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Ageing of reduced sensitivity RDX and compositions based on reduced sensitivity RDX, an update

by

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1-**Introduction**

In the field of Energetic materials, Cyclotrimethylene Trinitramine (RDX or Research Development eXplosive), since its discovery (Second World war) has been extensively used in military applications because of ease of manufacture, acceptable low cost, and good performances.

It is only in recent years, that a quality of reduced sensitivity RDX, called I-RDX® has been described. This quality of RDX, when incorporated in cast Plastic Bonded Explosives compositions (cast PBX) such as PBX N 109, confers reduced shock sensitivity as acknowledged by gap test as measured for example on :

-US cast PBX: PBX N-109, PBXN-108, PBXAF-108, PBXN-111,
-French Cast PBX: HBU88, B2211, B2213

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Reduced Sensitivity RDX have since then been described by other producers because such a quality of RDX is of interest to the Insensitive Munitions community who strives toward reducing the vulnerability of Munitions.

The use of less sensitive munitions is really of importance as it makes ammunition less vulnerable towards all type of stimuli and that is why most of NATO countries have adopted IM (Insensitive Munitions) policies for their armament, in order to save live and material, plus enhance military capabilities.

The first example of Reduced Sensitivity RDX was given with a grade of RDX called I-RDX® produced by EURENCO (a subsidiary of SNPE group), and obtained by a specific and unique recrystallisation process ; this product has been industrially produced at Sorgues plant for more than 40 years…

This insensitive character of I-RDX® has been proven to be highly reproducible as acknowledged on HBU88, B2213 and PBXN-109 (as illustrated for PBX N 109 in table 1).

Table 1

Name	composition	sampling	Barrier pressure (Mean value)	Standard deviation
PBXN-109	I-RDX® = 64% Al = 20 % HTPB = 16 %	15 different lots of I-RDX tested during 2002-05	53.7 kbar (51.2-56.4)	2 kbar

This proven reproducibility is of very high interest for the development of Insensitive Munitions (IM).

It is also of major interest to be sure that the lower shock sensitivity is maintained through ageing.

It has been proved that for cast PBX compositions prepared with I-RDX®, there is no change of shock sensitivity as measured by NOL-LSGT, as well for compositions prepared with aged RDX as for compositions prepared with “fresh” raw material [1].

On the contrary, in the case of RDX produced by the Bachmann process, there are evidences of reversion of shock sensitivity [1].

These results are consistent with behaviour already observed by Eglin and Picatinny on new melt cast formulations and also on PBX N 109 either prepared with Holston crystallized RDX or Woolwich (Royal Ordnance, UK) RDX recrystallised in presence of HMX [2].

Results obtained on PBX N-109 do show [2] that elevated temperature and humidity does not appear to be affecting the mechanical properties in PBX N-109 but does appear to be affecting the shock sensitivity of the explosive.

What are the properties of RDX that form a basis for the alteration with time of the shock sensitivity in cast PBX? is it linked to the Bachmann process ?

One hypothesis is that the reversion of shock sensitivity may be linked to the presence of HMX.

We will present in this paper the results of studies done to try to understand what may be the role of HMX.

2-Influence of the presence of HMX in RDX

We will distinguish two different cases:

-HMX is just “mechanically “added to already crystallised pure I-RDX®,

or

-HMX is added before the crystallisation step, we will call it HMX co crystallised with RDX (which is in fact the case for RDX prepared by the Bachmann process).

2.1-HMX added to I-RDX®

A PBX N 109 composition has been prepared with standard I-RDX® in which some HMX has been added (2% level).

The shock sensitivity of this composition has been measured (NOL-gap test) on freshly prepared composition and after ageing (3 months at 60°C). The results are presented in table 2

Table 2

Composition	LSGT result	remarks
PBX N 109 2% HMX added	53.7 kBars	T0
	51.2 kBars	3 months at 60°C

In this case, there is no evidence of alteration of shock sensitivity after ageing.

2.2-HMX co crystallised with RDX

In order to measure not only the influence of HMX co crystallised with RDX, but also the influence of its concentration in starting material, two levels have been evaluated (0.5 % and 5% of HMX).

HMX (0.5 and 5%) has been added to crude Woolwich RDX before crystallisation step; the products obtained are described in paragraph 3.

A PBX N 109 composition has been prepared with each of the two products, and the shock sensitivity of these compositions has been measured (NOL-gap test) on freshly prepared composition and after ageing (3 months at 60°C). The results are presented in table 3

Table 3

Composition	LSGT Result		
	Initial	After 3 months at 60°C	
PBX N 109	53.7	51.2	0.5%HMX
	40.4*	44.4	5% HMX

*Measured after 3 months at RT

The PBX N 109 prepared with RDX co crystallised with 5 % of HMX is more shock sensitive. From results presented in paragraph 3, we do have evidence of evolution after ageing in this case.

The result of shock sensitivity on a PBX N 109 composition prepared with aged RDX (co crystallised with 5% HMX) will be presented.

2.3-discussion

From the results presented here, it appears that:

-If HMX is mechanically added to I-RDX®, there is no evidence of alteration of shock sensitivity even after ageing.

-If HMX is present during the crystallisation process, even starting with Woolwich RDX, there may be alteration of shock sensitivity.

This alteration is only observed for high levels of HMX, and an explanation is to be proposed in paragraph 3.

What may explain this behaviour?
In order to find answers, work at crystal level has been realized.

3- Studies at crystal level

3.1-Origin of the low shock sensitivity of I-RDX®

If low shock sensitivity is acknowledged on cast PBX, the intrinsic characteristic (s) of crystal responsible of the lowering of shock sensitivity of cast PBX based on I-RDX® is not known despite all the efforts to find a correlation between a crystal property (or a set of crystal properties) and response to shock stimuli in the composition.

A technical meeting on reduced sensitivity RDX under the authority of AC 1326 subgroup I, and assisted by NIMIC, was held in MEPPEN end of 2003 [3]. Its objective was to consider possible techniques to allow discrimination of the normal and insensitive grades.
It led to the proposal of the organization of a Round Robin inter-laboratory study to examine a suitable test method or methods to distinguish the reduced sensitivity form of RDX.
There will be a technical meeting to be held just before 2006 IMEMTS meeting to review the results obtained in the Round Robin inter-laboratory study and a presentation will be given during the 2006 IMEMTS meeting.

If reversion of shock sensitivity after ageing (for Bachmann based RDX and more generally HMX co crystallised with RDX) also seems to be acknowledged, the intrinsic characteristic(s) of crystal responsible is (are) also to be determined.

3.2- Physico-chemical characterization of crystals

The three different qualities of RDX involved in this study are:

- I-RDX® (with 2% HMX "mechanically" added)
- Co crystallised Woolwich RDX with 0.5 % HMX
- Co crystallised Woolwich RDX with 5% of HMX

The I-RDX® is to be considered as representative of industrial standard production quality and has been already extensively described, even its ageing in presence of HMX [1].

The co crystallised products have been characterized in term of grain size distribution, HMX content (global and according to grain size), density, solvent content, internal defects (matching refractive index microscopy)…, and the results are presented in tables 4 and 5

Table 4

RDX quality	0.5% HMX	5% HMX	I-RDX®*
Melting point (°C)	205	203	205
Acidity (%)	0.01	0.01	< 0.01
Insolubles (%)	0.01	0.02	0.01
Inorganics (%)	≤ 0.01	0.02	≤ 0.01
Inoluble Particules (%) > 0.40 > 0.25	0 0	0 0	0 0
Sieve granulation (% pass) > 0.800 > 0.315 > 0.149 > 0.074	0 1 61 75	0 1 65 81	0 1 64 75
Laser granulation mean (µm)	223 (figure 1)	222 (figure 2)	248 (/)
Density (kg/m^3)	1.7965	1.8040	1.796
Solvent content (ppm)	350	520	350
Matching refractive Index microscopy	Figure 3	Figure 4	/

*typical values

Table 5

RDX	HMX content (%)			
	0.5% d'HMX		5% d'HMX	
global	0.29-0.52		4.7-5.5	
By Sieve fraction	Mass %	HMX (%)	Mass %	HMX (%)
> 800µm	0	/	0	/
315-800µm	0.8	0.09	0.6	0.94
150-315µm	64.6	0.61	66.3	2.42
80-315µm	20.5	0.54	17.0	5.00
< 80µm	14.1	1.05	16.1	12.55

Discussion

The co crystallised products, except for the HMX content, are very similar from the physico-chemical point of view: very comparable granulation, same level of internal defects.

The HMX content according the sieve fraction, do show that HMX is mainly, but not exclusively in the fines. The higher content in the fines is consistent with the fact that crystallisation of HMX (due to its lower content and also lower solubility) do occur lately in the crystallisation process.

Therefore, HMX crystallisation will occur earlier when there is 5% than when there is only 0.5 %; and we may have here a reason for the difference in behaviour of cast PBX in LSGT test.

How do crystallise HMX ? totally separately from RDX ? or is there any co crystallisation occurring ? This point will be discussed in paragraph 3.4.

3.3-Advanced Characterisation methods

A Differential Scanning Calorimetry (DSC) method has been developed in order to distinguish in between regular and insensitive RDX at crystal level.

Conditions have been found that allow to make a difference in between the different qualities of crystallised RDX and examples of DSC for normal and insensitive RDX are given in figures 5 and 6.

Based on peak temperature of decomposition, in these conditions, it is possible have a correlation with LSGT results on PBX N 109 composition as exemplified in figure 7.

This method has been applied to the products of the present study, and the results are presented in table 6

Table 6

RDX quality	Ageing conditions for RDX crystals	Number of cards estimated by DSC on RDX crystals	LSGT result (number of cards) measured on PBX N 109
I-RDX®	/	130	140
0.5 % HMX	To	< 130	140
	6 months RT	145	/
	3 months 60°C	/	145
5% HMX	To	< 130	/
	3 months RT	/	170
	3 months 60°C	/	160
	6 months RT	170	/
	6 months 60°C	195	/

RDX co crystallised with 5 % HMX, has been found by this technique, insensitive when freshly prepared, and to present reversion of shock sensitivity with time.

It has been shown [1,4] by Nuclear Quadrupole Resonance spectroscopy (NQR) a correlation between the crystal quality and shock initiation pressure of the corresponding cast PBX. Additional results obtained by this technique will be presented.

3.3-HMX localisation,

Additional effort has been done to try to answer to the question: how is HMX distributed when we do have co crystallisation with RDX.

Is there any HMX included in the RDX crystal.

Work done by DSC on isolated crystals shows, based on the endotherm at 190°C and attributed to the RDX/HMX eutectic that to some extend, there is evidence of RDX/HMX co crystallisation (figure 8). Corresponding results will be presented.

We may have here a reason for higher sensitivity to shock of Bachmann RDX and more generally co crystallised RDX with HMX. A minimum percentage of HMX appears to be necessary to degrade the shock sensitivity of RDX.

4-Conclusions

Eurenco (a subsidiary of SNPE), through a specific recrystallization process, produces industrially, with very high reproducibility a unique, low shock sensitivity RDX called I-RDX®

The low shock sensitivity of cast PBX conferred by I-RDX®. is of great value for the development of insensitive munitions.

It has been previously shown:

- for I-RDX®. that:ageing of the raw material itself and cast PBX compositions prepared either with fresh or aged I-RDX®. do not alter in any case the low shock sensitivity of the cast PBX compositions,

- and for recrystallised RDX from Bachmann process, we may have alteration of shock sensitivity after ageing.

The present study do show that:

-Co crystallisation of Woolwich RDX with HMX may also lead to more sensitive RDX, so HMX present at the crystallisation step may be a factor of instability, Bibliography

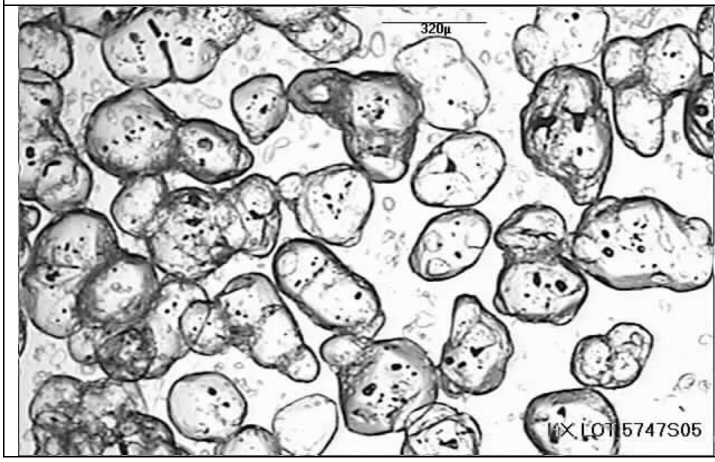
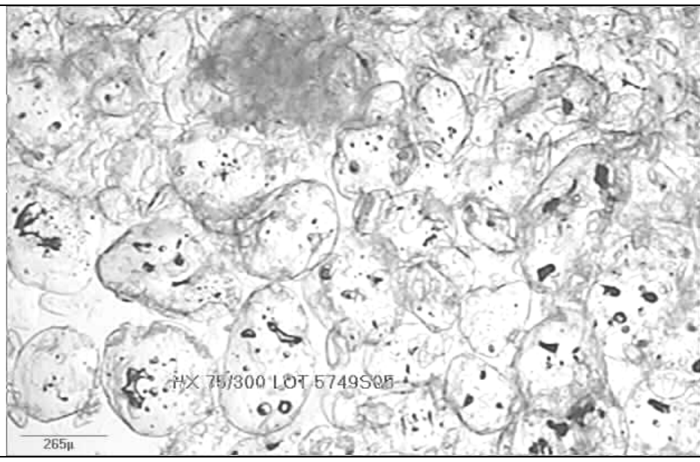
[1]C. SPYCKERELLE, A. FRECHE and G. ECK, Ageing of I-RDX®. and of compositions based on I-RDX®., 2004 Insensitive & Energetic Materials Technology Symposium, San Francisco, November 15-17, 2004

[2]M. BEYARD, variations of PBX N-109 shock sensitivity, NIMIC Reduced sensitivity RDX technical Meeting Meppen 17-20th November 2003

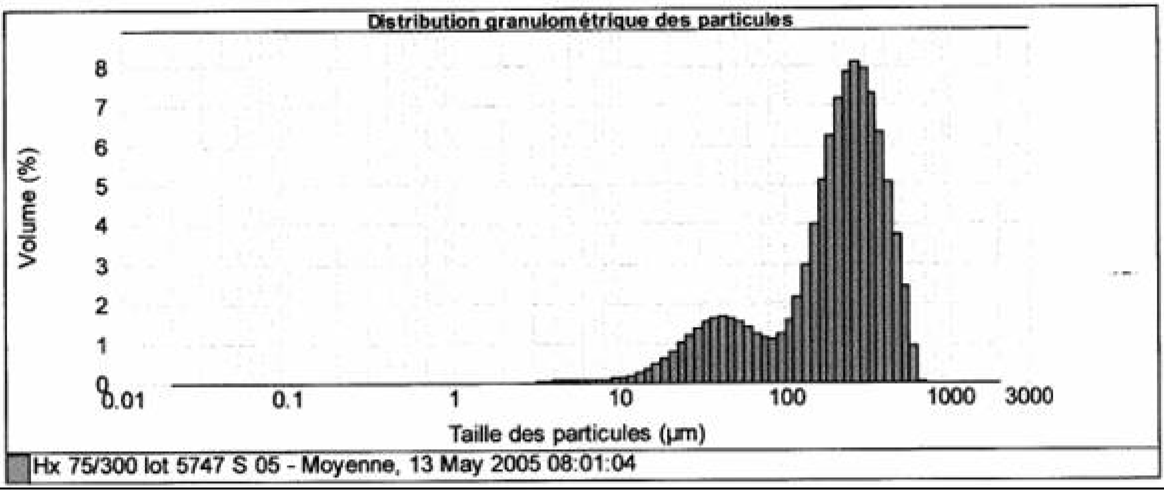
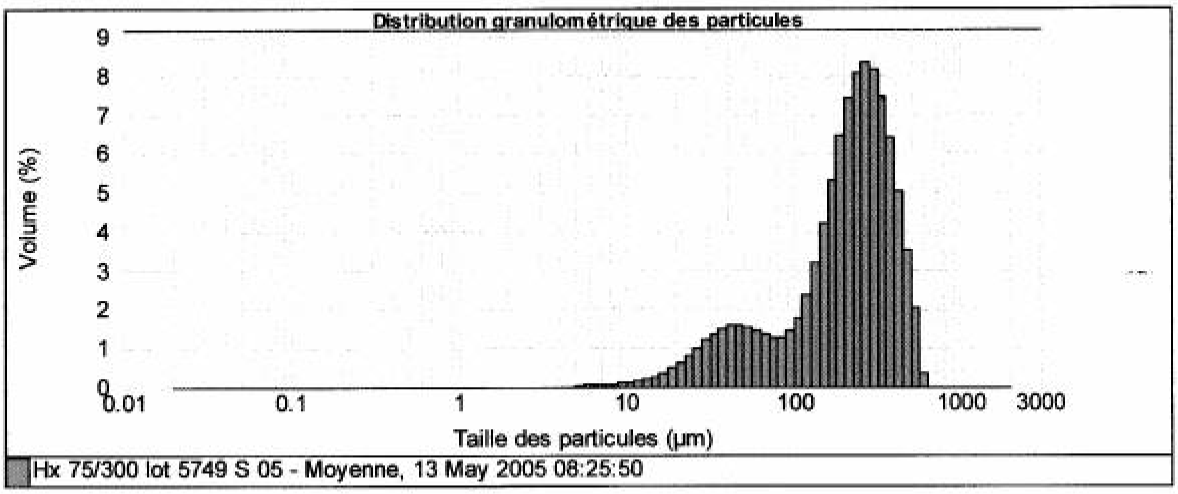
[3] Reduced Sensitivity RDX Technical Meeting, in support of NATO AC/326 SG1-Energetic Materials, 17-20th November 2003, WTD91, Meppen, Germany

[4] S.M. CAULDER, M. BUESS, A.N. GARROWAY, and P.J. MILLER, correlating RDX Nitramine Crystal quality with shock sensitivity, NIMIC Reduced sensitivity RDX technical Meeting Meppen 17-20th November 2003

Figures 1 and 2

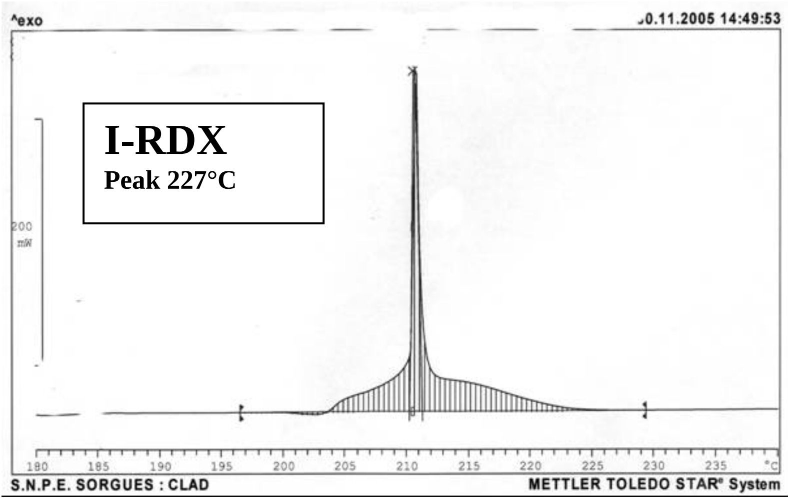
0.5% HMX	5% HMX
	

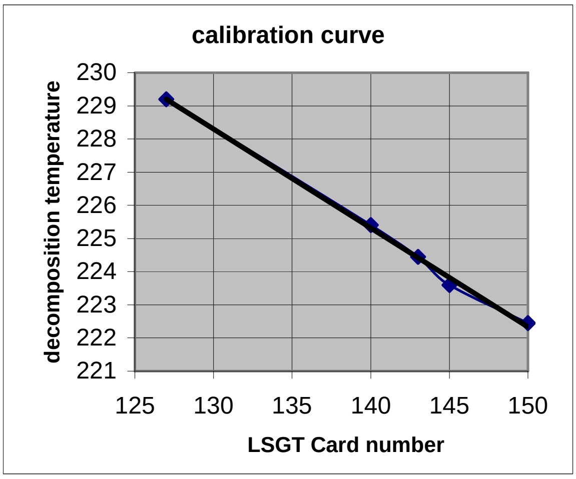
Figures 3 and 4

0.5% HMX

5% HMX


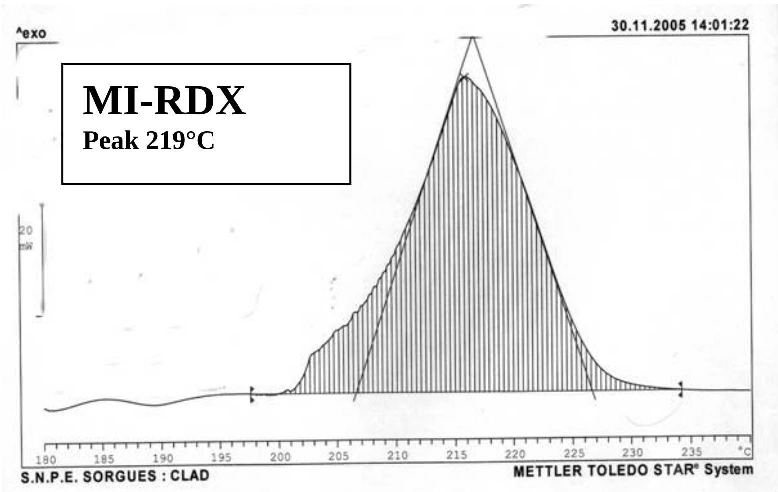
Figures 5, 6 and 7

I-RDX ®





MI-RDX



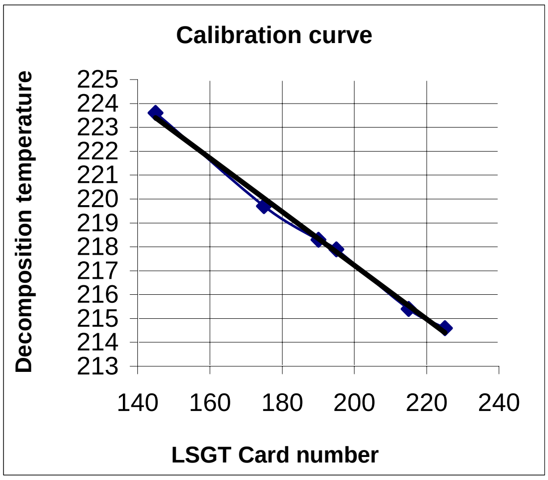


Figure 8 : DSC analysis (search for HMX)

Pure I-RDX ®	RDX + 0.5% HMX	Isolated Crytals of RDX from RDX/HMX co crystallisation