**Innovative thermoplastic propellants for gun ammunition applications**
*From the definition of formulations to pilot scale production*

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## 1. Context

Since 1981, as part of the reduction of munition vulnerability, some studies based on composite propellants has been leaded by SNPE Company (French company of Propellants and Explosives). These new formulations of propellants include thermoplastic binder(s) in the formulation with or without nitrocellulose. These formulations are also composed of energetic charges to reach performances. In 2008, formulations were developed by including a new energetic charge in Thermoplastic propellant compositions. In 2015, DGA Land and System has established a developing program to select, scale up, manufacture and characterize some Thermoplastic propellants for a given application. This program was built to have a real cooperation between DGA Land System, Eurenco, Nexter and ArianeGroup teams in order to reach a scale in TRL from 2-3 to 3-4. The selection of the formulation and propellant geometry had to take in account increasing requests towards more and more successful for a given artillery system. Teams evaluate the feasibility of a MURAT and high performing propelling system for a given ammunition and projectile.

## 2. Issues

As part of this study, teams were focused on the development of a gun propellant formulation with thermoplastic binder(s) by taking into account:

- Ballistic performances and their compatibility with ammunition (pressure, impetus, acceleration and muzzle velocity)
- Artillery erosion phenomena,
- Environmental stakes (REACH regulation and absence or small quantities of solvent during shaping)
- Reusable/recycling product and/or raw materials
- Vulnerability of munitions
- Maintenance of manufacturing processes / cost reduction.

The developing program challenge is to tend to reach a combination of all the specifications to find the best compromise. For example erosivity of a given tube tends to increase with the flame temperature. For nitrocellulose base propellants it is well known that a higher impetus produce higher flame temperature which causes erosivity phenomena. In this program one challenge is to develop a propellant with lower flame temperature for a given impetus compare to nitrocellulose base propellants (cf. Figure 1).

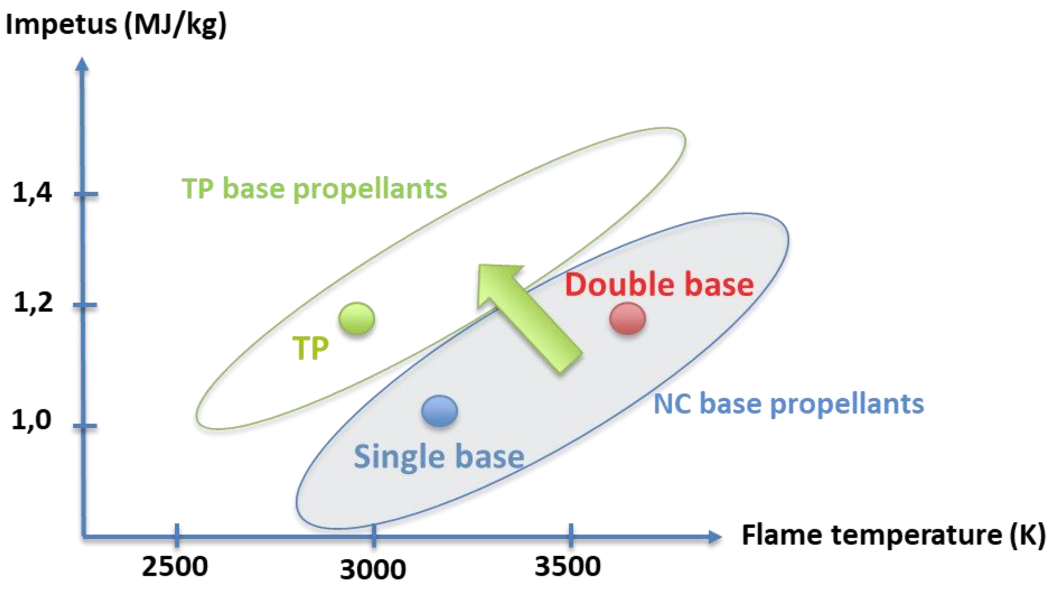


*Figure 1 : evolution of impetus versus flame temperature for thermoplastic and nitrocellulose base propellants*

The workpackage of this program has been split in two parts. The first part was dedicated to feasibility evaluation of propelling system. Technical approach is progressive, the purpose is to end in propelling system evaluation in munition. MURAT characteristic of this propellant will be also evaluated. The second part is about industrialization feasibility of the manufacturing process of this gun propellant. In this developing program manufacturing process uses have been gone from laboratory scale to pilot scale. Production process used is sensitive of extruded material viscosity, production transposition of propelling system on an adapted production tool is technical challenge.

## 3. Technology choice

To develop low munition vulnerability characteristics, project team has selected a family of propellant formulation based on thermoplastic binders with energetic charges without nitrocellulose. To combine all issues introduces previously, manufacturing process has been selected to be a continuous one. This process has to use as less as possible solvent during the manufacturing steps.

During this developing program twin screw extruders have been used to manufacture thermoplastic propellants.

The installation of each twin screw extruder consists of 3 elements:

- Feeders used to introduced quantitatively raw materials
- Twin screw extruder, sheath and screw are composed of several interchangeable modules enabling mixing and transfer zone adjustment which depends on the consistency (viscosity) of the dough.
- Pilote automaton, feeder piloting, safety elements of the twin screw extruder, regulation system (velocity of the screw, temperatures, pressure…)

Product consistency control during extrusion and at the end of the process is one of the most important parameter to get, directly at the end of the step, a propellant whose consistency satisfy the two following obligations:

- Ability of extrusion
- Product shape conservation

Process and composition adjustments are necessary to answer different obligations.

## 4. Predimensioning calculations and Selection of formulation

Some thermochemical calculations, simulations were done to determine the impetus and the geometry of the propellant necessary to satisfy the following munition specifications:

- Available volume inside the munition for propellants
- Ballistic route
- Tube diameter
- Pressures
- Projectile mass
- Targeted muzzle velocity
- Maximum impulsion

Predimensioning calculations were realized to determine:

- The formulation based on thermoplastic binder(s) and energetic charges to have an impetus close to a double base propellant with a lower flame temperature (cf. Figure 1)
- Geometries of propellant which are compatibles with all munition specifications

The exercise of predimensionning were done with a given muzzle velocity, projectile weight and geometry family (cylinder 7 holes or 19 holes). Variation of the propellant weight was studied in function of maximum breech pressure and geometry parameters (average web: W). Figure 2 illustrates results got to calculation study. Limits are illustrated with discontinuous red line. One represents the maximum breech pressure which is limit of system. The other illustrate respectively the minimum and the maximum weight of propellants in the munition.

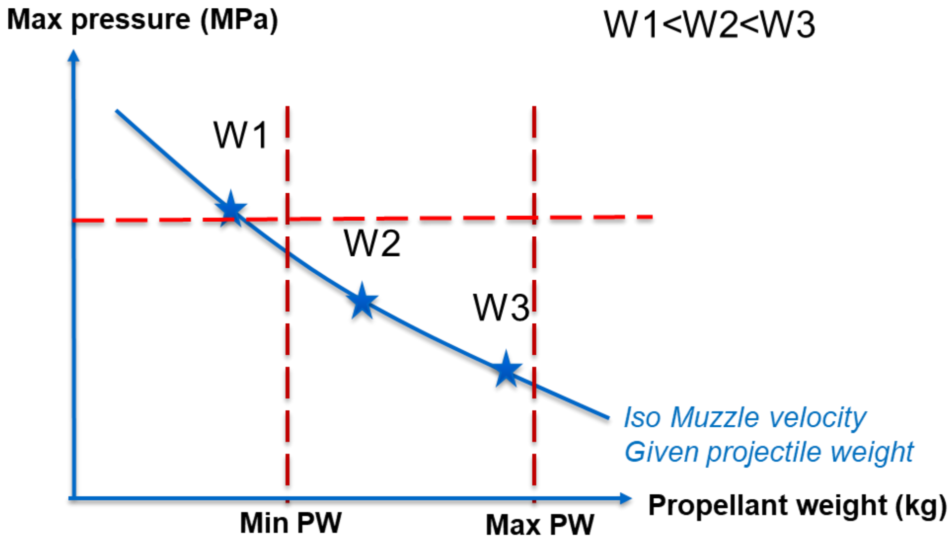


*Figure 2 : Variation of Maximum breech pressure in function of propellant weight according given muzzle velocity and projectile weight for propellant geometry*

This exercise was done with different muzzle velocities. Table 1 introduces the geometry variations of propellant grains according to:

- Their ability to be loaded in system. Weight ratio is the ratio of the weight of propellant reached in a given configuration necessary to reach the maximum pressure acceptable by system versus targeted average weight.
- Muzzle velocity ratio which is the ratio of the muzzle velocity calculated with geometry and ability of the propellant grains to be loaded versus targeted muzzle velocity

| Web (mm) | Weight ratio (%) | Muzzle velocity ratio (%) | Loading ability |
|---|---|---|---|
| 1.4 | 93 | 96 | |
| 1.5 | 97 | 98 | OK |
| 1.6 | 101 | 99 | |
| 1.7 | 106 | 101 | Non OK |
| 1.8 | 110 | 102 | |

*Table 1 : Variation of muzzle velocity ratio, weight ratio and loading ability with thermoplastic propellant grains web.*

The results showed for 19 perfored holes geometry, a compatible TP base propellant with an average web of 1.5-1.6mm with targeted muzzle from 98% to 99%. Length and diameter of the grains have been determined too.

Some formulations were done in lab scale to study Thermoplastic base propellants feasibility with a content of energetic charges more than 80%w and different energetic charges granulometries. Granulometries ($D_{50}$) vary from 10µm to 200µm. Table 2 showed photographies of carpets obtains after mixing thermoplastic base formulation thank to a rolling mill with different granulometries of energetic charges.

| Energetic charges content | Granulometry 1 | Granulometry 2 | Granulometry 3 | Granulometry 4 |
|---|---|---|---|---|
| >80%w with additive (processing aids) |  |  |  |  |
| >80%w |  |  |  |  |

*Table 2 : Feasibility of Thermplastic base carpet with different granulometries of energetic charges with a lab rolling mill*

Thank to this study, it has been shown that energetic charges with granulometry 2 is the most appropriate to be processed in twin screw extrusion with processing aid.

Thermoplastic base propellant composition is showed in

| Components | %w |
|---|---|
| Energetic charges | >80 |
| Energetic plasticizer | 0-20 |
| Thermoplastic polymers | 5-20 |
| Additive | <1 |

*Table 3 : thermoplastic base propellant composition*

## 5. Thermoplastic base propellant development with a laboratory scale twin screw

For safety reason, Team project has firstly evaluated the non-reactivity of the Thermoplastic base propellant when it is stressed by a friction aggression. For that a basic friction sensitivity characterization using Julius Peters apparatus (BAM machine) was used as well as a shear to rotating friction test. Results of these two tests showed non-reactive ignition of the product in a given configuration. Thank to these results and some added characterization, characterizations results, project team has designed twin screw profile by using 1D calculations of pressure rate and temperature, 3D mixing simulation and 3D calculated speed field tools. This step was important to evaluate:

- Process safety parameters check
- Mixing quality
- Local product retention detection
- Temperature, pressure and strength profile

Figure 3 introduce corotative twin screw configuration used for the different runs.

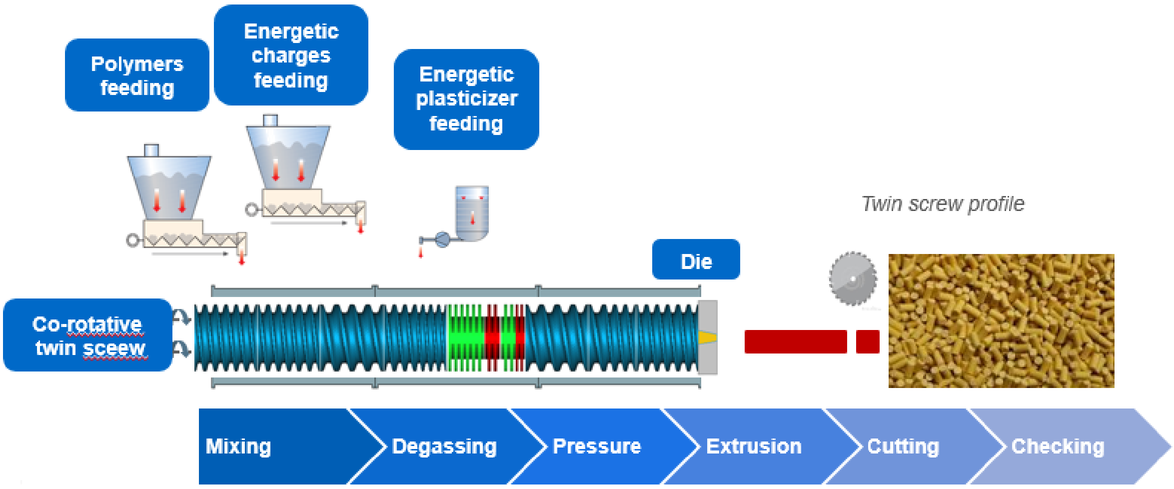


*Figure 3 : laboratory twin screw configuration*

Main characteristics used during different runs were:

- Extrusion flow rate ~ 3 to 5 kg/h
- Representative feeders for liquid and solid components
- Incremental active charge rate rising (>80%)

For each runs parameters are followed such as:

- Pressure at end of die (bars)
- Screw torque (%)
- Screw speed (RPM)

Figure 4 introduces parameters curves followed in twin screw extrusion as well as their evolution in function of time and process steps.

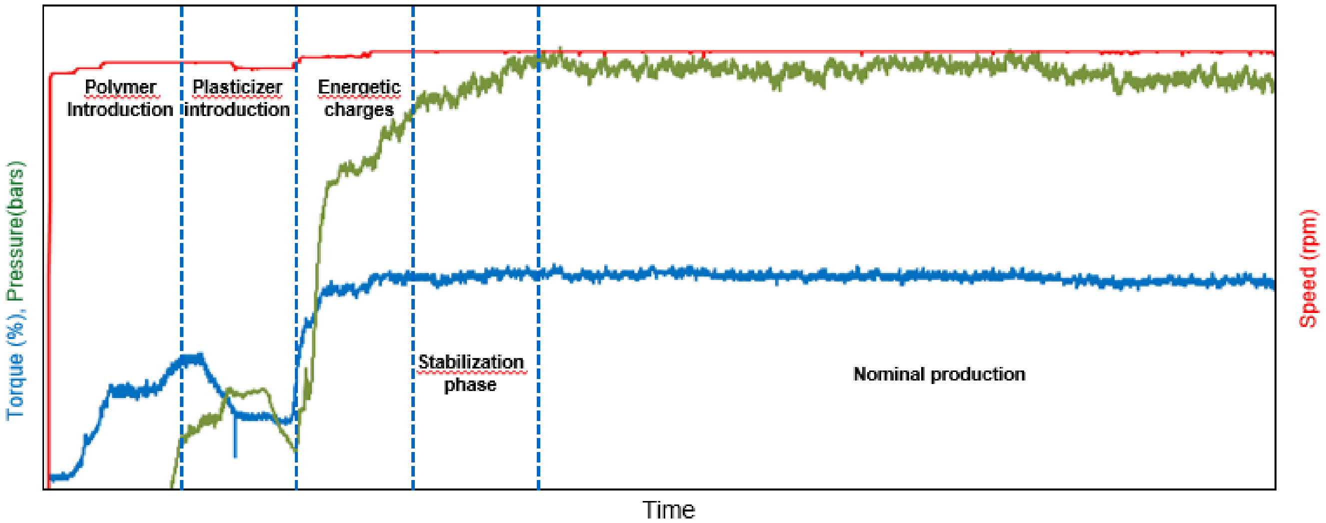


*Figure 4 : twin screw extruder parameters followed in function of time*

Stabilization phase of a given run is composed of 4 phases

- Phase 1: introduction of thermoplastic binder(s) which cause a high increase of the machine torque. It is usually to wait for getting the product out of the die before introducing plasticizer.
- Phase 2: Introduction of plasticizer which cause an important and quick reduction of machine torque. Pressure in die increase continuously which mean a die filling.
- Phase 3: introduction of energetic charges which cause an increase of pressure and machine torque in die. It is due to the increase of the dough viscosity inside the machine.
- Phase 4: vacuum which has no impact on torque machine but interfere with the die pressure.

At the end of this phase, the whole process parameters are stabilized, extruded product is collected and then cut into grains.

About 10 runs were necessary to produce 50kg of Thermoplastic base propellant. A perfect screening parameter reproducibility has been shown for the whole production.

The structure of the Thermoplastic propellant grains is introduced in Figure 5 and compared to a double base propellant grain. These pictures reveal granular structure of the Thermoplastic propellant grain caused to the presence of energetic charges. Double base propellant structure is more locally homogeneous as it is composed of mainly gelatinized nitrocellulose with nitrated oil.

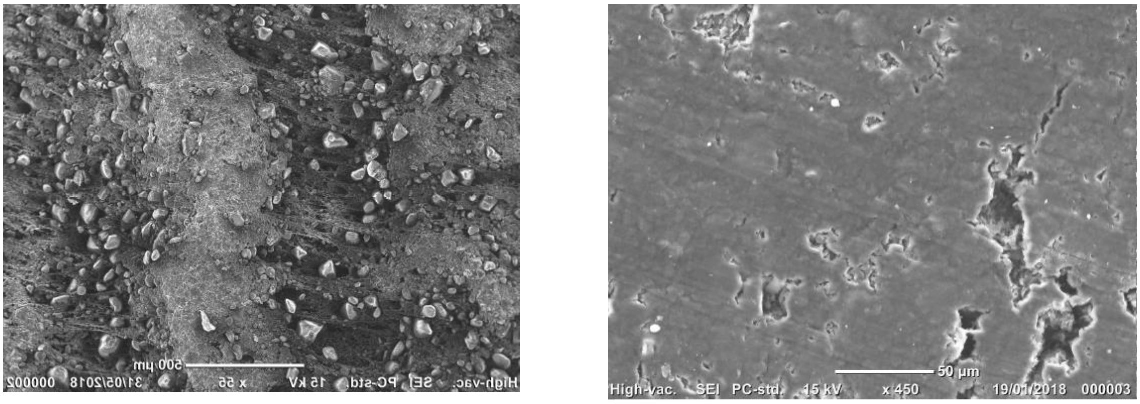


*Figure 5 : Scanning electron microscopy pictures of thermoplastic grain propellant (left) and double base propellant (right)*

## 6. Thermoplastic base propellant characterization

Thermoplastic base propellant grains have been characterized. Table 4 introduces physico-chemical characterization as well as the potential results. Density and potential are presented as a ratio of given propellant result versus double base propellant one.

| | Self-combustion temperature (°C) | $H_2O$ content (%) | Density ratio (%) | Heat explosion ratio (%) |
|---|---|---|---|---|
| Thermoplastic grain propellant | 180 | 0,14-0,19 | 100 | 80 |
| Double base propellant | 167 | 0,43 | 100 | 100 |

*Table 4 : Physico-chemical and potential properties of Thermoplastic base propellant grains and double base one.*

Self-combustion temperature of Thermoplastic base propellant is higher than double base one. This results seems to be coherent with a less sensitive propellant (MURAT). Heat explosion is 20% less important to Thermoplastic propellant compare with double base one. This result shows that the available energy in propellants is less important for thermoplastic base propellants compare to double base one. Some closed vessel test are necessary to study pressure development behavior of these two propellants.

At low pressure (<300MPa) some closed vessel characterization were done to compare Thermoplastic and double base propellant. Results at a given loading density (200 kg/m$^3$) from these tests showed:

$$\frac{P_{MAX}\ TP\ Propellant}{P_{MAX}\ Double\ base\ propellant} = 1{,}03$$

$$\frac{D\ TP\ Propellant}{D\ Double\ base\ propellant} = 0{,}6$$

$$\frac{T_C\ TP\ Propellant}{T_C\ Double\ base\ propellant} = 1{,}8$$

With $P_{Max}$ (MPa): Maximum pressure reached in closed vessel
D (m$^3$.kg$^{-1}$.s$^{-1}$): Maximum gaz flow
Tc (s): Combustion time

At low pressure (<300MPa), Maximum pressure reached by Thermoplastic or double base propellant are similar but combustion time and gaz flow are different. Thermoplastic propellant seems to generate less gaz flow compare to double base one. This characteristic seems to be connected with the increase of combustion time for Thermoplastic propellants.

Closed vessel tests were performed at different temperatures ( -40, 20 and 63°C) to evaluate temperature coefficients. Determination of temperature coefficient ($\pi_v$) is realized from the following equation:

$$\pi_v(\theta \rightarrow +20) = \{[v_{100MPa.(\theta)} - v_{100\ MPa.(+20)}]/[\theta - 20]\}$$

This equation introduce temperature coefficient based on combustion speed (v).

According to results for all the temperature range studied, thermoplastic propellant temperature coefficients are inferior to Double base coefficient. It means that temperature has less impact on ballistic results for thermoplastic propellant compare to double base one. This characteristic is searched to have a constant performance of munition whatever temperature conditions.

At -40°C some mechanical tests were performed to evaluate propellant friability/damaging. This test consists projecting a temperature conditioned propellant grain at a given velocity (45m/s) on a defined wall. After the choc we collect grain and its potential residue of friability. During this test no damaging of thermoplastic propellant grains was noted whereas double base propellant grains was damaged. This results show a good behavior of thermoplastic propellant grains at the impact resistance.

## 7. Thermoplastic base propellant development with a pilot scale twin screw

A scale up of thermoplastic propellant production is planned in this developing program. This scale consists in the transfer of the production from a laboratory twin screw extruder to a pilot one.

Some adaptations dedicated to the thermoplastic propellant production were necessary to be sure to produce in safety conditions reproducible products. The workshop in where the pilot twin screw extruder is located was initially designed for continuous mixing products for others applications. Purpose of the adaptation work was particularly done to be able:

- Feeding of the whole raw materials in the twin screew with appropriate flow and specific quantity tolerance.
- Temperature mixing control of thermoplastic propellants
- Collection of extruded products at the end of the die

These scale up cause some necessary adaptation and optimization during testing runs. All parameters were studied (Pressure at the end of the die, Torque of the screw, Speed, feeding condition…)

## Conclusion

New propellants based on thermoplastic binder(s) with energetic charges were developed by French collaboration between DGA Land Systems, Nexter, Eurenco and ArianeGroup. This propellant was designed to answer a given system conditions. The whole simulation and calculation work was necessary to fix the geometry as well as the formulation of the propellant to reach targeted performances such as:

- Ballistic performances and their compatibility with ammunition
- Decrease of artillery erosion phenomena,
- Environmental stakes (REACH regulation and absence or small quantities of solvent during shaping)
- Reusable/recycling product
- Vulnerability of munitions

Development done in laboratory scale with twin screw extruder showed us production feasibility of thermoplastic gun propellants with good reproducibility. Products characterizations showed a non-standard behavior of this product compared with a double base propellant. It appears clearly that:

- Thermoplastic gun propellant could be less sensitive to external stimuli
- Temperature coefficient are flatter in case of thermoplastic gun propellant
- Thermoplastic gun propellant seems to have better mechanical properties for impact resistance

A scale up of thermoplastic gun propellant was planned in the developing program. A pilot. Twin screw extruder was chosen and adapted to produce thermoplastic propellant.

## 8. Outlooks

Some complementary characterizations are necessary to have a better understanding on this new gun propellants. Other igniter systems will be explored to match with Thermoplastic gun propellants ignition properties at low pressure (Maximum gaz flow and combustion time). Some studies will have to be done to explore relationship between heat of explosion, propellant formulation (base nitrocellulose or composite) and pressurization behavior.

Some firing tests in the given system will be planned to evaluate the behavior of this propellant compared with traditional one.