France)

Abstract: A number of different quench media were evaluated in order to improve the characteristics of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) obtained via nitration of 2,6-diaminopyrazine-1-oxide (DAPO). After a first screening phase, seven aqueous solutions containing a selected additive were used to quench the nitrating mixture in scale-up experiments. Complete characterization of the resulting LLM-105 indicated that nitrate salts as additives, especially ammonium and potassium nitrate, provided a high quality product, without requiring any further recrystallization. Notably, both particle morphology and thermal stability were significantly improved over the ones obtained using the standard pure water quench. This new DAPO-LLM-105 has been compared to the conventional DMP-LLM-105 and showed similar characteristics with even better insensitivity data.

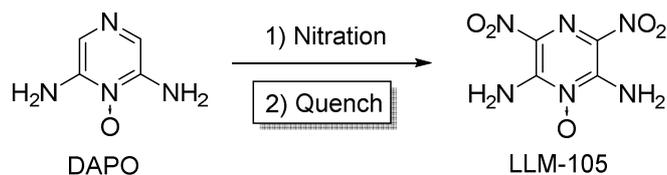
1 Introduction

The synthesis of 2,6-diamino-3,5-dinitropyrazine-1-oxide, known as LLM-105 (or ANPZO, NPEX-1, PZO), was first described by Pagoria [1]. In terms of high performance and low sensitivity, LLM-105 offers one of the best trade-offs to date. For example, its decomposition temperature approaches 350°C, while its power is estimated to be about 20% more than that of TATB [2]. For these reasons, prospects have been raised for applications that require moderate performance and high insensitivity: insensitive explosives or munitions [3], deep oil well perforation [4].

Even if other routes have been described [5], there are now two main syntheses of LLM-105. The first one starts from 2,6-dimethoxy pyrazine (DMP) and comprises 3 steps [6], all involving explosive products. After dinitration, then amination, the resulting 2,6-diamino-3,5-dinitropyrazine (ANPZ) is oxidized with hydrogen peroxide to LLM-105. The resulting product ('DMP-LLM-105') is known to be obtained as cubic, relatively coarse particles, contaminated by a small amount of ANPZ [7]. The second route that has been disclosed more recently consists in the dinitration of 2,6-diaminopyrazine-1-oxide (DAPO), that is readily obtained in 2 steps from iminodiacetonitrile [8]. At the end of the nitration, quenching in ice/water or cold water precipitates LLM-105 ('DAPO-LLM-105'). This new pathway (scheme 1) is attractive for a number of reasons: i) the last nitration step is the only one that involves an explosive derivative; ii) the product seems essentially pure, circumventing the issue of residual ANPZ from the DMP route; iii) cost reduction is anticipated [9].

However, its major drawback is the morphology of the crystals. The usual process generates very small particles that are less easily handled and need specific protective equipment. Moreover, most applications require reasonable particle sizes. Therefore, studies have been undertaken in order to improve the crystal size and shape, through a modification of the quenching medium. It was found that the use of some concentrated acids reduced the crystal aspect ratio [10]. The procedure required further dilution with water, and important quality data were lacking, such as thermal stability at demanding conditions. Prolonged high temperature exposures are required for oil and gas applications for example, and One-Dimensional-Time-to-Explosion (ODTX) experiments are very useful in evaluating the safety of systems, for example in the field of low vulnerability ammunitions.

Herein, we report our own direct quenching studies using aqueous solutions containing various additives. The results show a dramatic improvement in both the morphology and the thermal stability under pressure of DAPO-LLM-105, when quenched in aqueous ammonium and potassium nitrate.



Scheme 1. Synthesis of LLM-105 via the DAPO route ('DAPO-LLM-105').

2 Experimental Section

2.1 General information

DAPO was synthesized as described [11]. For ammonium nitrate, the additive-free A9642 reference from Aldrich was used. For comparison purposes, DMP-LLM-105 samples were synthesized from 2,6-dimethoxy pyrazine according to literature procedures [6,12] (400 g-scale).

Nitrate concentration was determined by ^{14}N NMR, using equilibrium N_2 signal as a natural internal reference for ^{14}N NMR chemical shifts and concentration [13]. The DSC measurements were performed on a TA instruments Q Series Differential Scanning Calorimeter Q200 from 20°C to 450°C using 10°C/min heating rate, in non hermetic crucibles, under air flow. For particle size distribution measurement, samples were dispersed in water and sonicated without surfactant. The vacuum thermal stability (VTS) was determined by measuring the evolved gas production (at standard temperature and pressure) upon heating of a powdered sample (5g) for 70 hours at 140°C (120°C for HMX), in a 20 mL test tube. Sensitivity tests were performed with a 10kg drop-weight apparatus similar to the BAM fallhammer system. Electrostatic discharge (spark) sensitivity experiments were performed with the ESD2008 system from the OZM Research company. Friction tests results were obtained with the classical Julius Peters apparatus. The specific thermomechanical limit test (TLT) is a small uniaxial press which has been designed to determine safety margins for molding processes. Small quantities (typically 2g) are heated at a rate of 2°C/min under 50 MPa to determine the temperature of explosion. To quantify time-to-explosion values in severe conditions, samples were heated at 220°C under 50 MPa, until decomposition. The latter experiment is similar to the known ODTX test.

2.2 Screening experiments

A 50 mL flask filled with 95-98% sulfuric acid (20 mL). 2,6-Diaminopyrazine-1-oxide (2.35 g, 18.6 mmol) was then added portionwise with stirring. After solubilization, 99-100% nitric acid (2.35 mL, 56 mmol) was slowly added to the brown solution, while the reaction mixture was maintained under 30°C with cooling. Stirring was kept for 2 h at 25°C before quenching. These conditions yielded in total around 2 g (50%) of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105).

For the quenching studies, aliquots (usually one fourth) of the nitrating mixture were successively poured dropwise in a stirred aqueous solution of the considered additive, while the temperature was controlled between 25-35°C with cooling. Any issue during the quench (foaming, overheating...) was reported. After the quench was complete, the mixture was held at 20°C for 15 min. The slurry was filtered at room temperature, and the resulting solid was washed with water twice, then with saturated aqueous sodium hydrogen carbonate, and finally with water. After vacuum drying, DSC, NMR and SEM analyses were performed to assess the tested additive.

2.3 Scale-up experiments

Different experiments were carried out at 100 to 500 g scale. The procedure used for the product described in Table 2, entry 7, is given below as a typical procedure:

To 95-98% sulfuric acid (4.9 L) 2,6-diaminopyrazine-1-oxide (577.3 g, 4.58 mol) was added portionwise under stirring. The temperature was controlled to stay below 30°C. Then, 99% nitric acid (865.5 g, 13.74 mol) was slowly added to the brown solution, while the reaction mixture was maintained under 32°C by cooling. Stirring was kept for 2 h at room temperature. The nitrating mixture was added portionwise to a stirred 2.7 M ammonium nitrate solution (17.1 L). The quench temperature was kept around 30°C with cooling. The slurry was filtered at room temperature, and the resulting solid was washed with water twice, then with saturated aqueous sodium hydrogen carbonate, and finally with water. The crude product was transferred in another vessel for a hot water treatment (80°C with stirring). A subsequent MEK/water mix (9:1) treatment was applied in some cases (entries 2-5) but it had no influence on the final characterization data. After filtration and drying, the yield in 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) was 474 g (48%).

The product matched the described [9] analytical data for DAPO-LLM-105. Selected data: DSC decomposition onset (347-350°C). ¹H NMR: δ = 9.06, 8.78 ppm. ¹³C NMR: δ = 144.6, 124.9 ppm. ¹⁵N NMR: δ = -16.5, -107.1, -140.0, -292.5 ppm. C₄H₄N₆O₅ (216.11); C 22.47 (calc. 22.23); H 1.84 (1.87); N 38.70 (38.89)%.

3 Results and Discussion

3.1 Screening experiments

Nitration of DAPO was carried out in a concentrated sulfuric and nitric acid mixture, before quenching in an aqueous solution of the tested additive. Mineral or organic acids, ammonium and nitrate salts, as well as selected organic compounds (nicotinamide, urea) were investigated as morphology modifiers. The yields were around 50% (ca. 2 g of precipitate).

In order to qualitatively assess each additive, several criteria were defined: behavior during quench, particle morphology and size (SEM), chemical purity (NMR), thermal analysis (DSC). This screening enabled the identification of several additives that offered a reasonable trade-off between all criteria, thus constituting valuable candidates for further developments. Additives not soluble enough to significantly modify the crystallization (succinic acid), or leading to very small particle sizes (ammonium phosphate and carbamate), were rejected. Formic acid, though worth consideration, was rejected because of its known propensity to be entrapped in LLM-105 [10]. Urea as the additive produced particles similar to the ones obtained with trifluoroacetic acid (TFA). The latter was preferred since it is being used as the solvent during oxidation of ANPZ to DMP-LLM-105. Finally, the following seven quench additives were selected: TFA, citric acid, ammonium sulfate, ammonium formate, ammonium nitrate (AN), sodium nitrate, potassium nitrate.

3.2 Scale-up experiments

The synthesis of LLM-105 was scaled-up to 100-500 g, using the selected quench additives. Precipitation in pure water (i.e.: no additive present in the quench) was also included in the study for comparison purposes. Our aim was to fully characterize, by standard analytical techniques, the product obtained at a reasonable scale, but also to obtain quantitative thermal stability data in severe conditions. Weight loss at 120°C, vacuum thermal stability at 140°C, and specific thermomechanical tests (including an ODTX-type experiment) were thus added to the analyses already performed at small scale. Results are summarized in table 1, together with comparison data obtained for DMP-LLM-105 (oxidation of ANPZ, entry 11) and HMX (entry 12).

Table 1. Scale-up experiments using the selected quench additives.

Entry	Quench additive ^[a]	Synthesis scale (g)	Yield (%)	Particle size [D (v, 0.5), μm]	Decomposition temperature (DSC onset, $^{\circ}\text{C}$)	Vacuum thermal stability @ 140 $^{\circ}\text{C}$ /70h (cc/g)	Reaction temperature in the thermomechanical limit test @ 50 MPa ($^{\circ}\text{C}$)	Time-to-explosion @ 220 $^{\circ}\text{C}$ /50 MPa (min)	Nitrates content by ^{14}N NMR (wt %)
1	None (pure water)	350	52	23	350	0.11	231	17	<0.01
2	TFA	100	47	47	349	0.28	231	14	<0.01
3	Citric acid	100	52	39	348	0.28	227	10	<0.01
4	Ammonium formate	100	50	39	345	0.11	237	13	<0.01
5	Ammonium sulfate	100	48	36	350	0.19	230	13	<0.01
6	Ammonium nitrate	350	46	59	349	0.06	270	50	0.035
7	Ammonium nitrate ^[b]	500	48	49	349	0.06	260	54	0.025
8	Ammonium nitrate ^[c]	350	50	39	349	0.13	257	44	0.06
9	Sodium nitrate	350	47	37	347	0.13	236	23	0.115
10	Potassium nitrate ^[d]	350	44	56	347	0.05	265	39	0.015
11 ^[e]	N.A. (DMP-LLM-105)			48-53	344-345	0.09-0.10	245-270	51	0.025
12	N.A. (HMX 0-100 μm)			20	280	0.05 ^[f]	220-225	3-5	N.A.

[a] Concentration in additive: 5.4 mol.L⁻¹, unless otherwise stated. [b] Concentration: 2.7 mol.L⁻¹ [c] Concentration: 1.35 mol.L⁻¹ [d] Concentration: 2.3 mol.L⁻¹ [e] Data measured on 400g DMP-LLM-105 batches. [f] at 120 $^{\circ}\text{C}$ /70h

Yields were consistently around 50%, with only a little influence by the type of additive. However, experiments at lower ammonium nitrate concentrations (entries 7-8) produced slightly higher yields. This may be due to a higher solubility or to decomposition processes of LLM-105 in the acidic, nitrate-rich medium. It was shown that the higher the concentration, the higher the mean particle size. The fine particles (< 20 μm) content was also dramatically reduced using a concentrated ammonium nitrate quench (figure 1).

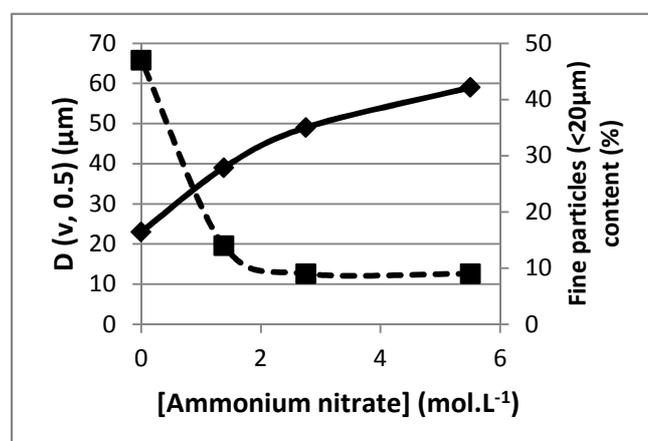


Figure 1. Influence of the AN quench concentration on particle mean size (plain line) and fine particle content (dashed line).

The observed behavior allows the particle size to be tuned by modifying the ammonium nitrate concentration in the quench solution. Overall, quenching in aqueous solutions of the

selected additives always produced coarser particles than in pure water (mean size: 36-59 μm vs 23 μm). The laser scattering measurements were confirmed by SEM analyses (figure 2 - a micrograph of DMP-LLM-105 was also included for comparison).

Concerning the particle morphology, grain powder appeared mostly as aggregates of various individual crystallites. The best aspect ratio, i.e. the most isotropic shape, was obtained when using nitrate compounds, leading either to smaller particles with sodium nitrate or larger particles with potassium nitrate. An increase of ammonium nitrate concentration was seen to improve the aspect ratio. TFA quench additive produced particles with a particular tablet-like shape and sometimes containing an empty cavity inside as revealed by focused ion beam scanning electron microscopy (FIB-SEM) experiments.

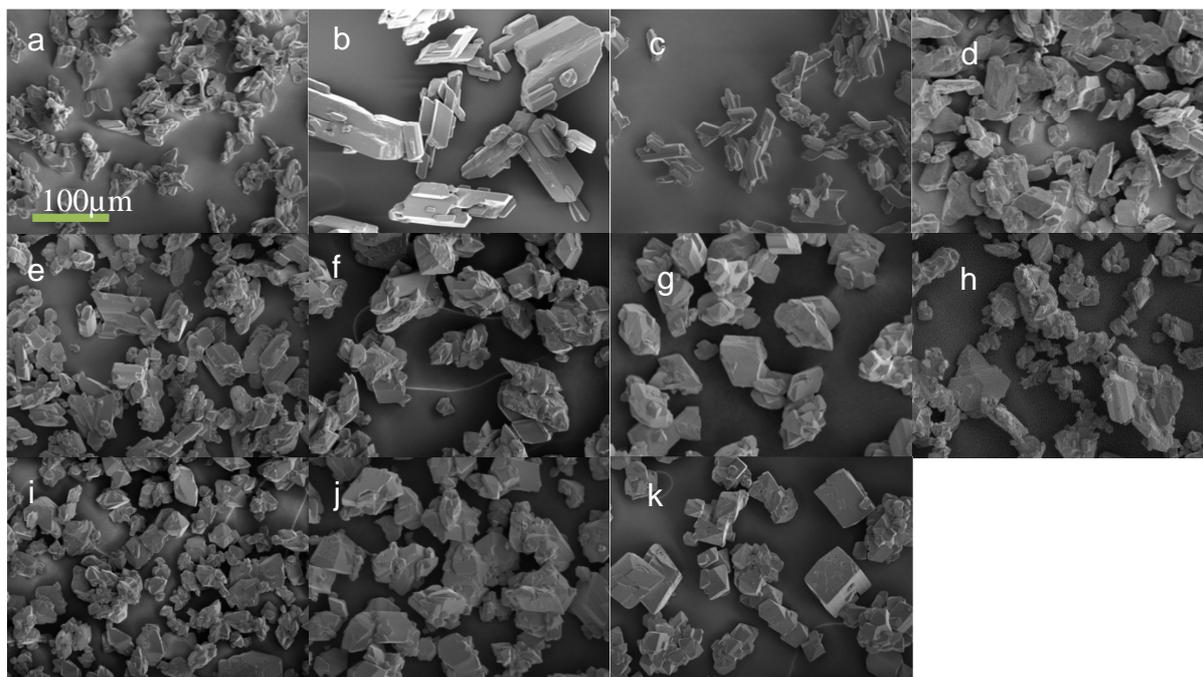


Figure 2. SEM micrographs of samples from scale-up experiments obtained with different quench additives referring to table 2. a) Water; b) TFA; c) Citric acid; d) Ammonium formate; e) Ammonium sulfate; f) Ammonium nitrate 5.4M; g) Ammonium nitrate 2.7M; h) Ammonium nitrate 1.35M; i) Sodium nitrate; j) Potassium nitrate; k) typical DMP-LLM-105.

All quench additives resulted in high-purity LLM-105 samples, as indicated by elemental analyses and ^1H NMR spectra, that only showed trace impurities. This was confirmed by HPLC analyses on several samples, that were found >99.5% in LLM-105 (area ratios), and by ion chromatography, that showed only traces of various anions. DSC results also conformed to literature data, with a decomposition onset between 345 and 350 $^{\circ}\text{C}$ (figure 3).

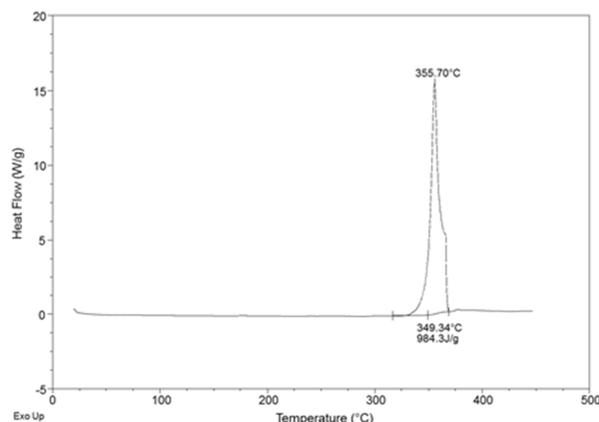


Figure 3. DSC thermogram of DAPO-LLM-105 – Quench additive: ammonium nitrate (table 2 – entry 6)

Other characterizations were carried out to validate the product quality. Our attention was particularly drawn to the thermal stability of the different samples. Thermal stability in severe conditions is a major parameter when considering applications for new insensitive explosives. Therefore, other tests were performed for all samples: vacuum thermal stability (VTS) at 140°C, and a specific thermomechanical limit test (TLT) at 50 MPa. This allowed us to identify any unwanted issues (degassing, decomposition of trace impurities, polymorphism under pressure...) in low and high pressure conditions. The aim was also to obtain quantitative data on the thermomechanical behavior of LLM-105, that we could compare to known explosives.

These characterizations proved more informative than the standard ones, producing more discrepancies between the samples obtained from different quench additives. The lowest VTS figures (at 140°C) were obtained for ammonium nitrate and potassium nitrate-quenched samples and compared well with the limited data available in the literature for recrystallized LLM-105 (DMP route, VTS at 120°C) [14]. Concerning the thermomechanical limit test, we were grossly able to classify the additives into two groups.

DAPO-LLM-105 obtained with water, TFA, citric acid, ammonium sulfate or formate exhibited thermal stabilities at 50 MPa close to, or just above, HMX/NTO/FOX-7 (all in the range 220-227°C). The second group was constituted of ammonium nitrate or potassium nitrate-quenched DAPO-LLM-105 which reacted around 260°C and therefore exhibited a thermal stability similar to that of DMP-LLM-105. Interestingly, the sodium nitrate-quenched sample showed less improvement than its ammonium and potassium counterparts.

Selected samples were further subjected to time-to-explosion measurements (ODTX-like experiments). The first results concerning the thermal stability in severe conditions were confirmed. Further experiments showed that even slightly washed ammonium nitrate-quenched samples (on-filter treatment with water and hydrogen carbonate solution) exhibited satisfactory thermal stabilities. Conversely, even repeated hot water treatments (in-vessel, with stirring) did not improve the poor thermal stability of water-quenched samples. This indicated that the nature of the quench solution is the most relevant factor to control the quality of DAPO-LLM-105. In this respect, ammonium nitrate and potassium nitrate-quenched products showed a markedly improved thermal stability over samples obtained from any other tested media, while still exhibiting particles with a reasonable aspect ratio.

Importantly, this work shows that high-quality, thermally stable LLM-105 samples can be obtained directly from synthesis, without requiring any further recrystallization. Avoiding recrystallization is highly desirable, since it may produce very small or needle-like particles [14,15], and may entrap the recrystallization solvent in the crystals. Needle particles are also known to produce low density PBXs after formulation [16].

3.3 Comparison of DAPO- vs DMP-LLM-105

Typical analytical and thermal stability data for DMP-LLM-105 have been included in table 2 for comparison purposes (entry 11). Results are very similar to the ones obtained for ammonium and potassium nitrate-quenched DAPO-LLM-105. Particle morphology and size are also much closer for these two types of products, while water-quenched DAPO-LLM-105 particles are significantly smaller and more elongated (figure 2a). Typical DSC decomposition onset temperatures for DAPO-LLM-105 are always 3 or 4°C higher than for DMP-LLM-105. Sensitivity data have been compared also. Table 2 describes impact and spark sensitivity thresholds determined by the classical up-and-down method (Bruceton method). We found that DAPO-LLM-105 and especially nitrate-quenched DAPO-LLM-105 are less sensitive to impact than DMP-LLM-105. Regarding the spark sensitivity threshold, DMP- and DAPO-LLM-105 were comparable, except for the more sensitive TFA-quenched sample. All LLM-105 are insensitive to friction (Julius Peters apparatus).

Table 2. Sensitivity data for selected DAPO- and DMP-LLM-105 samples.

Synthesis route	Quench additive (corresponding entry in table 2)	Drop-weight impact sensitivity ^[a]	Spark sensitivity ^[b]
DAPO	Ammonium nitrate (entry 6)	48.4 cm	136.4 mJ
DAPO	Ammonium nitrate (entry 7)	48.5 cm	113.3 mJ
DAPO	Sodium nitrate (entry 9)	39.3 cm	99.6 mJ
DAPO	Potassium nitrate (entry 10)	45.9 cm	98.3 mJ
DAPO	TFA (entry 2)	28 cm	69.0 mJ
DMP	N.A.	19-24 cm	110 mJ

[a] 10 kg hammer (RDX: 10 cm). [b] OZM ESD2008 apparatus

4 Conclusions

Quenching of DAPO-LLM-105 in aqueous nitrate solutions allows the direct synthesis of a high quality product. Both the particle size and aspect ratio are significantly improved over the classical water quench, without requiring any recrystallization process. Moreover, ODTX-like experiments showed a dramatic increase of the thermal stability for ammonium nitrate and potassium nitrate-quenched samples. On the whole, these particular DAPO-LLM-105 are similar to DMP-LLM-105, with the advantage of avoiding the presence of residual ANPZ, and slightly better insensitivity characteristics [17]. The nitrate-quench procedure was scaled up to around 500 g, thus raising high prospects for the development of LLM-105 following the DAPO route, a route that was suffering from serious drawbacks before this work.

References

- [1] P. F. Pagoria, Synthesis of 2,6-Diamino-3,5-dinitropyrazine-1-oxide, Report UCRL-JC-117228, Lawrence Livermore National Laboratory, Livermore, CA, USA **1994**.
- [2] T. D. Tran, P. F. Pagoria, D. M. Hoffman, B. Cunningham, R. L. Simpson, R. S. Lee, J. L. Cutting, Small-Scale Safety and Performance Characterization of New Plastic-Bonded Explosives Containing LLM-105, *12th International Detonation Symposium*, San Diego, 11-16 August **2002**.
- [3] a) F. Guo, Y. Liu, D. Liu, Y. Yu, Optimization of the Synthetical Craft of 2,6-Diamino-3,5-dinitropyrazine-1-oxide, *Chin. J. Explos Propellants*, **2006**, *29*, 17-19. b) D. Price, GrIMEx: Development of a Novel, Green IM Comp B Replacement, *Insensitive Munitions and Energetic Materials Technology Symposium*, Nashville, 12-15 September **2016**.
- [4] H. Yan, H. Jia, M. Zhang, F. Miao, W. Wang, B. Liu, Y. Wang, X. Yao, Explosive for Ultrahigh Temperature Petroleum Perforating Bullets, and Preparation Method thereof, CN 105418340 A, Mountain Northwest Huaguanlu Chemical Industry Ltd, China **2015**.
- [5] a) E.-C. Koch, Insensitive Explosive Materials: 2. 2,6-Diamino-3,5-dinitropyrazine-1-oxide ANPZO, MSIAC Limited Report L-159, Brussels, Belgium **2009**; b) X. Zhao, Z. Liu, An Improved Synthesis of 2,6-Diamino-3,5-dinitropyrazine-1-oxide, *J. Chem. Res.* **2013**, *37*, 425-426.
- [6] P. F. Pagoria, G. S. Lee, A. R. Mitchell, R. D. Schmidt, The Synthesis of Amino- and Nitro-Substituted Heterocycles as Insensitive Energetic Materials, *Insensitive Munitions and Energetic Materials Technology Symposium*, Bordeaux, 8-11 October **2001**.
- [7] A. Pearsall, K. M. Hanson, S. P. Lad, J. Salan, Synthesis, Scale-Up, and Recrystallization Studies of 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105), *Insensitive Munitions and Energetic Materials Technology Symposium*, Munich, 11-14 October **2010**.

- [8] P. F. Pagoria, M. X. Zhang, Synthesis of Pyrazines Including 2,6-Diaminopyrazine-1-oxide (DAPO) and 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105), WO 123806 A1, Lawrence Livermore National Security, Livermore, CA, USA **2010**.
- [9] S. Jing, Y. Liu, J. Guo, Research on a New Synthesis of LLM-105 Using N-Nitrosobis(cyanomethyl)amine, *Centr. Eur. J. Energ. Mater.* **2016**, *13*, 21-32.
- [10] D. am Ende, P. F. Pagoria, S. Anderson, J. Salan, LLM-105 (DAPO Route) Morphology Study, *Insensitive Munitions and Energetic Materials Technology Symposium*, Rome, 18-21 May **2015**.
- [11] a) P. Pagoria, M. X. Zhang, Synthesis of Substituted Pyrazines, US Patent 9,458,115, Lawrence Livermore National Security, Livermore, CA, USA **2016**; b) P. Pagoria, M. Z. A. DeHope, G. Lee, A. Mitchell, P. Leonard, 'Green' Energetic Materials Synthesis at LLNL, *Proc. 15th seminar on New Trends in Research of Energetic Materials*, part I, pp. 55-65, Pardubice, 15-17 April **2012**.
- [12] a) Y. Liu, D. Liu, Z. Yang, Y. Zhang, Y. Tang, J. Wang, Characterization of a Heat-resistant Explosive ANPZO, *Chin. J. Energ. Mater.* **2012**, *20*, 721-725; b) Y. Wang, Z. Ge, B. Wang, Z. Ye, Y. Li, Y. Shang, Preparation and Thermal Properties of Fine LLM-105 with Different Crystal Form, *Chin. J. Energ. Mater.* **2011**, *19*, 523-526; c) T. D. Tran, P. F. Pagoria, D. M. Hoffman, J. L. Cutting, R. S. Lee, R. L. Simpson, Characterization of 2,6-Diamino-3,5-Dinitropyrazine-1-Oxide (LLM-105) as an Insensitive High Explosive Material, *33rd International Annual Conference of ICT*, Karlsruhe, 25-28 June **2002**.
- [13] S. Delile, T. Maillou, P. Palmas, V. Lair, M. Cassir, Optimization of the Electrochemical Reduction of Nitromethane for the Development of an Integrated Portable Sensor, *Electrochimica Acta* **2013**, *99*, 94-101.
- [14] H. Li, B. Cheng, S. Liu, F. Nie, J. Li, Recrystallization and Properties of LLM-105, *Chin. J. Energ. Mater.* **2008**, *16*, 686-688.
- [15] H.-B. Li, B.-B. Cheng, H.-Z. Li, F.-D. Nie, Synthesis of 2,6-Diamino-3,5-dinitropyrazine-1-oxide, *Chin. J. Org. Chem.*, **2007**, *1*, 112-115.
- [16] D. M. Hoffman, K. T. Lorenz, B. Cunningham, F. Gagliardi, Formulation and Mechanical Properties of LLM-105 PBXs, *39th International Annual Conference of ICT*, Karlsruhe, 24-27 June **2008**.
- [16] E. Pasquinet, N. Pin, A. Forzy, P. Palmas, J. Rideau, A. Beaucamp, E. Lalière, M.-L. Perdrigeat, S. Quéré, C. Barthet, A. Guillaume, *Propellants Explos. Pyrotech.*, **2019**, *44*, 785-791.