ECH polymerization – Qualification of a solvent compatible with REACh regulation

Geneviève Eck, Marion Fourdinier, Thibaud Alaime, Céline Bedos, Vincent Chauffour

EURENCO, 1928 route d'Avignon, CS 90109 Sorgues- 84275 VEDENE, France
g.eck@eurenco.com – Phone : +33642117722

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 some other 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.

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 by 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 work performed on the replacement of different identified critical components has already been presented at the 2018 IM & EM Technology symposium that was held in Portland on April 23-26, 2018.

This paper will focus on the work performed on DCE for which long term research studies are needed in order to find a sustainable replacement product.

2- TECHNICAL RESULTS

2.1- Introduction

Thus DCE replacement is ongoing according to two different pathways:

- Middle term replacement
- Long term replacement

Middle term replacement

- ✓ Another organic solvent that is not yet impacted by REACh regulation and that is compatible with the polymerization reaction conditions 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
- ✓ The 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.

The results will be detailed hereafter for the middle term replacement.

2.2- Middle term replacement of DCE

2.2.1- Lab scale results

Two solvents, A and B, other than DCE have been tested at lab scale.
The experiments have been performed on 350 g. of ECH in the following conditions:

- ➔ Reaction medium temperature set between TR_1 and TR_2 for all experiments
- ➔ Double jacket temperature set at T_1 or T_2 in order to measure the impact of the cooling on the polymerization
- ➔ Addition rate of ECH regulated by the reaction medium temperature

For all experiment, special attention was paid to

- ➔ The initiation of the polymerization and the temperature peak that is observed when the reaction starts. This phase is the most difficult one to control.
- ➔ The propagation phase of the polymerization which corresponds to the stabilization phase of the reaction
- ➔ The characterization of the polymer PECH: Average mass in number Mn, average mass by weight Mp and hydroxyl content.

The table 1 summarizes the most relevant results obtained for the polymerization of ECH in different solvents. These results are compared to those for DCE.

Ref.	Solvent	DJ T°[(a)] (°C)	PECH characterizations			
			Mn	Mp	I	OH content (eq/kg)
Average at industrial scale			*1790*	*1890*	*1.05*	*0.80*
DCE-1	DCE	T_2	1670	1890	1.13	0.80
DCE-2	DCE	T_1	1750	1890	1.08	0.75
A-1	A	T_2	1690	1910	1.13	0.86
A-2	A	T_1	1770	1910	1.08	0.84
A-3	A	T_1	1820	1960	1.08	0.80
B-1	B	T_1	1770	1900	1.08	0.83
B-2	B	T_2	1750	1910	1.09	0.78
B-3	B	T_1	1770	1910	1.08	0.81

(a) DJ = Double jacket

Table 1: ECH polymerization – Results in different solvents

The figures 1 and 2 present the temperature of the reaction medium for the initiation phase and the propagation phase.

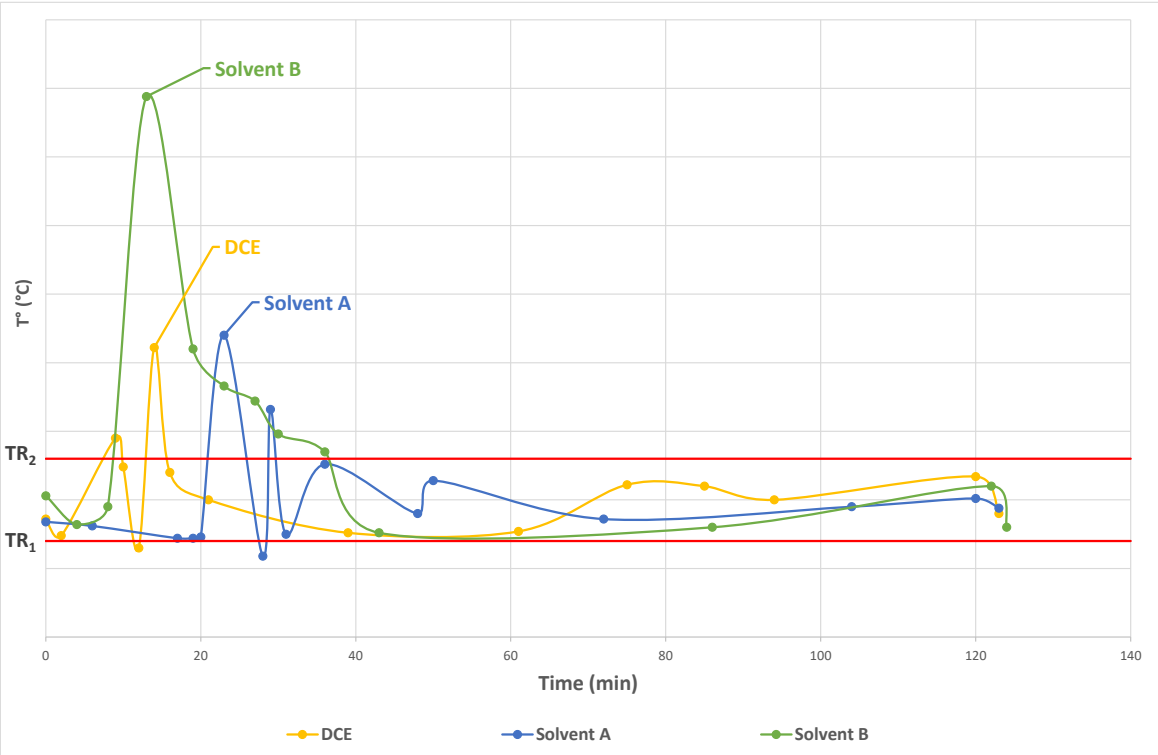

Figure n°1: ECH polymerization at lab scale - Results for a cooling temperature of T_1

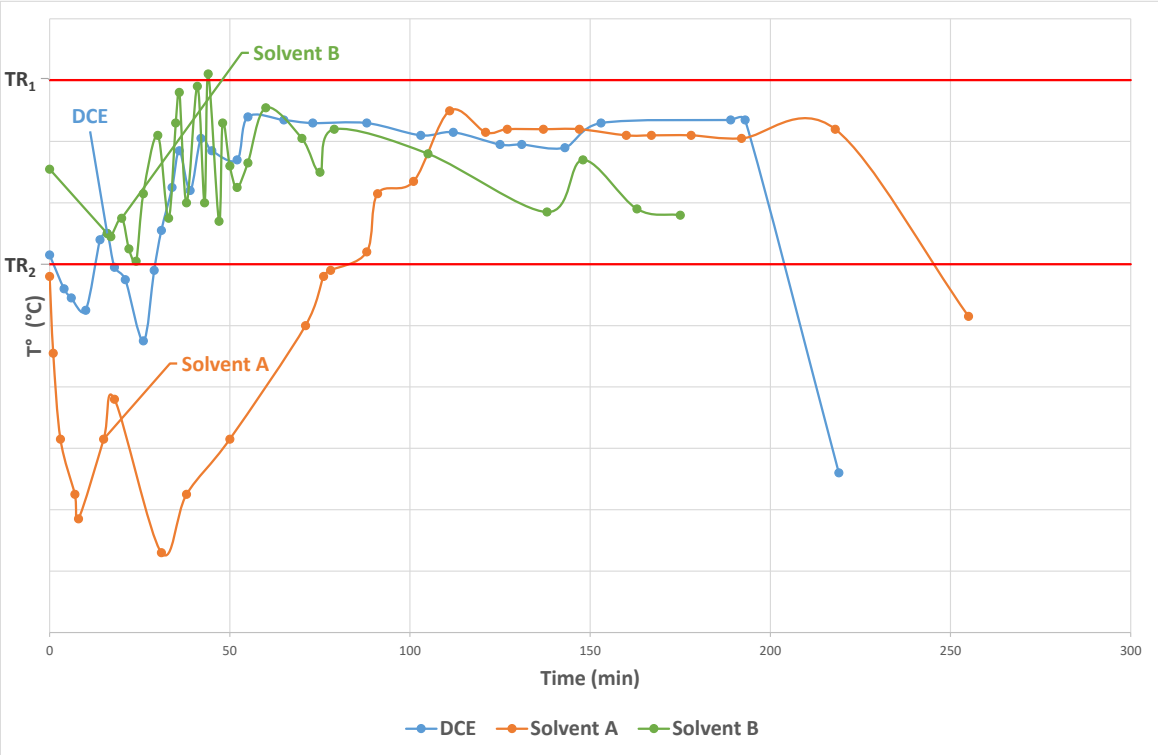

Figure n°2: ECH polymerization at lab scale - Results for a cooling temperature of T_2

Based on the results of the characterizations presented in the table 2:

- ➔ Mn/Mp are reproducible for a same solvent and the same polymerization conditions. Moreover the impact of the polymerization conditions on Mn/Mp seems negligible
- ➔ Hydroxyl contents are reproducible for the experiments performed in the same conditions but might be impacted by the polymerization conditions.

The cooling temperature has, as expected, an impact on the reaction medium temperature peak during the initiation phase:

- ➔ For a double jacket temperature stabilized at T_1, we observed a temperature peak whatever the solvent
  - This exothermic phenomenon is more important for solvent B than for DCE or solvent A.
  - The peak temperature is slightly shifted in time for solvent A compared to DCE and solvent B, suggesting a slower initiation of the reaction
- ➔ For a double jacket temperature stabilized at T_2, the temperature peak for the initiation phase is controlled differently depending on the solvent
  - We observed a good control for DCE and solvent B
  - For solvent A, we had to apply many "cooling down / heating" series in order to control the reaction medium temperature

Based on all experimental observations, the solvent B has been chosen for the scale up.

2.2.2- Scale up

The polymerization has been scaled up to around 600 g. of ECH.

The results are summarized in table 2.

They show that the cooling at T_1 seems giving better results than the cooling at T_2.
This will have to be confirmed before scaling up to the industrial scale.

ECH quantity	Solvent	DJ T°[(a)] (°C)	PECH characterizations			
			Mn	Mp	I	OH content (eq/kg)
Average at industrial scale			*1790*	*1890*	*1.05*	*0.80*
350 g.	B	T_1	1770	1900	1.08	0.83
350 g.	B	T_2	1750	1910	1.09	0.78
600 g.	B	T_1	1570	1870	1.19	0.79
600 g.	B	T_2	1560	1760	1.13	0.92

(a) DJ = Double jacket

Table 2: ECH polymerization – Scale up in solvent B

2.2.3- Process file for scaling up to industrial scale

Based on:
- ✓ The material balance for production, presented in table 3
- ✓ The heat balance explained in table 4
- ✓ The sequence of manufacturing steps
- ✓ The production time

It has been shown that the polymerization of ECH in solvent B is fully compatible with the available industrial equipment with only a few modifications.

	Vessel N°1	Vessel N°2
Raw materials	Initial loading	Recovered or engaged quantities
ECH	M1	0 kg
Solvent B	M2	M2
Initiator	M3	0 kg
Catalyst	M4	Reacted
PECH		M1
Washing ingredients		M5

Table 3: ECH polymerization at industrial scale – Material balance

Synthesis phase	Heat balance [(a)]	
Loading and heating	Q_{Total} (kcal)	72%
	t (min)	80%
	$\Phi_{cooling\ medium}$ (kg/h)	100%
Polymerization	Q_{Total} (kcal)	99.8%
	t (min)	100%
	$\Phi_{cooling\ medium}$ (kg/h)	100%
Solvent extraction	Q_{Total} (kcal)	97.6%
	t (min)	96%
	$\Phi_{heating\ medium}$ (kg/h)	100%

(a) Values for solvent B in % of that for DCE

Table 4: ECH polymerization at industrial scale – Heat balance

3- CONCLUSION AND WAY AHEAD

For EURENCO, one of the most important remaining issue induced by REACh regulation is the replacement of DCE, the polymerization solvent for the synthesis of PECH. Long term research studies are needed in order to find a sustainable replacement product.

A middle term solution has already been found since it has been shown that DCE could be replaced by solvent B. The obtained PECH has the same characteristics than the current one produced at industrial scale.

In parallel, EURENCO is working on long term solutions which means on new polymerization process. The first results are quite promising.