Cast PBX energetic fillers recycling: Approaches and results

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1- INTRODUCTION

For many years, EURENCO has been producing a complete range of high explosives as well as the plastic-bonded explosive based thereof. Nevertheless, most of these compositions use chemically cured binder based on Polybutadiene structure which are difficult to degrade. This becomes a problem in the case of an ammunition at the end of its life. To try to find solutions, numerous studies have been conducted over the last decades to develop a system that could be easily demilitarized. One option is to take advantage of the hydrolysing properties of some polymers to degrade the binder and recycle or reuse the energetic fillers at the end of the ammunition service life.

Thereby, Eurenco has worked on the development of a castable plastic-bonded explosive formulation, chemically degradable with the possibility to separate the binder from the explosive by a post treatment.

The objective of this paper is to present the latest results available in term of feasibility, recycling performance and characteristics of a polyurethane degradable system.

2- Hypothesis definition and validation of the concept

Following preliminary bibliographic research on alternative hydrolysable polyurethane binder, EURENCO opted for a system with ester component polymers. Indeed, ester components increase the hydrolysing properties of the polymer, which can then be easily degraded to recover the energetic ingredients of the composition.

So, based on the numerous studies conducted on this kind of binder, the different ingredients have been selected and tested. Thus, the main polymer of the composition as well as the plasticizer were both composed of ester components.

Once the new ingredients of the binder selected and the compatibility between these new materials and the energetic molecule proved (HMX in this case), a preliminary test has been conducted at lab scale to validate the concept.

Thus these new ingredients have been introduced in a reference formulation, widely used for industrial applications.

The main characteristics of the cast PBX are given in Table 1.

Characteristics	PBX-1
Binder / Graphite / HMX (%)	13 / 1 / 86
Viscosity (Poises)	40 000
Density (g/cm^3)	1,702
Hardness, Shore A	69
Stress maximum (MPa)	0,70
Strain at maximum stress (%)	7

Table 1: Characteristics of the 1st PBX

Comparatively, the mechanical properties obtained with the reference formulation and this first trial were similar, whereas the viscosity was far too high for an industrial application.

Nevertheless, the cured composition has been subjected to a hydrolysis treatment to validate the hypothesis previously made. Thus, after several days of treatment in solution 1, under specific conditions, followed by filtration, washing and drying steps, a grey powder has been extracted.

Figure 1: PBX-1 sample after treatment

Based on different analysis (HPLC, DSC, microscopy …), the HMX after treatment was 99% pure, undamaged, with no trace of binder and no modification of its thermal behaviour. Thus, the reaction yield for this first composition was 98%.

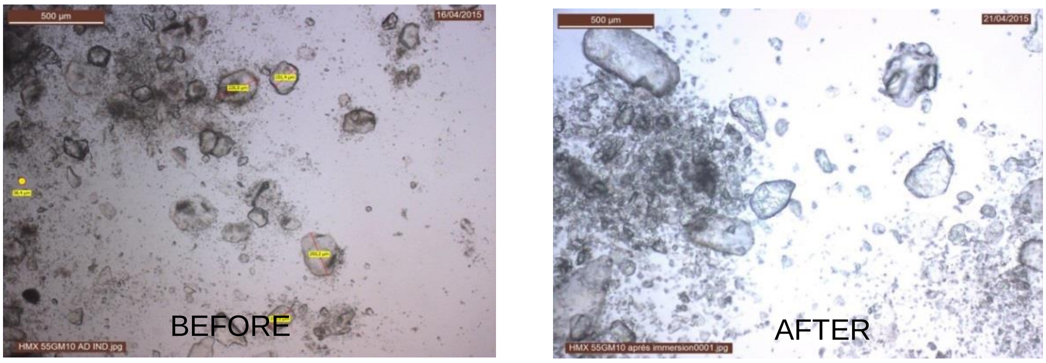

Figure 2: Pictures of HMX before and after hydrolysis

Thus, the hydrolysis treatment of this first composition gave promising results with a 98% reaction yield. However, its viscosity was not suitable for industrial application. An optimization study has then been conducted to find the best trade-off between viscosity, characteristics and degradability.

3- Optimization of PBX based on hydrolysable polyurethane binder

There are different ways to improve the feasibility of a composition and, in this case, to decrease its viscosity. Preliminary studies and trials made on the amount of plasticizer, the addition of processing agents, or the reduction of the HMX content (from 86 to 84%) did not give the expected results, or at least did not decrease the viscosity enough to be suitable for an industrial application.

- Optimization of viscosity

Thus, the amount of HMX has been significantly reduced to 80% to achieve a suitable viscosity. This second PBX was made at lab scale as well, according to the same process parameters than the first one, and this time its viscosity was considerably reduced.

The main characteristics of the cast PBX are given in Table 2.

Characteristics	PBX-2
Binder / Graphite / HMX (%)	19 / 1 / 80
Viscosity (Poises)	5 500
Density (g/cm^3)	1,697
Hardness, Shore A	10
Stress maximum (MPa)	Unusable
Strain at maximum stress (%)	Unusable

Table 2: Characteristics of the 2nd PBX

Based on these results, the viscosity of this second PBX was perfectly acceptable while its mechanical behaviour was not satisfactory. Thus, among other options, it has been decided to fix the HMX rate between 80 and 84% with the type of binder previously defined to combine both suitable viscosity and processability and good mechanical properties.

- Compromise between HMX rate and viscosity

As mentioned above, this cast PBX must be a good compromise between viscosity and mechanical properties. Nevertheless, the viscosity of cast PBX is linked to the HMX rate in the composition. Thus, different PBX have been made at lab scale to define the maximal HMX rate to reach a viscosity under 10 000 Poises. The results are given in figure 3.

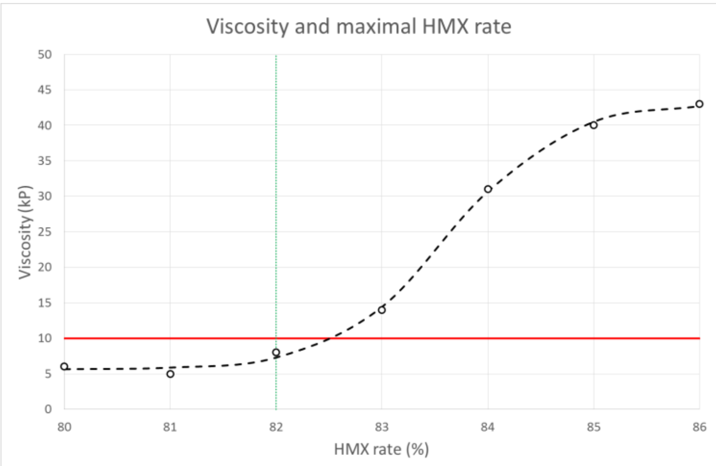

Figure 3: Viscosity and maximal HMX rate evolution

Thus, the maximal HMX rate to keep a suitable viscosity was fixed at 82% for the rest of the project. Nevertheless, the polymerization of these compositions were not appropriate and the test specimens still unusable.

One of the solution chosen to achieve a proper polymerization was to work on the type of catalyst and its rate.

- Compromise between polymerization and viscosity

The increase of the catalyst rate in a composition has a significant impact on the polymerization but can also has a negative effect on the viscosity and curing time. Nevertheless, among the catalysts available, a specific one has an exponential kinetic effect with slow action at the beginning of the reaction. Thus, the use of this catalyst would have a limited impact on the viscosity of the product.

So, three cast PBX have been processed at lab scale with different catalyst rates and compared with a composition made with the first catalyst.

Results are given in table 3.

Characteristics	**PBX-3 Catalyst 1 Rate 1**	**PBX-4 Catalyst 2 Rate 1**	**PBX-5 Catalyst 2 - Rate 2**	**PBX-6 Catalyst 2 Rate 3**
Viscosity (P)	7 500	6 100	5 600	5 300
Curing time (days)	30	30	14	14
Hardness (Shore A)	36	47	32	62
Smt (MPa)	0,30	0,40	0,20	0,50
emt (%)	26	14	30	14

Table 3: Influence of type and rate of catalysts on polymerization and mechanical properties

Based on these results, for the same rate, the benefits of the second catalyst were highlight with an increasing of the hardness and the mechanical properties and a reduction of viscosity.

Moreover, a significant reduction of the curing time was also observed with the increase of the second catalyst rate. However, the rate 3 has been fixed as a minimum to get closer to usual mechanical properties and to guarantee suitable viscosity and curing time.

Thus, based on these first trials, HMX as well as catalyst rates have been defined to combine both suitable viscosity and curing time. The last part of the work on the composition was dedicated to the mechanical properties optimization.

- Optimization of mechanical properties

To improve the mechanical behaviour of this cast PBX, the influence of the NCO/OH ratio as well as the addition of a short chain polyol have been studied. More PBX have been made at lab scale with different NCO/OH ratio and amount of short chain polyol to reach higher maximum stress. Nevertheless, no improvement could have been noticed with these compositions compared to the PBX-6, mentioned in table 3.

Despite the fact that the mechanical properties were a little low compared to other compositions, the choice was made to move forward with the PBX-6, to:

- Evaluate the energetic performances of the composition,
- Validate the feasibility of the hydrolysis treatment previously defined.

4- Evaluation of energetic performances of the hydrolysable composition

To validate the PBX-6 composition and test its energetic performances, a last PBX has been produced at industrial scale. Different samples have been made to test the insensitivity of the composition, as well as its vulnerability and safety characteristics.

Results are given in table 4.

Characteristics	**PBX-7**
Binder / Graphite / HMX (%)	17 / 1 / 82
Viscosity (Poises)	6 000
Density (g/cm^3)	1,714
Hardness, Shore A	66
Stress maximum (MPa)	0,50
Strain at maximum stress (%)	13
Impact sensitivity (J)	41
Friction sensitivity (N)	353
Self-ignition temperature (°C)	248
Shock sensitivity (number of cards)	160 (STANAG 4488 – Annex B)
Detonation velocity (m/s)	8 200

Table 4: Characteristics of the industrial PBX

Based on these results, the safety and energetic performances of this cast PBX were acceptable with good impact and friction insensitivities and relatively high self-ignition temperature. Moreover, its detonation velocity was satisfactory, although the HMX rate has been significantly reduced and its shock sensitivity was acceptable compared to other compositions.

In addition, some samples have also been subjected to a storage at high relative humidity (RH 100%) and a temperature of 52°C for eight days to guarantee the humidity resistance of the composition. No impact on the density has been highlight as well as no evolution of the weight of the samples could has been noticed.

Thus, from all the previous results, the composition developed has been validated in terms of feasibility, insensitivity and energetic performances. Despite the fact that its mechanical properties remain to be improved, this composition has been used for the second part of this project related to the hydrolysis treatment.

5- Hydrolysis treatment on the optimized composition

The same process parameters have been applied for the hydrolysis treatment of this composition and the reference formulation mentioned in chapter 1.

Nevertheless, the hydrolysis reaction was not satisfactory as no degradation of the composition could has been noticed after a 14 days treatment.

Figure 4: Samples at T0, T0 under agitation and at the end of the treatment

Indeed, after washing and drying steps, the product from reaction was still hard, absolutely unusable, as shown in figure 5.

Figure 5: Sample after 14 days hydrolysis treatment, washing and drying steps

Thus, the different modifications made on the final cast PBX had a significant and negative effect on the hydrolysable properties of the composition. Indeed, to find the best compromise between viscosity, polymerization and mechanical properties, different adjustments had had to be made.

So, after the optimization of the composition, the second part of the study involved an improvement of the hydrolysis treatment, to get closer to the results previously obtained on the composition before the optimization work.

6- Optimization of hydrolysis parameters

There are various possibilities to improve the hydrolysis parameters. The different options chosen were the study of the impact of concentration and type of solution (solution 1 and solution 2), the reaction temperature, the composition rate and the treatment duration. More than fifteen trials have been performed, analysed and products from the reaction characterized.

According to the first trials, the temperature of the reaction had no significant influence on the reaction yield and the final characteristics of the product subjected to both solutions 1 or 2. This parameter has been fixed for the rest of the study.

Then, a second campaign of trials was dedicated to the selection of the solution given the most promising results. Based on these results, the second solution tested provided the best results. Indeed, if the reaction yields obtained on the trials made with both solutions under the same conditions were equivalent, the products from reaction with the second solution were more satisfactory.

Thus, products from reactions with the second solution were grey powder while the initial solution gave powder with clusters and residual traces of binder, as shown in figure 6.

Figure 6: Samples from hydrolysis with initial solution (left) and second solution (right)

Moreover, the purity of the energetic fillers seemed to be higher with the second solution, as the DSC test made on all samples gave better results with the second solution than with the initial one, compared to the DSC curves of the reference HMX.

As an example, the following table gives a comparison of the onset and peak temperatures of trials made with solution 1 and 2 and the reference HMX.

Results	Solution 1	Solution 2	HMX untreated
Onset temperature (°C)	263	278	278
Peak temperature (°C)	267	286	282

Table 5: DSC results comparison between products from hydrolysis reactions and HMX

Thanks to these first results, the temperature as well as the solution have been defined. Then, the last part of the study was related to the improvement of this reaction yield and the optimization of the reaction productivity.

Thus, around ten additional trials have been made, with different concentrations of solution 2, different duration and different quantities of composition to increase the productivity. According to these test results, an optimal concentration of solution has been defined to reach reaction yield higher than 70%. To finish, the last trials permitted to increase the quantity of composition per treatment as well and significantly reduce the duration of hydrolyse with no effect on the reaction yield.

The table 6 gives a comparison between the initial treatment and the optimized conditions.

	Initial to Optimized conditions
Solution	1 → 2
Temperature	=
Composition quantity	↗ (+ 1 600 %)
Duration	↘ (- 99 %)
Reaction yield	↘ (- 27 %)

Table 6: Initial and optimized hydrolysis conditions comparison

Thus, hydrolysis conditions have been significantly optimized. However, these improvements had an impact on the reaction yield, even if it remains acceptable.

So and to finish, additional analysis have been performed on the last sample after optimized hydrolysis to compare all its characteristics with the reference HMX. The different results obtained were fully satisfactory.

Figure 7: Sample subjected to optimized hydrolysis

Thus, the different trials made on the cast PBX formulation and the hydrolysis parameters had permitted the development of a composition suitable for industrial application, which can be degraded to recover the energetic fillers, under optimized conditions mixing good productivity and satisfactory reaction yield.

The next and last step on this project will then be the revalorisation of the energetics fillers in another composition and its characterisation.

7- Future work and perspective

To simulate the treatment of a munition at its end-life, the optimized composition will be cast in two shells. After polymerization, the cured PBX will be subjected to water jet cutting to remove the composition from the shells. The shells will then be analysed and reused if possible while the wastewater will be treated, after filtration step.

Then, the composition in the form of mud will be subjected to the hydrolysis treatment with optimized conditions. As previously, the energetic fillers will be characterized and they will finally be reused in a second composition which will also be characterized for its energetic performances and mechanical properties.

Thus, these energetic fillers, as well as the shells would have extended lives.

The synoptic of the cast PBX energetic fillers recycling approach is given in the figure below.

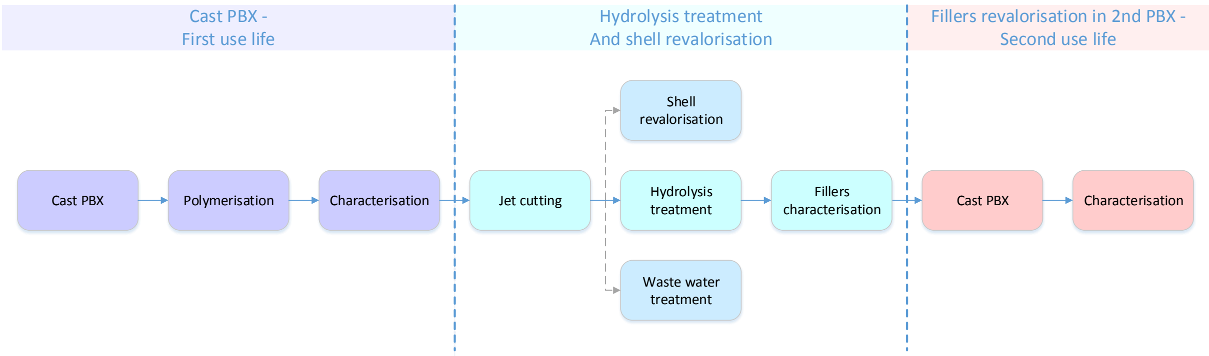

Figure 8: Synoptic of the revalorisation

8- Conclusion

For the majority of its formulations, EURENCO has to face the issue of demilitarisation or ammunition dismantling at the end of use life. However, based on another type of formula using polyester component polymers, it is possible to degrade the binder and recycle or reuse the energetic fillers.

Thus, this project involved two approaches. The first part of the work was dedicated to the optimisation of the composition to combine good feasibility with suitable viscosity, acceptable mechanical properties and good insensitivity and energetic performances. Once this composition defined, the second part of the work was related to the optimization of the hydrolysis conditions. Indeed, with the improvement of the composition, the initial hydrolysis treatment were no longer effective.

So, the hydrolysis conditions have also been optimized to find the best compromise between feasibility, reaction yield and productivity.

Thus, the different trials made on the cast PBX formulation and the hydrolysis parameters led to the development of a composition suitable for industrial application, which can be degraded to recover the energetic fillers, under optimized conditions mixing good productivity and satisfactory reaction yield. In this way, the revalorisation of the energetics fillers for a second use life is made possible.

9- Acknowledgement

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10- Rerences

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