

Investigation of the effect of ageing of RDX containing HTPB and GAP bonded high explosive charges on their thermal and shock sensitivity

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Results from the German part of the EDA Project Insensitive Munitions and Ageing' (IMA) 'B 0219 GEM2 ERG'

Abstract

Insensitive ammunition is intended to reduce the collateral damage that, for instance, occurs as a result of fire or bullet impact on ammunition during transport and storage in battle field environments. In the framework of the project »Insensitive Munitions & Ageing« of the European Defense Agency (EDA) researchers were investigating the aging of a variety of energetic materials with respect to changes in sensitivity against thermal and shock impact threads. Six contributing European countries worked together on this project: France (was also project-leading country), Germany, The Netherlands, Sweden, Finland, Czech Republic. This paper presents the German part. The other parts can be found in these proceedings under the paper numbers 11, 12, 13, 14, 16, 17.

The German part concentrated on high explosive charges manufactured with two types of RDX, of different sensitivity. Four charges have been manufactured at Fraunhofer ICT:

- Standard RDX bonded with HTPB-IPDI and DOA as plasticizer;
- Insensitive RDX bonded with HTPB-IPDI and DOA as plasticizer;
- Standard RDX bonded with GAP-N100 and BDNPF_A as plasticizer;
- Insensitive RDX bonded with GAP-N100 and BDNPF_A as plasticizer.

All four charges used bimodal particle size distributions of the RDX types. The so-named

standard RDX (named S-RDX) was obtained from Dyno Industrier Norway, the insensitive RDX (I-RDX™) as well as the GAP (glycidyl azide polymer) diol was purchased from Eurenco, Sorgues, France. The HTPB (hydroxyl terminated polybutadiene) was of quality R45M obtained from Sartomer. The isocyanates are from company Bayer (now Lanxess), Germany. To assess thermal sensitivity ARC (Accelerating Rate Calorimetry) and heat flow microcalorimetry (HFMC) were used. To test shock sensitivity two methods have been applied: (i) the ICT 21 mm gap test with cylindrical samples, 21 mm in diameter and 42 mm long; (ii) the ISL bullet impact test with cylindrical samples, 30 mm in diameter and 50mm long, instrumented to record the travel times of the shock wave inside the sample. The samples with these geometries required have been manufactured and aged at Fraunhofer ICT. For the thermal tests no specified geometry was necessary.

For the ageing, the ageing plan was designed using the general van't Hoff (GvH) rule and the principle of Thermal Equivalent Load (TEL). The gap test samples were aged at 80°C and 90°C with the following ageing times and the corresponding times at 25°C:

80°C: 0 days, 16 days, 35 days, 60 days
Corresponding in years at 25°C with factor 2.5 in GvH rule
25°C: 0 years, 6.8 years, 15 years, 25 years

90°C: 0 days, 6 days, 15 days, 25 days
Corresponding in years at 25°C with factor 2.5 in GvH rule
25°C: 0 years, 6.3 years, 16 years, 26 years

The bullet impact samples were aged only at 80°C at the same ageing times as for the gap test samples. The ageing was performed in desiccators in air with the samples tightly wrapped in aluminium foil. The ageing in air was chosen to have the worst case situation. Ageing in air should lead to a hardening of the HTPB bonded samples, which may have a negative influence on the shock sensitivity. The hardening of all samples was found in determining the Shore A hardness.

For the thermal sensitivity the samples have been aged in argon and in air. Differences have been found between S-RDX and I-RDX bonded in HTPB-IPDI, but only small changes with GAP-bonded charges. It seems that in argon the decomposition is generally a bit faster than in air and that I-RDX formulations react somewhat faster than S-RDX formulations. The shock sensitivity has not changed in all cases. This has been found with gap test and with bullet impact test.

Keywords

Ageing sensitivity of RDX charges; I-RDX, ageing according to general van't Hoff rule; ARC, heat flow microcalorimetry for thermal sensitivity; shock sensitivity by gap test and bullet impact.

1. Abbreviations

ICT	Fraunhofer Institute for Chemical Technology
ISL	German-French research institute Saint Louis
AIT	autoignition temperature, determined at 5°C/min or at 20°C/min heat rate in wood metal bath
ARC	Accelerating Rate Calorimeter
BDNPA_F	1 :1 mixture of bis(2,2-Di-Nitro Propyl) Acetal and bis(2,2-dinitropropyl) Formal, energetic plasticizer or energetic liquid filler
DMA	Dynamic mechanical analysis
DOA	dioctyl adipate, plasticizer
DSC	differential scanning calorimetry;
EFP	explosive formed projectiles
GAP	glycidyl azide polymer, energetic binder
GvH	generalized van't Hoff rule
HA	shore A hardness
HEC	high explosive charge
HFMC	heat flow microcalorimetry, performed with microcalorimeters
HG	heat generation Q
HGR	heat generation rate dQ/dt
HTPB	Hydroxyl terminated polybutadiene, pre-polymer, binder
IPDI	isophorone diisocyanate, curing agent for HTPB
N100	polyisocyanate, curing agent for GAP
NQR	nuclear quadrupole resonance
PID	proportional-integral-differential, temperature control algorithm
Qex	heat of explosion
RDX	Hexogen, energetic filler
SA	sample amount
SCJ	shaped charge jet
VST	vacuum stability test, standard stability test performed in vacuum

2. Introduction

Insensitivity of ammunition against impacts by bullets, fragments, EFP (explosive formed projectiles), SCJ (shaped charge jet) and thermal threats (all types of cook-off) is an ongoing demand. To achieve this demand two ways are possible: (i) mitigation of the threats by construction measures; (ii) sensitivity reduction of the energetic materials

against the impacts. Probably the best is to combine both lines. After finding an insensitive energetic material for use in ammunition the question arises, if its insensitivity is maintained during the in-service time period. This is the question about the ageing behaviour of insensitive energetic materials. Investigation methods should be sensitive to changes in thermal and shock sensitivity. Further on, methods should be found, which could be used for understanding of changes.

3. Investigated sample materials

Four high explosive charges (HEC) were manufactured at ICT.

GAP-N100 bonded I-RDX and GAP-N100 bonded S-RDX

75% RDX (I-RDX or S-RDX),

15% binder GAP - N100 + 10% plasticizer BDNPF_A

HTPB-IPDI bonded I-RDX and HTPB-IPDI bonded S-RDX

80% RDX (I-RDX or S-RDX),

12% binder HTPB (R45M) - IPDI + 8% plasticizer DOA + antioxidant (AO)

Used lot names of the high explosive charges (HEC)

GHX 147 I-RDX-GAP-N100-BDNPA_F
 GHX 148 S-RDX-GAP-N100-BDNPA_F
 HX 458 S-RDX-HTPB-IPDI-DOA + AO
 HX 459 I-RDX-HTPB-IPDI-DOA + AO

I-RDX and S-RDX were applied with particle sizes of class 1 and 5 to form bimodal high explosive charges. It has to be noted that I-RDX is produced by the Woolwich process, therefore nearly no HMX is formed as side product in RDX. On the other hand the S-RDX from Dyno (now Chemring, Saetre, Norway) was produced by the Bachmann Process, by which an appreciable amount of HMX can occur as side product in RDX, up to 10 mass-%.

Table 3.1: Data on the used RDX qualities

RDX type		Mean particle size [µm]	R friction [N]	S impact [Nm]	HMX content [mass-%]
RDX from SME - Eurenco (produced according to Woolwich process)					
I-RDX, class 1	coarse	225	96	7.5	0.01
I-RDX M3C, class 5	fine	10.5	112	7.5	0.01
RDX from Dyno (Chemring) (produced according to Bachmann process)					
S-RDX, Type I, class 1	coarse	195	160	7.5	0.84
S-RDX, Type I, class 5	fine	17.6	168	10	0.52

4. Basic stability test data of the HEC

The Table 4.1 summarizes the basic stability data and the values on impact and friction sensitivity. There is no real influence from the two RDX types recognizable. Only for GHX 147 the impact sensitivity seems better than with the other materials. The VST data for the GAP bonded formulations are a little higher than for the HTPB bonded formulations. This is caused by the energetic binder GAP, which contributes to the gas generation. But all VST data are far below the limit value, which is here 2 ml/g gas evolution.

Table 4.1: Basic stability data and values and on impact and friction sensitivity.

Test method	unit	GHX 147	GHX 148	HX 458	HX 459
AIT at 5°C/min	°C	215	214	210	211
AIT at 20°C/min	°C	228	227	224	223
Impact sensitivity S (BAM method)	Nm	20	15	15	15
Friction sensitivity R (BAM method)	N	324	324	358	358
VST at 100°C 40 h (STANAG 4556)	ml/g	0.063	0.074	0.025	0.008

AIT autoignition temperature; determined in Wood metal bath with 0.2 g sample amount, forced heating starts at 100°C; performed with two heating rates in air.

VST vacuum stability test, standard method to determine chemical stability via gas generation in vacuum. The evolved gas volume per g sample amount is given at standard conditions (0°C, 1 atm); condensable volatiles as water are nearly without influence in final result.

S limit impact energy causing ignition or burning.

R limit friction force causing ignition or burning.

5. Performed ageing

The two RDX types each comprising of two samples (fine and coarse) were aged as well as the four HEC formulations. The HEC formulations were aged in exsiccators only in air by heating them in oven cabinets. The samples for bullet impact (30mm in diameter, 50 mm long) were aged only at 80°C and only the samples with I-RDX were used. For the gap test of the HEC samples (21mm in diameter, 42 mm long) the ageing was performed at 80°C and 90°C also in air only but with all four HEC formulations.

The RDX samples were aged under air and under argon. The ageing under argon simulates the inner bulk material, to which nearly no oxygen will penetrate. The argon was applied to the vials via a high performance glove box with very low residual oxygen content in ppm range. The material was placed in small vials inserted in bigger ones with 30 mm inner diameter, which have been placed in PID temperature controlled aluminium ovens, see Fig. 5.1 and Fig. 5.2.

Table 5.1: Overview on applied ageing temperature and ageing times. The ageing times have been determined with the Generalized van't Hoff (GvH) rule on the base of the principle of the Thermal Equivalent Load (TEL) /1/. The TEL corresponding times at 25°C are given also.

RDX samples (all four)

Accelerated ageing at	90°C:	15 d	30 d	under air <i>and</i> argon.
Corresponding years at	25°C:	15	25	calculated with GvH, F=2.5
Corresponding years at	25°C:	52	104	calculated with GvH, F=3.0

HEC sample

Test bodies (30 mm in diameter, 50 mm long) for flat projectile impact at ISL, only the I-RDX containing HEC types

Accelerated ageing at 80°C:	16 d	35 d	60 d	in air
Corresponding years at 25°C:	6.8	15	25	calculated with GvH, F=2.5

Test bodies (21 mm in diameter, 42 mm long) for gap-test at ICT; all four HEC types

Accelerated ageing at 80°C:	16 d	35 d	60 d	in air
Corresponding years at 25°C:	6.8	15	25	calculated with GvH, F=2.5

Accelerating ageing at 90°C:	6 d	15 d	25 d	in air
Corresponding years at 25°C:	6	15	25	calculated with GvH, F=2.5

DMA test samples (50 mm long, 10 mm wide, 4 mm thick), aged in the shape of the test samples.

Accelerated ageing at 90°C:	7 d	13 d	30 d	27 d	34 d	in air
Corresponding years at 25°C:	7.4	14	21	29	36;	with GvH, F=2.5

Accelerated ageing at 80°C:	17 d	33 d	50 d	67 d	84 d	in air
Corresponding years at 25°C:	7.2	14	21	28	36;	with GvH, F=2.5

Accelerated ageing at 70°C:	43 d	82 d	125 d	168 d	211 d	in air
Corresponding years at 25°C:	7.3	14	21	28	36;	with GvH, F=2.5



Fig. 5.1: Ageing of RDX samples in small vials inserted in the ageing vials. Left: ageing in air, not sealed stoppers, regularly opening of the vials to let fresh air in. Right: Ageing under argon with sealed stoppers and clamped to avoid lifting of stoppers by internal over pressure.



Fig. 5.2: Example of a PID temperature controlled aluminium block oven for ageing of samples in vials.

6. Applied investigation methods

The Table 6.1 lists the investigation methods used and the institution where the method was performed.

Table 6.1: Investigation methods and performing institution. For ARC, HFMC, heat conduction, shore hardness as samples the test bodies from gap test were taken

Method	Purpose / what to investigate	done at
<i>For I-RDX and S-RDX</i>		
Ageing	to simulate ageing during in-service	ICT
ARC	Thermal decomposition behaviour, suitable for the discrimination between the RDX qualities	ICT
HFMC	Thermal decomposition behaviour	ICT
DSC measurements	Thermal decomposition behaviour	ISL
Density measurements	Changes can influence cook-off and may indicate defect healing	ISL
X-ray scattering	Crystallite analyses for strain and defects	ICT
NQR measurements	Changes in defect structure with ageing	ISL
<i>For the HEC GHXsss and HXsss</i>		
Ageing	to simulate ageing during in-service	ICT
ARC	Thermal decomposition behaviour > suitable for slow cook-off screening	ICT
Heat flow microcalorimetry	Thermal decomposition behaviour	ICT
DMA measurements	Glass transition range, loss factor analysis	ICT
Shore hardness	Surface changes	ICT
Heat conductivity	Changes could influence cook-off behaviour	ICT
Gap-Test (21 mm in diameter)	Shock sensitivity, with detonation pressure as probing parameter	ICT
Instrumented projectile impact	Shock sensitivity, with projectile velocity (impact energy) as probing parameter	ISL

ARC	Accelerating Rate Calorimetry, to determine adiabatic selfheating;
DMA	dynamic mechanical analysis, mechanical behaviour in linear deformation range;
DSC	differential scanning calorimetry;
HFMC	heat flow microcalorimetry, performed with microcalorimeters from TA Instruments (type TAM II and TAM III);
NQR	nuclear quadrupole resonance;

7. Summarized results

Ageing of all RDX samples in air and in argon

I-RDX: significant colour changes in both atmospheres, aged samples become darker;

S-RDX: clearly less change in colour, they become only slightly darker;

Results related to thermal sensitivity obtained with DSC at very small heat rate no (0.1 °C/min)

No ageing influence with I-RDX;

slight change with S-RDX coarse, but the decomposition is shifted to higher temperatures (formally an improvement);

Results from NQR measurements with I-RDX and S-RDX, aged in argon and air

No ageing influence with I-RDX and S-RDX recognizable;

Results of adiabatic self heating (ARC) with the RDX samples

Clearly recognizable differences between S-RDX and I-RDX;

the two S-RDX samples, coarse and fine, have lower onset temperatures than I-RDX samples; coarse and fine S-RDX are distinguishable, coarse has lower onset temperature than fine; coarse and fine I-RDX have nearly the same onset temperature;

Results of adiabatic self heating (ARC) with the HEC formulations

HEC with HTPB binder:

differences with formulations containing I-RDX und S-RDX,
with I-RDX the decomposition starts at higher temperatures;

HEC with GAP binder

differences between formul. with I-RDX and S-RDX are small,
GAP determines the decomposition;

Shore A hardness (HA) (determined with the gap test an projectile impact bodies)

Difference in hardness between GAP-N100 and HTPB-IPDI samples;

GAP-N100 formulations have higher hardness;

the trend in ageing behaviour is different between the two binders

GHXsss initial HA(0): 62.2; final HA(te): 64.7 reaches a plateau value

HXsss initial HA(0): 41.7; final HA(te): 44.7 continues to increase.

Results from heat conduction measurements with the test bodies of projectile impact

No ageing influence found.

Results from DMA measurements

No influence on loss factor curve by the type of RDX. However, strong influence of the binder.

X-ray (Röntgen) diffraction

fine RDX S-RDX: first the distortions (tension) increase then they decrease;
I-RDX: distortions (tensions) are relieved steadily;

coarse RDX S-RDX: tension producing distortions increase steadily;
I-RDX: distortions are relieved steadily;

Microcalorimetric measurements with HFMC

Decomposition of I-RDX is somewhat faster in argon compared to air;
 The same holds for the I-RDX-HTPB formulation;
 S-RDX-HTPB formulation decomposes more slowly than I-RDX-HTPB formulation.

Density distributions (only coarse RDX lots studied)

No significant changes with I-RDX and S-RDX
 (distribution widths: 0,007 and 0,026 g/cm³),
 but with ageing shifts of the distributions to somewhat lower values (about 0.001
 g/cm³ with both RDX types).

assumption

trapped solvent from processing diffuses out from the particles during
 ageing, but without void healing.

The kinetic of the diffusion process seems different after ageing in argon
 and air; maybe in air some oxidation occurs, which increases somewhat the
 density compared to argon ageing;

Shock sensitivity of the four formulations

21 mm gap test samples (ICT)	no ageing influence found;
30 mm projectile impact (ISL)	no ageing influence found;

from the results of gap test

S-RDX formulations are more sensitive than I-RDX formulations;

Difference in initiation pressure (no-go) about 8 kbar in 21 mm gap test with
 all four formulations.

8. Conclusion

Some micro-methods (X-ray, density distribution, adiabatic selfheating, microcalorimetry) have revealed changes with ageing. It seems that with I-RDX mainly reduction of distortion caused tension occurs but in S-RDX the distortion increases with ageing. The reasons are unclear. However these 'micro' changes with ageing seem not so effective that changes in shock sensitivity will be induced. Two tests for shock sensitivity have not revealed an ageing influence or a sensitivity change. Nevertheless it remains to find explanations for the found changes and differences between ageing in air and ageing in argon.

9 References

- /1/ Bohn M.A., "Prediction of Equivalent Time-Temperature Loads for Accelerated Ageing to Simulate Preset In-Storage Ageing and Time-Temperature Profile Loads", Paper 78 in Proceedings of the 40th International Annual Conference of ICT, Karlsruhe, Germany, June 23-26, 2009. ISSN 0722-4087. Fraunhofer-Institut fuer Chemische Technologie (ICT), D-76318 Pfinzthal, Germany.