Impacts of REACh, ITAR and other regulations on Energetic Materials Sustainability

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1- INTRODUCTION

EURENCO has for many years been producing a complete range of high explosives as well as the compositions based thereof.

Most of these compositions require the implementation of solvents or various components such as plasticizers, catalysts, binders or bonding agents. In the last years, the availability of these components has become more and more critical because of European or US regulations. Many European companies have to face to these regulation.

Thus EURENCO has identified the chemical components considered as critical in its production process. Some of them have been or will be banned by REACh (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation. The other products are subject to exportation limitations such as ITAR (International Traffic in Arms Regulations) and EAR (Export Administration Regulation) or sometimes by producers themselves which are reluctant to provide products for military applications.

Depending on the component and also the type of regulation, different strategies have been applied to deal with this new issue:

- Find new suppliers of the same component
- Replace the critical component be another one that is supposed to be chemically and/or functionally equivalent

Thus the impact of these regulations could be minor as well as of great importance which means that this can lead to the complete requalification of the composition.

The objective of this paper is to present a summary of the work performed in this area.

2- IDENTIFICATION OF THE CRITICAL COMPOUNDS

2.1- Components impacted by REACh regulation

REACH is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals.
In principle, REACH applies to all chemical substances except polymers; not only those used in industrial processes but also in our day-to-day lives, for example in cleaning products, paints as well as in articles such as clothes, furniture and electrical appliances. Therefore, the regulation has an impact on most companies across the EU.

Thus companies must identify and manage the risks linked to the substances they manufacture and market in the EU which means that companies could be involved as manufacturers, importers or even downstream users.

In the long run, the most hazardous substances should be substituted with less dangerous ones. Thus most of European companies need to anticipate.

EURENCO starts to make a list of critical compounds few years ago. The table 1 presents some of the more relevant compounds.

Impacted compounds	Use	Regulation impacts on the supply	Strategy
DBP Dibutyl Phtalate (CAS 84-74-2)	- Plasticizer	- Prohibited by REACh since 2015	- Replacement
DCE Dichloroethane (CAS 107-06-2)	- Polymerisation solvent	- Impacted by REACh - Not to be used after 2021	- Search for a new polymerization solvent
Tetrachloroethylene (CAS 127-18-4)	- Jellification solvent	- Prohibited by REACh since 2016	- Search for a new solvent

Table 1: EURENCO compounds impacted by REACh regulation

2.2- Components impacted by ITAR or EAR regulations

As for the components impacted by REACh regulation, a list of critical compounds impacted by ITAR or EAR regulation has been made. Some of these compounds are detailed in table 2.

Impacted compounds	Use	Regulation impacts on the supply	Strategy
HTPB R45HT2	- Polymer	- Produced in the USA under EAR licence - Difficulties for renewing the end user statement	- Find new suppliers
Copolymer SBS	- Thermoplastic copolymer	- Long supply period - Difficulties due to the final use (Military application)	- Find an European source
TEPAN tetramethylen pentamine acrylonitrile (CAS 68412-45-3)	- Bonding agent	- Impacted by ITAR regulation	- Find new suppliers
$BiPhi_3$ or TPB Triphenyl Bismuth (CAS 603-33-8)	- Polymerization catalyst	- Impacted by ITAR regulation	- Find new suppliers

Table 2: EURENCO compounds impacted by ITAR or REACh regulations

The problem is slightly different than the one for REACh regulation. The objective for components impacted par ITAR or EAR regulations is to find through a new European supplier the same chemical compounds.

3- TECHNICAL RESULTS

3.1- Components impacted by REACH regulation

Various compounds are impacted: two solvents and one plasticizer.

The difficulty is to find another chemical compound that should have an equivalent function to the old one and that does not have any impact on the final application.

3.1.1- DBP replacement

Dibutyl phthalate was used as a plasticizer in the nitrocellulose varnish used for final coating of modular artillery charges (MACS) and combustible cartridge cases (CCC). As DBP was part of Annex XIV with a sunset date in 2015, a new varnish has been formulated where DBP was replaced by a plasticizer widely used in the cosmetic industry.

Chemical compatibilities were successfully assessed against other products. Measured combustion quickness, ash percentage and permeability were consistent with former definition data.

The overall qualifications of MACS and CCCs were performed, taking into account not only the change in coating but also various changes in the product configuration and the production processes.

3.1.2- DCE replacement

Dichloroethane (DCE) is the solvent for the polymerization of epichlorhydrine (ECH) to get PECH Polyepichlorhydrine), the intermediate polymer in GAP (Glycidyle azide polymer) production. DCE is impacted by REACH regulation and will be authorized for use up to the end of 2021.

Polymerization reactions are based on active species which makes not easy to find a new solvent, furthermore if this new solvent has to be "green" and environmentally friendly.

That is why the replacement of DCE has been undertaken in two parts:

- ➔ Middle term replacement by a standard organic solvent:
  - Another organic solvent that is not yet impacted by REACh regulation and that is compatible with the polymerization reaction conditions and has been tested at lab scale and proved to yield to a polymer with characteristics (Mn / Mp and OH content) equivalent to those of an industrial polymer
  - Process file is also ready for scale up to the industrial workshop.

- ➔ Long term replacement: Research studies are carried on in order to find new ways to polymerize ECH (Epichlorhydrine). Up to now, the early results are very promising.

3.1.3- Tetrachloroethylene replacement

Tetrachloroethylene was used for the jellification of the copolymer SBS in the formulation C1322 used for the production of base-bleed grains. In 2013 this solvent was in the REACh candidate list with a sunset date in April 2016. The replacement of this solvent has been studied in collaboration with a bespoke solvent supplier:

- ➔ Drafting of specification
- ➔ Proposition of new candidates for tetrachloroethylene replacement
- ➔ Proposition by the solvent supplier of 3 alternatives (Biosane 161420, Biosane 1611165 and Butylal)
- ➔ Validation of Biosane 161420 based on physical characteristics such as the saturated vapor pressure and the enthalpy of vaporization.

3.2- Components impacted by ITAR / EAR regulations

To date, the components impacts by ITAR or EAR regulations are mainly polymers, bonding agents or catalysts.

3.2.1- HTPB R45HT2

HTPB R45HT2 is the most used polymer in EURENCO cast PBX compositions. Up to 2016, this product was supplied from a single supplier based in USA and thus impacted by EAR regulation. A new European supplier has been found. According to our specifications, the technical characterizations of the HTPB proposed by the European source are very close to those of US HTPB as presented in the table 3.

Characterizations	Units	Specifications	US HTPB	European HTPB
Viscosity at 30°C	mPa.s	< 6500	5000	4000-5500
OH content	mg KOH/g	/	47.1	44-51
OH content	meq/kg	0.73< <0.90	0.84	/
Mn (g/mol)	g/mol	/	2800	2900
Density at 20°C	/	/	0.901	0.90-0.92

Table 3: Characteristics comparison between HTPB from 2 different suppliers

The qualification in composition of this new source of HTPB is in progress according to:

- ➔ Measurement of the chemical compatibilities with most important granular products (RDX, HMX, NTO)
- ➔ Evaluation in cast PBX compositions in 8 L mixer in order to check the implementation feasibility
- ➔ Evaluation in cast PBX compositions in 35 L industrial mixer to check the implementation feasibility and characterize the compositions
- ➔ Ageing studies at 60°C
- ➔ Evaluation in the proprietary bi-component process

The most relevant results are detailed hereafter.

3.2.1.1- Qualification at 8 L. scale

The qualification has been performed on 6 different cast cured compositions in order to scan a large set of ingredients (See table 4).

For all these compositions, characterization results on:
- Density
- Hardness
- Mechanical properties at +20°C, -45°C and +60°C
- Sensitivity to friction and impact

have been found conform to the specifications and equivalent to those for standard industrial compositions.

Ingredients	B2238B	B2211B	PBXN-109	B2214B	B2263A
RDX	✓	✓	✓		✓
HMX				✓	
NTO				✓	
PA		✓			
Al		✓	✓		
HTPB	✓	✓	✓	✓	✓

Table 4: Compositions for qualification of a new source of HTPB

3.2.1.2- Qualification at 35 L. scale

The next step was to scale up at a 35 L. mixer the following compositions: B2238B, B2263A and PBXN-109.

Results are available for the first two compositions and are in progress for the composition PBXN-109.

The results on both compositions show a good reproducibility from lab scale to pilot scale. Furthermore they are encouraging for scaling up to industrial mixer and make us confident to substitute the US source by the European source.

3.2.2- Copolymer SBS

SBS is a copolymer Styrene-Butadiene-Styrene. A second source of supply had to be found because of the end use (Military application) that is a problem with the current supplier.
The qualification of a new European source of SBS (Named “source n°2” in the following paragraphs) has been successfully done according to:
- ➔ Validation of SBS n°2 compliance with EURENCO specification
- ➔ Validation of SBS n°2 in the production process of C1322
- ➔ Validation of the final composition

3.2.2.1- Compliance of the new source of SBS with the specifications

SBS n°2 has been found compliant as presented in the table n°5.

Characterizations	Units	Specifications	SBS n°2 sample 1	SBS n°2 sample 2
IR	/	Conform to the reference	Conform	Conform
Glass T° by DSC	°C	-98 ≤ ≤ -86	-88.5	-88.4
Volatile matter	%	≤ 0.3	0.03	0.00
Ash content	%	≤ 0.25	0.00	0.00
Viscosity in solution	Poises	9 ≤ ≤ 15	13	14

Table 5: Characterization of SBS n°2

3.2.2.2- Validation of the new source in the final composition

No unexpected behavior has been observed in all production process steps of the composition C1322.

Physico-chemical characteristics as well as safety characteristics have been measured and compared to those obtained with the composition produced from SBS n°1.
The final composition is conform to the specifications and the results of the measurements are quite identical to those on the reference composition. The most important results are summarized in table 6.

Thus the new source has been fully qualified and approved for industrial use.

Characterization	Specification	SBS n°1	SBS n°2
Density (kg/m^3)	1540 / 1600	1560	1567
Glass temperature (°C)	≤ -84	-84	-90.5
Mechanical properties at 20°C ▪ Sm (MPa) ▪ Em (%)	 ≥ 3.5 ≥ 5	 4.3 11.9	 4.5 17.2
Impact sensitivity (J)	/	34	50.1
Friction sensitivity (N)	/	27 + at 353	217
Vacuum stability 130°C/193h. (cm^3/g)	/	0.47	0.21

Table 6: Final validation of SBS n°2

3.2.3- TEPAN

TEPAN (tetramethylen pentamine acrylonitrile) is used as a bonding agent in the formulation of cast PBX or composite rocket propellants. Since it is supplied from USA, it is impacted by ITAR regulation.

Two French alternative suppliers have been identified and samples of TEPAN have been supplied (Named “TEPAN n°2” and “TEPAN n°3” to be compared to TEPAN n°1).

The qualification of these two new sources of TEPAN according to:

- ➔ Characterization of TEPAN
- ➔ Validation of TEPAN at 8 liter mixer scale
- ➔ Validation of TEPAN at industrial scale

3.2.3.1- Characterization of TEPAN n°2 and n°3

Both TEPAN are conform to EURENCO specifications. As an example, the table 7 shows the results for TEPAN n°2.

Characterization	Specification	TEPAN n°1 (Reference)	TEPAN n°2
Total amine content	11/15 eq/kg	13.7	13.7
Water content	≤ 0.50 %	0.28	0.28
IR	Conform to the reference	See figure 1	See figure 1

Table 7: Compared characterizations of TEPAN n°1 and TEPAN n°2

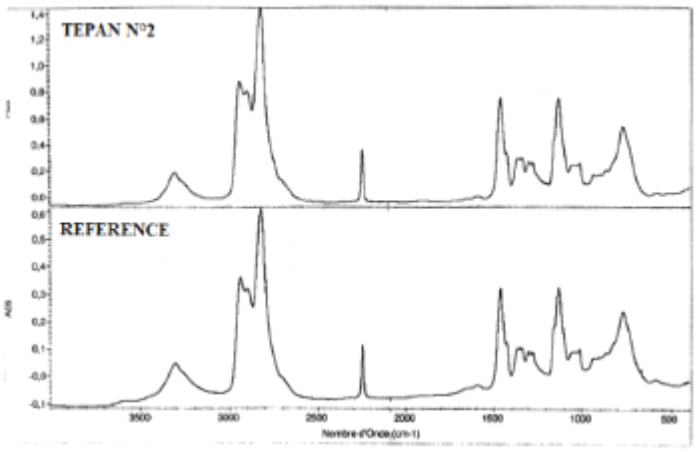

Figure 1: IR spectrum of TEPAN n°2 compared to the US reference

3.2.3.2- Validation of TEPAN in compositions

Both qualities have been tested in formulations at lab scale and the compositions based on TEPAN n°2 and n°3 have been found to be conform with the specifications.

The more relevant results for TEPAN n°2 are summarized in table n°8.

TEPAN quality	TEPAN n°2	
Formulation tested	B2238	B2214B
Viscosity	Compliant with industrial scale	Compliant with industrial scale
Density	1.572	1.636
Mechanical properties ▪ Smt (MPa) ▪ Emt (%)	 0.96 9.3	 0.60 10.6

Table 8: Validation of TEPAN n°2 in composition

- The feasibility data such as the viscosity are compatible for scale up at industrial mixer.
- Densities are as expected for both tested compositions
- Mechanical properties for B2214B are consistent with those at industrial scale for B2214B
- Mechanical properties for B2238 are slightly different (emt little bit low) but it might be due to the scale at which the experiment has been performed.

3.2.4- TPB (Triphenyl bistmuth)

TPB is a catalyst for polymerization of cast cured formulations. Up to 2012 it was supplied in USA. A new supplier has been qualified (Named later “TPB n°2”). TPB n°2 has been tested in PBXN-109 composition. The most relevant characteristics of PBXN-109 prepared with TPB n°2 are presented in the table 9.

Characteristics	PBXN-109 with US TPB[(a)]	PBXN-109 with TPB n°2[(b)]
Density	1669/1683	1669
Mechanical properties at 20°C ▪ Sm (MPa) ▪ Em (%)	 0.33/0.76 19/55	 0.61 19
Shore hardness	44/64	62

(a) Industrial results (36 mixes)
(b) Results at 8 liter scale

Table 9: Qualification of TPB n°2 on PBXN-109

4- CONCLUSION

Most of the issues encountered by EURENCO in France that are induced by the REACh regulation, have been solved, or are about to be solved. For some products (DCE as example) long term research studies are needed in order to find a sustainable replacement product.
Since REACh is still updating, fundamental work will be always necessary to propose environment friendly solutions.

Among the products which are subject to ITAR or EAR authorizations, the most important remaining action is related to the HTPB European supplier, where a long term program is self-supported by EURENCO and remains to be completed.

Moreover, triphenyl bismuth (TPB) could constitute a critical product, even if a non US supplier has been qualified, as no European producer was found.