Less Sensitive and "Green" Propellant

Charles F Wiehahn

Rheinmetall Denel Munition,
Somerset West, South Africa

Abstract

Single base propellants containing DNT (dinitrotoluene) are not IM compliant and typically fail the Bullet Impact (BI), Fragment Impact (FI) and Shaped Charge Jet Impact (SCJI) IM tests. The DNT and other ingredients such as DBP (dibutylphthalate) and DPA (diphenyl-amine) are suspected carcinogenic substances and in combination with the large quantities of solvents released into the atmosphere during the processing these formulations are not environmentally friendly or "green". We have embarked on a project to develop a less sensitive and green propellant to replace the existing SSE single base propellant. Three different propellant families were investigated as possible IM candidates to replace the present propellant formulation. In the 1st formulation the DNT was directly replaced with an increase in the DBP concentration. The 2nd formulation was a triple base formulation containing DEGDN instead of NG and the 3rd formulation contained the energetic plasticiser TEGDN. All 3 formulations processed well and were evaluated for their sensitivity and IM properties.

1 INTRODUCTION

1.1 BACKGROUND

Single base propellants that contain approximately 10% DNT are not IM compliant and are especially sensitive to shock. Such propellants typically fail the Bullet Impact (BI), Fragment Impact (FI) and Shaped Charge Jet Impact (SCJI) IM tests. The DNT, DBP and DPA these propellants typically contain are all suspected carcinogenic substances. A further problem is the large quantities of solvents released into the atmosphere during the processing of these propellants. There is a world-wide drive towards "green" propellants as well as less sensitive propellants and we have launched a project to develop a less sensitive and green propellant to replace the existing single base propellant formulation.

Various formulations were evaluated with the aim of replacing the DNT, DBP and DPA with "green" substances that are also less sensitive to shock to comply with the IM specifications as well. A further aim was to reduce or totally eliminate the large quantities of solvents normally released into the atmosphere during the processing. Three different propellant families were proposed as possible less sensitive and/or "green" candidates. In these formulations the DPA was replaced as stabiliser with EC (ethylcentralite) or Acardite II. The DNT and DBP were replaced as plasticisers with TEGDN (tri-ethylene glycol dinitrate) or DEGDN (di-ethylene glycol dinitrate). We also replaced the mechanical mixture NC (13.15% N), typically used for single base propellants, with Piro M30 type of NC (12.6% N). Although the mechanical mixture NC has more energy than the Piro M30 type of NC, it does not process as well nor does it have the same mechanical properties.

1.2 SSE/MOD-1 – SINGLE BASE PROPELLANT WITH DBP

This formulation was intended to reduce the sensitivity only and comprised a single base formulation with the DNT directly replaced with an increase in the DBP concentration and an increase in the NC concentration to maintain the required energy level. A total of 100 kg of the SSE/Mod-1 formulation was processed and the propellant dough was extruded through the standard 7 perforation SSE dies. The propellant grains were pre-dried, steeped and final dried according to standard operating procedures for SSE propellant.

The propellant grains were tested and evaluated and passed both the traditional Bergman & Junk and Methyl Violet stability tests. The energy value and the relative vivacity both comply with the standard SSE propellant specification.

1.3 TRIPLE BASE SOLVENT-FREE DEGDN PROPELLANT FORMULATION

This propellant formulation, a triple base formulation containing DEGDN instead of NG, was intended to be both "green" and less sensitive. The traditional NG type of double base formulation would be too energetic for this application and therefore the less energetic, cooler and also far less sensitive DEGDN formulation was selected. The DBP in the SSE formulation was replaced by DEP (diethylphtlalate) and to achieve the required energy level NQ was added, making it a triple base formulation.

A total of 75kg of the DEGDN formulation was processed solvent-free and extruded through the standard 7 perforation SSE dies.

Testing and evaluation of the DEGDN propellant grains showed that the energy value of the formulation is slightly higher than the SSE specification and this could be beneficial. The density was very acceptable and the Methyl Violet stability values indicate that the formulation has good stability.

1.4 TEGDN PROPELLANT FORMULATION

1.4.1 Properties of TEGDN

TEGDN has the following properties that make it a promising energetic plasticiser to consider for insensitive medium energy propellant applications:

- TEGDN is a nitrate ester similar to DEGDN
- TEGDN is far less sensitive than NG and less sensitive than DEGDN
- TEGDN is of medium energy when compared to NG
- It has a good specific energy to flame temperature ratio

Since last year small quantities of TEGDN have been made at our Wellington factory and it is now readily available for experimental evaluation in propellant formulations.

1.4.2 SSE/TEGDN Propellant Formulation

The 3rd candidate formulation is a single base formulation with the DNT replaced with the energetic plasticiser TEGDN. The mechanical mixture NC (13.15% N), typically used for single base propellants, was replaced with Piro M30 type of NC (12.6% N) and the NC concentration was decreased in order to maintain the required energy level. The DPA was replaced by EC (ethyl centralite). A total of 50 kg of the TEGDN formulation was processed with the solvent process. The TEGDN formulation processed well and upon evaluation passed the Methyl Violet stability test and the energy value came out slightly higher than SSE specification.

The initial processing produced samples for sensitivity and IM testing. After encouraging results further iterations of both the TEGDN and DEGDN formulations were processed with different dies for web optimisation. The formulations were slightly modified as well.

In Figure 1 photo's of the propellant grains from the SSE/mod-1 propellant formulation which underwent the standard steeping process before final drying, the TEGDN grains produced by the solvent process and the DEGDN grains produced by the solvent-free process are shown. All 3 formulations were extruded through the same set of dies and the effect of die swell or shrinking and also steeping can be seen.

Figure 1: Propellants from Solvent Process versus Solvent-Free – Same Die

1.5 FRICTION AND IMPACT SENSITIVITY

The friction and impact sensitivity properties of the 3 less sensitive candidate propellant formulations and the SSE formulation itself were all performed together. The friction sensitivity was determined on the BAM friction apparatus according to UN test method 13.5.1 Test 3. The impact sensitivity of the experimental propellants were determined on the BAM drop hammer apparatus according to UN test method 13.4.2 Test 3(a) (ii). These tests were performed at our Phillippi laboratory facility. The samples were prepared for the testing by cutting the propellant grains into pieces of 4mm in diameter and 3mm thick.

The friction and impact sensitivity of the experimental propellants are listed in Table 1. A maximum mass of 36 kg was used for the friction tests and a mass of 2.0 kg was used for the impact tests.

Table 1: Sensitivity Properties of SSE, SSE/Mod-1, DEGDN and TEGDN Propellant Formulations

Propellant	Friction Sensitivity	Impact Sensitivity #L I E (J)	
	No Reaction (N)	Initial Formulation	Modified Formulation
SSE	> 360	10.7	10.7
SSE/Mod-1	> 360	11.8	-
SSE/DEGDN	> 360	12.8	13.9
SSE/TEGDN	> 360	11.4	15.6

Limiting Impact Energy

All 3 the experimental formulations as well as the standard SSE propellant are insensitive to friction. All 4 formulations have a limited sensitivity to impact under the conditions of the test and no meaningful differentiation can be made between the formulations. The real sensitivity to impact and shock will become apparent when the Bullet Impact and Shape Charge Jet Impact IM tests are performed.

1.6 CHEMICAL STABILITY / SHELF LIFE ACCORDING TO STANAG 4582

The aim of the investigation was to compare the stability and chemical shelf life of the less sensitive SSE propellant formulations with the standard single base SSE formulation. The chemical stability and shelf life of the 3 propellant formulations were determined according to the following 2 methods.

1 - STANAG 4582: *"Explosives, Single, Double and Triple Base Propellants, Stability Test Procedures and Requirements using Heat Flow Calorimetry".*

2 - AOP-48 Edition 2: *"Explosives, Nitrocellulose Based Propellants, Stability Test Procedures and Requirements using Stabilizer Depletion."*

The chemical stability testing of all 3 candidates and the SSE formulation were performed according to STANAG 4582. The HFC analysis, conducted with the TAMIII instrument, measured the heat flow of the propellant samples at 80°C for 10.6 days. The heat flow limit must not exceed 114µW/g during this period. The following is a summary of the results.

The heat flow of he SSE formulation and the 3 candidate formulations never exceeded the 114µW/g limit and therefore all 4 the propellant formulations will remain chemically stable for a minimum storage period of 10 years at an average temperature of 25°C. All 4 formulations also complied with the criteria set by AOP-48 stabilizer depletion test procedure and according to this method would also remain chemically stable for a minimum storage period of 10 years at an ambient temperature of 25°C.

1.7 BALLISTIC EVALUATION

1.7.1 Closed Vessel Data

After the initial propellant processing and sensitivity testing the propellants were processed and extruded through various dies for ballistic evaluation. Various web configurations were produced and fired in the closed vessel. A summary of the results that matched the reference propellant the best is given in Table 2. The relative vivacity of the TEGDN-5 formulation was slightly lower than the reference, but matched the energy very well (relative pressure). The DEGDN-8 formulation was nearly 4% more energetic than the reference.

Table 2: Closed Vessel Results of SSE, SSE/Mod-1, DEGDN and TEGDN Propellant Formulations

Propellant	Relative Vivacity (%)	Relative Pressure (%)
SSE Reference	100.0	100.0
Mod-1	98.0	98.6
DEGDN-8	96.8	103.7
TEGDN-5	95.3	100.9

1.7.2 Initial Gun Firings

Initial gun firings from a 76mm weapon were performed at Alkantpan during August. A summary of the results is given in Table 3. The DEGDN propellant matched the SSE reference propellant very well with regards to muzzle velocity and pressure. For the same charge mass the TEGDN propellant surprised us all by exceeding both the muzzle velocity and pressure by a considerable margin.

Table 3: Gun Firing Data of SSE, Mod-1, DEGDN and TEGDN Formulations

Propellant	Temp	Charge Mass (kg)	Vo (m/s)	Pressure (MPa)
SSE lot 260 (reference)	21℃	2.40	890.4	283.1
Mod-1	21℃	2.40	857.6	236.0
DEGDN-8	21℃	2.40	898.3	286.0
TEGDN-5	21℃	2.40	920.3	332.6

1.8 IM TESTING

Four different IM tests were performed at Boskop (Naschem) according to the specific STANAG's but with the propellants placed in the EMTAP mild steel tubes. The IM properties of the SSE/Mod-1, DEGDN and the TEGDN formulations were compared with that of the standard SSE formulation.

The following IM tests were performed:

- Bullet impact according to STANAG 4241
- Slow cook-off according to STANAG 4382
- Shape charged jet –standard Boskop setup using the 38mm shape charge
- Fast cook-off according to STANAG 4240

1.8.1 EMTAP Tube Test Apparatus

The *tube test apparatus* or the Emtap Tube or Emtap Holder as it is also called, is mostly used for the measurement of the explosiveness of energetic materials. Typically pellets of HE (High Explosive) material are pressed or machined to the correct dimensions to fit tightly into the tubes. These tubes are then subjected to the typical IM tests such as slow and fast cook-off, shape charge jet impact and bullet impact. It was decided to use these tubes as holders for the various propellant samples in order to carry out the various IM tests. Special propellant grains that fit snugly into the tubes could not be made and for this test the standard propellant grain configuration were used and packed as tightly as possible into the tubes. The tube test apparatus consists of a solid cold drawn mild steel tube of internal diameter 31.40 mm, length 253 mm and 6 mm wall thickness, sealed by threaded end caps. See Figure 2. The EMTAP mild steel tubes were used for all 4 types of IM testing.

Figure 2: EMTAP Tube Test Apparatus Filled with Propellant Grains

Tests using the EMTAP tubes were carried out according to the requirements specified in STANAG 4491 (Annexure C3) which specifies the tube material, dimensions, etc. and the evaluation of the different reaction categories. These different reaction categories are listed in Table 4.

Table 4: Description of Reaction Categories (STANAG 4491)

Category	Reaction Description	Observation
0	No reaction	Internal inspection
0/1	Burning/Decomposition	No disruption of test vehicle
1	Pressure burst due to burning/decomposition	Test vehicle ruptured but one fragment obtained
2	Deflagration	2 to 9 test vehicle body fragments
3	Explosion	10 to 100 test vehicle body fragments
4	Detonation	> 100 test vehicle body fragments showing evidence of detonation

1.8.2 Slow Cook-Off According To STANAG 4382

The Slow Cook-off tests were performed according to STANAG 4382, but at 25°C/hour as prescribed in paragraph 11.2 of the STANAG. The EMTAP tubes were rigged with thermocouple probes. All 4 propellant formulations gave similar category 2 reactions to the Slow Cook-off test. Photos of the results of the SSE and DEGDN propellants are shown in Figure 3.

DEGDN Propellant

SSE Propellant

Figure 3: Results of Slow Cook-off Test

1.8.3 Bullet Impact According To STANAG 4241

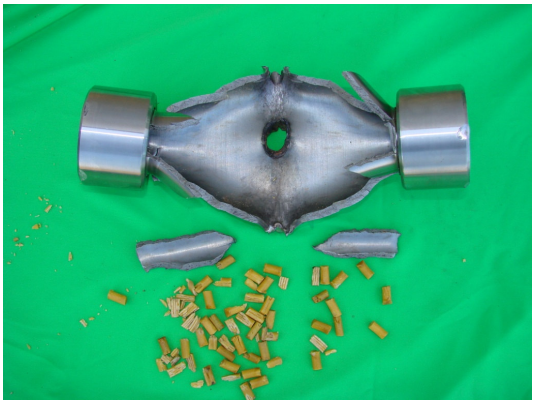
The test was carried out according to the procedure as specified in STANAG 4241 using a 12.7mm AP round. The test setup is given in Figure 4 below.

Figure 4: Bullet Impact Test Setup: EMTAP Tube with Witness Plates and12.7mm Gun

The SSE and SSE/Mod-1 propellant formulations gave similar category 2 reactions for the Bullet Impact test. The DEGDN and TEGDN propellant formulations, however, gave no reaction to the bullet impacts and the results are both category 0 reactions. Photos of the results are shown in Figure 5. In all 4 cases most or all of the propellant was recovered without having reacted during the bullet impact.

SSE Propellant

SSE/Mod-1 Propellant



DEGDN Propellant

TEGDN Propellant

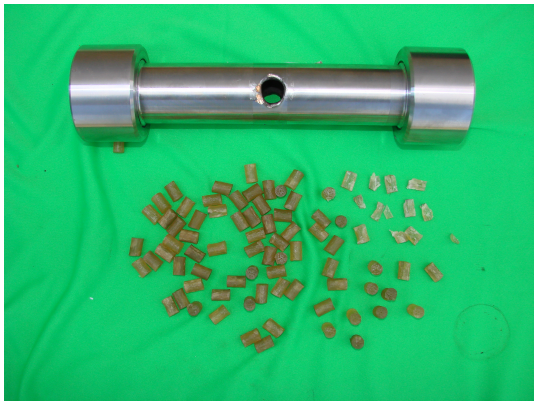


Figure 5: Results of Bullet Impact Test

1.8.4 Shape Charged Jet Impact According To STANAG 4526

The shape charged jet (SCJ) impact test was performed according to the standard Boskop test setup using the 38mm shape charge. This test setup complies with STANAG 4526. The test consists of subjecting the test item to a jet from a shaped charge and the effectiveness of the shaped charge is proportional to the square of the jet velocity times the jet diameter, the V^2d value, where V is the jet velocity and d is the jet diameter. The 38mm shape charge used for the testing produces a V^2d value of 80 $mm^3/\mu s^2$ which resembles a *Top Attack Bomblet* according to the threat hazard assessment (THA) guidelines.

The SSE and SSE/Mod-1 formulations gave similar reactions which bordered between a category 2 (deflagration reaction – 2 to 9 fragments) and a category 3 (explosion reaction – 10 to 100 fragments) type reaction. The DEGDN and TEGDN propellant formulations, however, gave no reaction to the shape charge jet impacts and the results were both category 0 reactions. The difference between the type of reactions of the SSE and SSE/Mod-1 propellants and the DEGDN and TEGDN propellant formulations were dramatic and good news when looking for a less sensitive replacement for the SSE formulation. In order to verify the results the Shape Charge Jet Impact tests were repeated on all 4 samples a few weeks later. The results were very similar and the tests can be seen as being repeatable. Photos of the test results are shown in Figure 6.

SSE Propellant

SSE/Mod-1 Propellant

DEGDN Propellant

TEGDN Propellant

Figure 6: Results of Shape Charged Jet Impact Test

1.8.5 Fast Cook-Off According To STANAG 4240

The fast cook-off test was performed on the propellant samples in the EMTAP tubes. The drums are welded together to form a stack. The bottom drum contains water with 10 liter of jet fuel added which forms the top layer. The holder with the propellant sample is placed on the grid as shown and tied to the grid with a piece of wire to keep it in place. The jet fuel is ignited electrically from the remote control room. The flame temperature is measured at 4 positions with thermocouples and the temperature must reach 550℃ within 30 seconds after ignition and maintain an average temperature of between 550℃ and 850℃ until all munition reactions have been completed.

The Fast Cook-off or fuel fire test setup and the positions of the 4 thermocouples are shown in Figure 7.

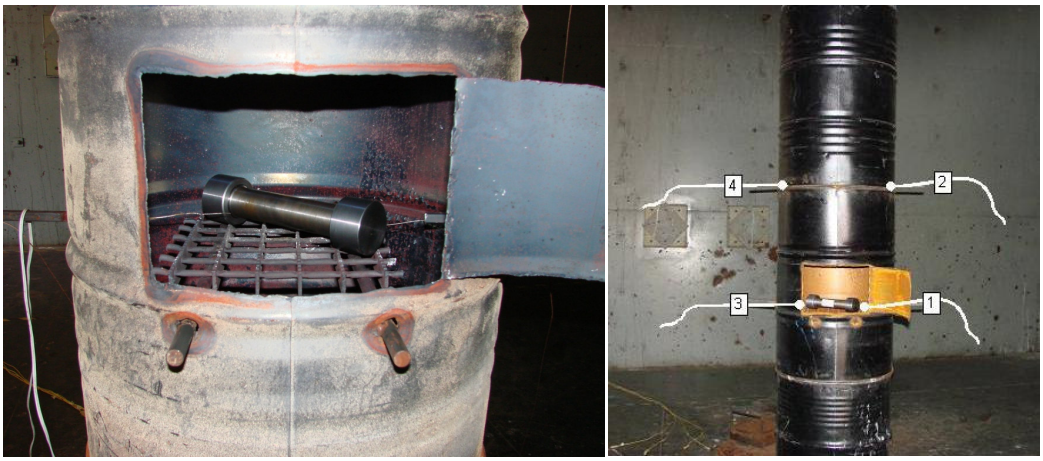


Figure 7: Fast Cook-off Test Setup with Tube on Grid and Thermocouple Probes

All 4 propellant formulations gave similar category 2 reactions to the Fast Cook-off test. Photos of the results of the SSE and TEGDN propellants are shown in Figure 8.

SSE Propellant

TEGDN Propellant

Figure 8: Results of Fast Cook-off Test

1.8.6 Summary of Test Reaction Types – SSE Replacement Candidates

The slow and fast cook-off tests, the bullet impact and shape charge jet attack tests were performed on the less sensitive SSE candidates. The propellant samples were packed in the EMTAP tube configuration. The results are summarised in Table 5 and the Slow Cook-off reaction temperatures are also given.

Table 5: Summary of IM Tests on SSE Replacement Candidates

Propellant	Slow Cook-off		Bullet Impact	Shape Charge Jet	Fast Cook-off
	Temp.	Reaction			
SSE	147ºC	2	2	2 / 3	2
SSE/Mod-1	153ºC	2	2	2 / 3	2
SSE/DEGDN	150ºC	2	0 / 1	0 / 1	2
SSE/TEGDN	146ºC	2	0	0 / 1	2

1.9 CONCLUSIONS

The following conclusions can be made in the search for a less sensitive replacement for the SSE propellant formulation:

- All 3 the less sensitive propellant candidates were successfully processed.
- The 3 candidates and the SSE formulation are not friction sensitive.
- The impact sensitivities of the 3 candidates and the SSE formulation are of the same order.
- All 3 candidates and the SSE formulation will remain chemically stable for at least 10 years according to both STANAG 4582 and AOP-48 test procedures.
- Both the DEGDN and TEGDN formulations passed all the IM tests and will be further evaluated as candidates to replace the SSE formulation.

1.10 FUTURE WORK

The following activities are planned for the next phase of the project:

- Web optimisation and ballistic evaluation of the DEGDN and TEGDN formulations will be performed.
- The 2 processes, solvent versus solvent-free, will then be evaluated.
- Finally a formulation will be selected, the process, dies, etc will be optimised and then the process will be industrialised.

1.11 ACKNOWLEDGEMENTS

- I would like to acknowledge my colleagues from Z-Area at RDM North (Boskop) for performing the IM tests and for the great reporting of the IM tests by means of photo's, videos and multi-media clips.
- Armscor must also be acknowledged for the funding of the project.

Contact Information:

Charles Frank Wiehahn
Rheinmetall Denel Munition,
Somerset West,
South Africa.
Tel: +27 21 850 3023
Fax: +27 21 850 3019
Mobile: +27 84 585 1925

E-mail: Charles.Wiehahn@rheinmetall-denelmunition.com