Improvement of high explosives crystal quality by crystallization

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As a leader in energetic materials, EURENCO has for many years been producing a complete range of high explosives as well as the compositions based thereof. Thus, EURENCO has a wide knowledge of explosives synthesis and more over in crystallization, granulation and coating of explosives; thereby offering customers a broad spectrum of products and qualities to fit most intended applications.

Manufacturing of particles is an important part of explosives production. The quality, size and shape of the crystals have large impact on the characteristics of the product. Inclusions and imperfections can reduce sensitivity significantly. Availability of particles with compact, preferably spherical, shape and of several different sizes, all with specific size distribution, is important to achieve high solid loading and high performance in formulations. It is also critical for good processing properties, e.g. good flowability, when formulating explosive materials.

Due to this, EURENCO put a lot of effort in the area of particle manufacturing in order to be able to offer customers a broad spectrum of products and qualities to fit most intended applications. This paper will present the most recent relevant results in the crystallization studies on:

- RDX with various available grades such as MI-RDX, the standard one, I-RDX®, the Insensitive one and VI-RDX, the new Very Insensitive RDX.
- NTO with a focus on a new high quality grade specifically adapted to high NTO content Ontalite for insensitive melt cast composition.
- FOX-7 with a new technique for manufacturing of small particle size for propellants.

1. Crystallization of various grades of RDX

Cyclotrimethylenetrinitramine (RDX) is a widely used crystalline high explosive. In recent years, UN countries have been more and more interested in a quality of Reduced Sensitivity RDX (RS-RDX) as it offers the potential to reduce the vulnerability of some RDX formulations towards shock. Leader in energetic materials, EURENCO has produced for many years the insensitive RDX I-RDX®. The benefit of this RDX quality towards the shock sensitivity in cast PBX composition is fully recognized [1] [2].
Numerous studies have been conducted for years in order to improve the sensitivity of explosive formulations and to understand the origin of the sensitivity of the RDX compositions.

It is now well known that many parameters could have a significant impact on the sensitivity of explosive formulations towards shock : the binder nature [3], [4], [5], the explosive particle size [6], [7], the explosive particle shape and / or surface [8], [9], defects, such as intragranular voids inside the explosive crystals [10], [11], [12]. Any heterogeneities in the material could lead to the formation of hot spots where the first chemical reaction occurs.
Moreover, it has been shown [6] that for low shock pressures the very fine particles are less sensitive. But such grade of RDX is hard or even impossible to process because of high paste viscosity.
Based on its knowledge on crystallization, EURENCO is able to produce various grades of RDX; from MI-RDX to I-RDX® (Insensitive RDX) and VI-RDX (Very Insensitive RDX).

1.1. Production

EURENCO has been producing at industrial scale for more than 40 years two main grades of RDX, MI-RDX and I-RDX®. I-RDX® is available with the same particle size distribution than conventional RDX (MI-RDX) depending on the manufacturing conditions such as the crystallization parameters.
VI-RDX is a new grade that has been developed at lab scale by the French German Institute of Saint Louis (ISL) and has been successfully transferred to pilot scale at EURENCO [13]. Using a well-controlled crystallization process, RDX particles with very few internal defects and smooth shapes have been obtained [14].

1.2 Compared characterizations

1.2.1 Microscopy

Pictures of RDX particles obtained by optical microscopy with matching refractive index are presented in figure 1. We observed less and less internal defects from MI-RDX to VI-RDX. While I-RDX® shows less internal defects than MI-RDX, VI-RDX presents quite no internal defects and round particles. Since the crystallization process for VI-RDX has been optimized to reduce the internal defects in the crystal, there are quite few inclusions in the particles although solution crystallization process often leads to solvent inclusions in the crystals.

MI-RDX I-RDX® VI-RDX

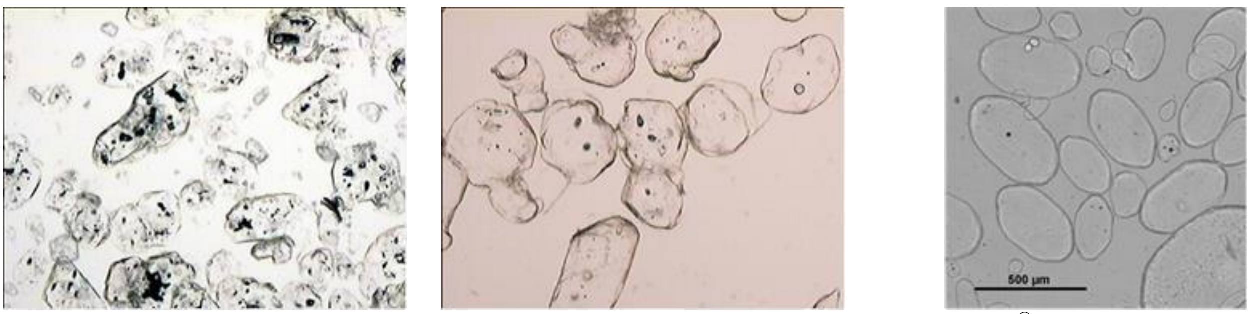

Figure 1: Optical microscopy with matching refractive index of MI-RDX, I-RDX® and VI-RDX

1.2.2 Volume fraction of inclusions

The volume fraction of inclusions is obtained from the particle apparent density measurement.
The particle apparent density was measured by the ISL sink-float method, a unique, accurate and quantitative tool that has already been successfully applied to different RDX grades from standard RDX to insensitive RDX [15] [16].
The apparent density distribution gives also the average apparent density for a RDX lot. Assuming that the heterogeneities in a RDX particle can only be HMX as an impurities or inclusions filled with air, it is possible to compute an average volume fraction of inclusions from the average apparent density and the average HMX mass fraction. It allows thus a correlation between the explosive particle microstructure and the shock sensitivity of the explosive PBXN-109 composition [16].
The results for MI-RDX, I-RDX® class 1 and VI-RDX are given in figure 2. I-RDX has around one-third less inclusions than MI-RDX but VI-RDX has two-thirds less inclusions than I-RDX.

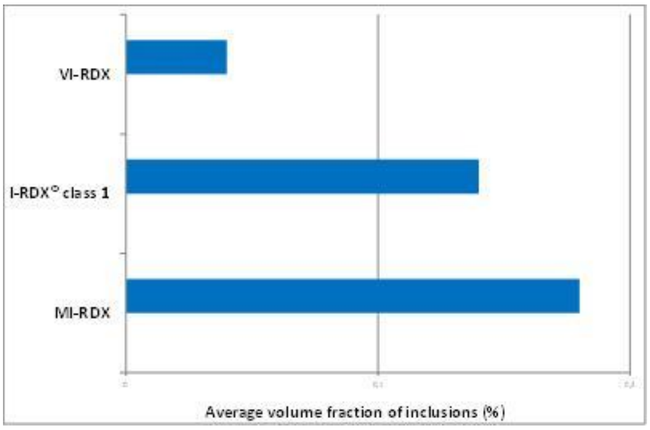

Figure 2: Average volume fraction of inclusions of MI-RDX, I-RDX® and VI-RDX

1.2.3 Shock sensitivity

The lab scale shock sensitivity tests are performed, according an ISL procedure, on a cast composition with 70% by weight of the explosive and 30% by weight of a wax. The use of wax allows an accurate control of the quality of the formulations which are homogeneous and free from residual extra-granular pores. The formulations are processed by casting under gravity and cooling under controlled conditions.
The behavior of the formulations towards shock is measured by impacting the samples with a flat ended steel projectile of diameter 20 mm, length 20 mm and mass 50 g. The projectile is launched with a nylon sabot using a powder gun. A protection wall and a 2 meters distance between the target and the gun muzzle avoid blast effects. The formulation sample diameter is 45 mm and its length is 50 mm. The shock transit time across the sample is recorded for several projectile impact velocities. The sharp decrease of the shock transit time, when sample detonates, provides the impact velocity threshold to get a full detonation of the sample [10].
The results obtained on the different grades of RDX are summarized in the figure 3. It gives, for each formulation, the lowest impact projectile velocity which leads to a detonation and the highest impact projectile velocity which does not lead to a detonation. These results clearly show that VI-RDX is much less sensitive than I-RDX®. Furthermore, the shock sensitivity of VI-RDX is similar to that measured on a very fine RDX (I-RDX® M5 grade with a single mode size distribution and a mean diameter of 5 µm). The gap between I-RDX® and VI-RDX is equivalent to the one between "standard" RDX and I-RDX®.

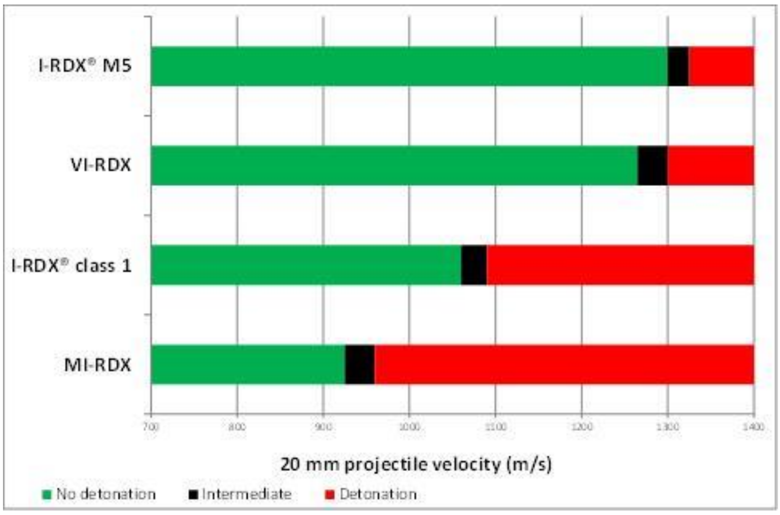

Figure 3: Shock sensitivity of MI-RDX, I-RDX® and VI-RDX – 20 mm projectile impact experiment

1.2.4 LSGT on PBXN-109 composition

In order to compare the new grade VI-RDX to MI-RDX and I-RDX®, a PBXN-109 composition has been prepared from the VI-RDX produced at EURENCO pilot scale. We got good process ability and mechanical tensile properties comparable to that for I-RDX® (Table 1).

Characteristics	*Results for VI-RDX*	*Results for I-RDX®*
Density (kg/m^3)	1696	1650 / 1700
Stress (MPa)	0.54	0.33 / 0.76
Max Strain (%)	20.6	19 / 55
Shore Hardness	61	44 / 64

Table 1: Mechanical properties of PBXN-109 with VI-RDX

LSGT test has also been performed. The figure 4 shows the results for the various grades of RDX, MI-RDX, I-RDX® and VI-RDX.

It is well known that I-RDX® grade significantly reduces the vulnerability of the PBXN-109 composition towards shock. VI-RDX slightly improves the vulnerability towards shock for the same composition.

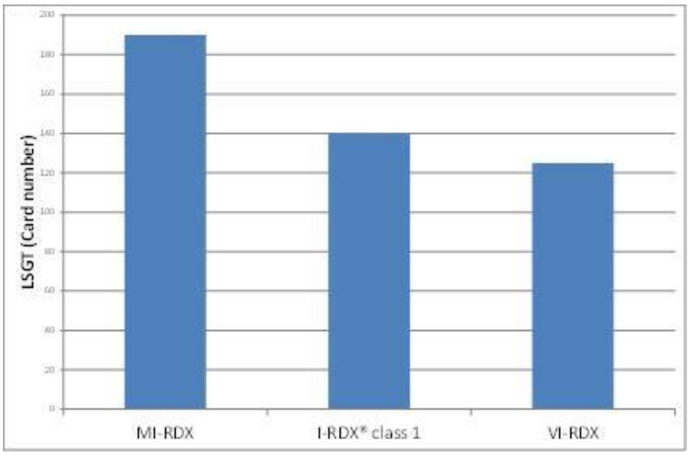

Figure 4: LSGT on PBXN-109 compositions for various grades of RDX

2 Crystallization of Various grades of NTO

In the field of Insensitive Munitions, EURENCO put a lot of effort on the development of compositions adapted to melt cast process. EURENCO IM compositions are mostly based on less sensitive explosives such as NTO and GUDN. Concerning NTO based compositions; EURENCO has developed optimized IM compositions using a high quality grade of NTO specifically adapted to high NTO content. This new grade is called NTO CF.

2.1- Production

EURENCO NTO standard production leads to two grades of coarse crystallized material, Class 1 and Class 2, (with a mean diameter around 450 µm for the class 1 and 350 µm for the class 2) and two grades of fine milled material, Class 3 and Class 4 (with respectively a mean diameter of around 50 µm and 12 µm). In most cases, these qualities are suitable for low NTO content Ontalites, either based on one grade (coarse) or on a mix of two grades (usually Class 2 + Class 3) of NTO with some adjustment between coarse and fine granulation.
But for very high NTO content, viscosity may be a real problem for casting and a special NTO quality may be recommended.
NTO CF is obtained from a controlled crystallization process. The crystallization parameters have been set up at lab scale and then validated at pilot scale.
NTO CF is now produced at the industrial scale. The improved process conditions yield to NTO with a high bulk density (more than 900 kg/m^3) which is a key parameter to lower the viscosity of the composition. The bulk density is perfectly controlled from pilot scale to industrial scale as shown in table 2.

Production scale	*Bulk density (kg/m^3)*	
	Average	*Standard deviation*
Pilot	934	17
Industrial	935	18

Table 2: Bulk density of NTO CF – From pilot scale to industrial scale

Moreover, the morphology is particularly appropriate for melt cast use (See figure 5).

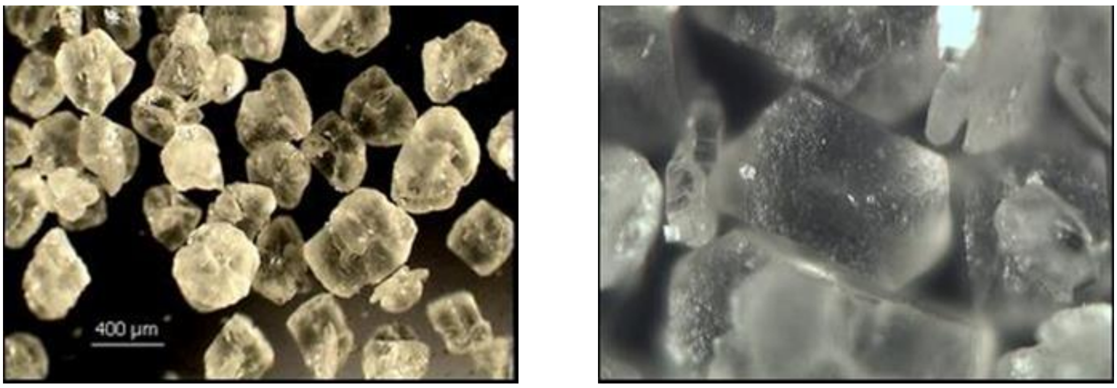

Figure 5: NTO CF – A high quality grade of NTO

2.2 Benefit of NTO CF on the viscosity of Ontalites

2.2.1 Non aluminized Ontalites

The viscosity of the composition is very dependent on the ratio between the coarse (Class 2) and the fine (Class 3) fraction. For example, if instead of NTO CF, regular NTO is used, the viscosity of the composition is more than twice higher for the Ontalite 65/35.

2.2.2 Aluminized Ontalites

In order to prove the benefit of NTO CF, aluminized Ontalites (NTO/TNT/Al/Wax : 40/30/20/10) were prepared at lab scale from different grades of NTO: NTO CF and a mix of NTO Class 2 and Class 3. The Efflux viscosity was measured on the compositions. It was shown that NTO CF significantly decreases the Efflux viscosity of the aluminized Ontalites (See table 3). Furthermore, no decantation has been observed on the melt compositions.
These results have been confirmed on NTO first produced at the pilot scale and then at the industrial scale.

Production scale of NTO CF	*NTO*	*Efflux Viscosity (s.)*
Lab scale	Class 2 / Class 3 : 70/30	8
	NTO CF : 100%	2
Pilot scale	NTO CF : 100%	2.6 / 2.9
Industrial scale	NTO CF : 100%	From 2.8 to 3.8

Table 3: NTO CF – Impact on the Efflux viscosity of aluminized Ontalite

3- New technique for manufacturing of small particle size FOX-7 for propellants

FOX-7 is 1,1-Diamino-2,2-dinitroethene (FOX-7) is an insensitive high power energetic material developed by The Swedish Defense Research Establishment (FOI) in the late 1990s and today produced by EURENCO Bofors AB in Sweden. Due to small-scale production, the cost of FOX-7 is relatively high, but since the production is based on commercial starting material and the synthesis is uncomplicated, the price will fall when production scale increases.

Theoretical studies predict that the performance of FOX-7 exceeds that of RDX. Since it is significantly less sensitive, particularly to impact and frictions stimuli, FOX-7 is an attractive ingredient for application in high performance, IM-compliant explosive compositions. Increasing the burning rate in propellants more than RDX does FOX-7 can also be used as a main ingredient of high performance propellants for tank ammunition.
EURENCO has since long been able to provide customers with four different grades of FOX-7, NSF 110 (20-40 µm), NSF 120 (50-100 µm), NSF 130 (100-200 µm) and NSF 140 (250-350µm), see figure 6.

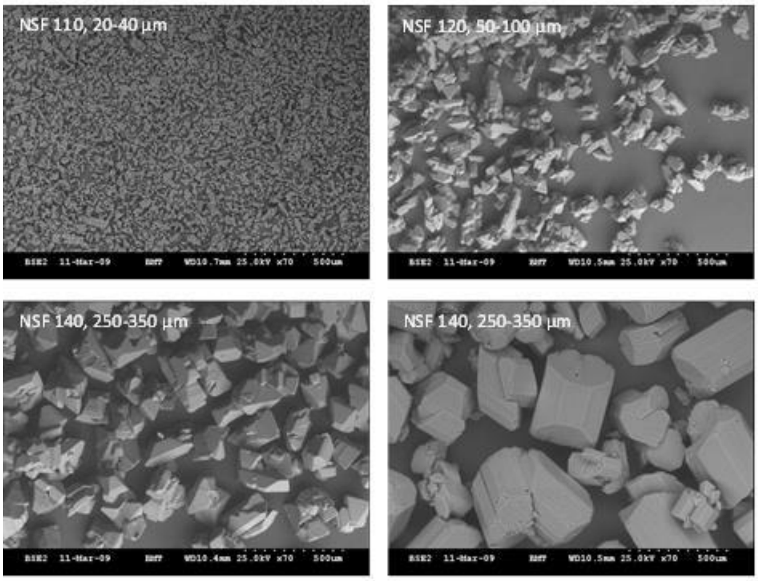

Figure 6: Fox-7 particles, magnification x200

To be able to meet customer demands for even smaller particles, the company has now further developed the particle production technique. Thanks to a new precipitation process, we are today able to produce particles with a size distribution of 3-15µm, see figure 7. The process is not yet fully scaled up, but samples and smaller quantities are available.

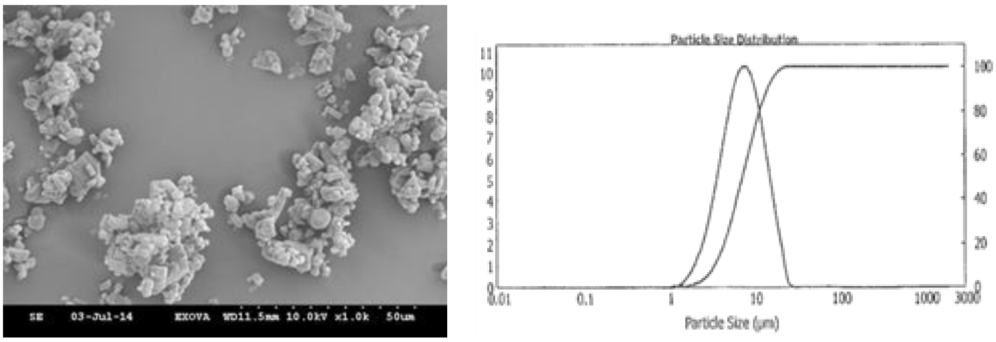

Figure 7: FOX-7, magnification x500 and particle size distribution

4- Conclusion

EURENCO is mastering the full range of Energetic Materials technologies, from new molecules syntheses to advanced processes such as crystallization.

Based on its knowledge on crystallization, EURENCO can offer to customers various grades of granular products such as:

- RDX: from standard RDX (MI-RDX) and the well-known I-RDX® to the new VI-RDX (Very Insensitive RDX) produced at pilot scale.VI-RDX shows round and smooth particles with very few internal defects and a shock sensitivity, measured on a cast composition, much better than MI-RDX and I-RDX®.

- NTO: In addition to the standard qualities (Classes 1, 2, 3 and 4), a new grade is available at industrial scale specially designed for melt cast composition with a high NTO content.
- FOX 7: This insensitive high power energetic material is now available in a wide range of granulations that fulfill perfectly the customer demands.

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