CIP-Eco-innovation Pilot and market replication
Grant Agreement number: ECO/12/332833

PLACARD

CARDANOL BASED PVC PLASTICIZERS

Deliverable N°	4.1
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Deliverable Responsible	Geoffroy Tillieux (EuPC)
Dissemination level	PU
Due date	
Submission date	
Status	

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1 Introduction

Plasticizers are organic esters added to polymers to facilitate processing and to increase the flexibility and toughness of the final product by internal modification of the polymer molecule.

Flexible polyvinyl chloride (PVC) accounts for 80–90% of world plasticizer consumption. The major applications of PVC where plasticizers can be used are: wire and cable, floor coverings, wall coverings, construction, automotive applications, packaging, medical applications, sporting goods, footwear, adhesive tapes and others.

Plasticizers are grouped into the following categories: phthalates, aliphatics (mainly adipates and hydrogenated phthalates), epoxy, terephthalates, trimellitates, polymerics, phosphates and others. Phthalic acid esters, generally known as phthalate plasticizers, are by far the predominant type of plasticizer produced and consumed in the world (78% of world consumption in 2012).

The demand for traditional plastizicers such as phthalate plasticizers could ease switch to eco-friendly, phthalate-free, plasticizers if the industrial and economical requirements for the use of an alternative plasticiser are achieved. These performance requirements of PVC articles are in relation to the duration of the service life of those articles. A significant proportion of the alternatives are not general purpose plasticisers but rather find limited or niche applications, particularly in applications for which DEHP has already been substituted in Europe as a result of past regulatory action (i.e. in toys, childcare products, etc.), or specific technical applications which benefits from isolated, key advantages of the selected alternative plasticiser (e.g. high or low-temperature applications).

This deliverable represents a comprehensive report with focus on business and technical strategic analysis and includes an in-depth analysis of the status of diferent types of plastizicers and markets. The report will be valuable in assessing opportunities and strategies in to introduce PLACARD in the plasticizer business.

2 Plasticizers Market

2.1 Overview

Phthalates accounted for just over 78% of the world consumption of plasticizers in 2012, down from approximately 88% in 2005; they are forecasted to account for 75.5% of world consumption in 2018.

China is the single-largest plasticizer market in the world, accounting for nearly 38% of world consumption in 2012; it also has the highest forecast consumption growth rate during 2011–2018, spurred by increased plasticizer consumption in goods for both domestic and export markets. Other Asian countries taken together, and including Japan, constitute the second-largest plasticizer consuming region, with nearly 21% in 2012, followed by Western Europe (16.0%) and North America (about 13%). Demand for plasticizers in North America is expected to grow at a moderate rate (2.2% per year) during 2011–2018. European demand growth is forecast at an average annual rate of 1.2% during 2011–2018; Western European demand will grow at about 1% while markets in Central and Eastern Europe are expected to grow at a higher rate of 1.9% annually.

The following pie chart shows world consumption of plasticizers:

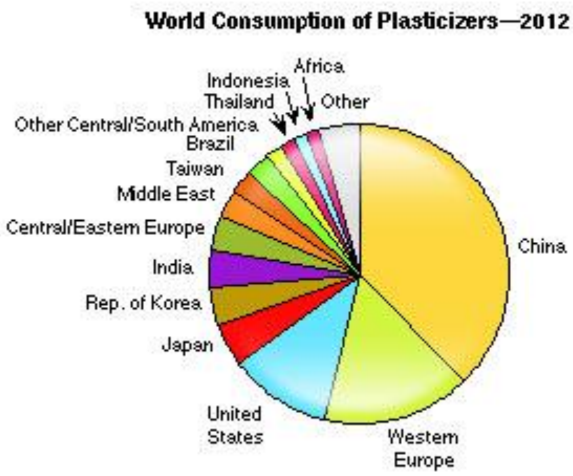
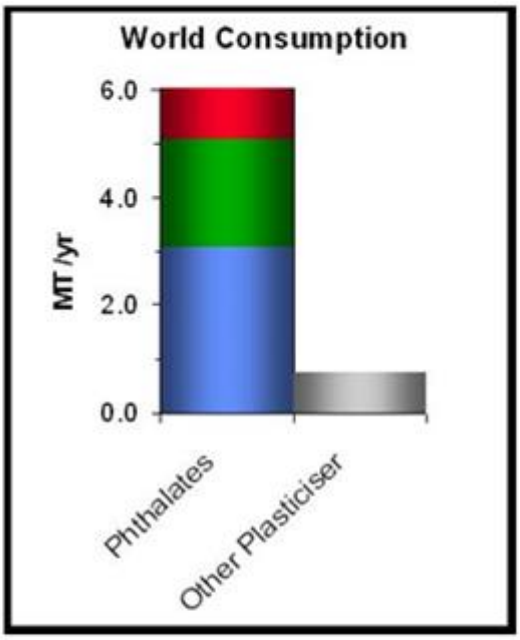


Figure 1: World Consumption of Plasticizers 2012
Source: Bizzari, S.N., Blagoev, M. & Kishi, A. IHS Chemical. (2013, January 1). *Chemical Economics Handbook – Plasticizers*. Retrieved from https://www.ihs.com/products/plasticizers-chemical-economics-handbook.html (on 2015, July 3).

Demand for most downstream plasticizer markets is greatly influenced by general economic conditions. As a result, demand for plasticizers largely follows the patterns of the leading world economies. The major end-use markets include construction/remodeling, automotive production and original equipment manufacture (OEM). Communication and building wire and cable, film and sheet (calendered and extruded), coated fabrics and dispersions (flooring and other) are the largest markets for plasticizers.



	Other phthalates include linears, DPHP, DIUP, DIBP, DBP
	DINP and DIDP
	DEHP
	Other Plasticizers includes adipates,Trimelitate, benzoates, DOTP,DINCH and citrates

Figure 2:World consumtion of plasticizers
Source: Sevenster, A. (2010, September 28). *World Consumption*. Presentation presented at the Fourth Andean Conference on “PVC and Sustainability”, Bogotá, Colombia.

As can be seen in the graph above DEHP is the most commonly used phthalate worldwide (50% of a world consumption of about 7 million tons of plasticizers per year).It is followed by DINP and DIDP (high molecular weight phthalate family), which are as well general purpose plasticizers. Other phthalates (in red) will be used in niches or as co-plasticizers. Please note that this category includes both low molecular weight plasticizers such as DIBP and DBP under scrutiny in Europe

World consumption of phthalate plasticizers is forecast to grow at an average annual rate of 2.4% during 2011–2018. World consumption of lower-molecular-weight phthalates is forecast to decline in many regions as a result of replacement, mostly by nonphthalates.

World consumption of other plasticizers (terephthalates, aliphatics, trimellitates, epoxy, polymerics, benzoates and phosphates) is forecast to grow at an average annual rate of 5.7% during 2011–2018. Terephthalates, benzoates and some aliphatics (mainly hydrogenated phthalates) are forecast to grow at rapid rates as they replace phthalates. Other aliphatic plasticizers, such as citrates and alkane sulfonic esters of phenol, are also expected to grow significantly during 2011–2018, albeit from smaller bases.

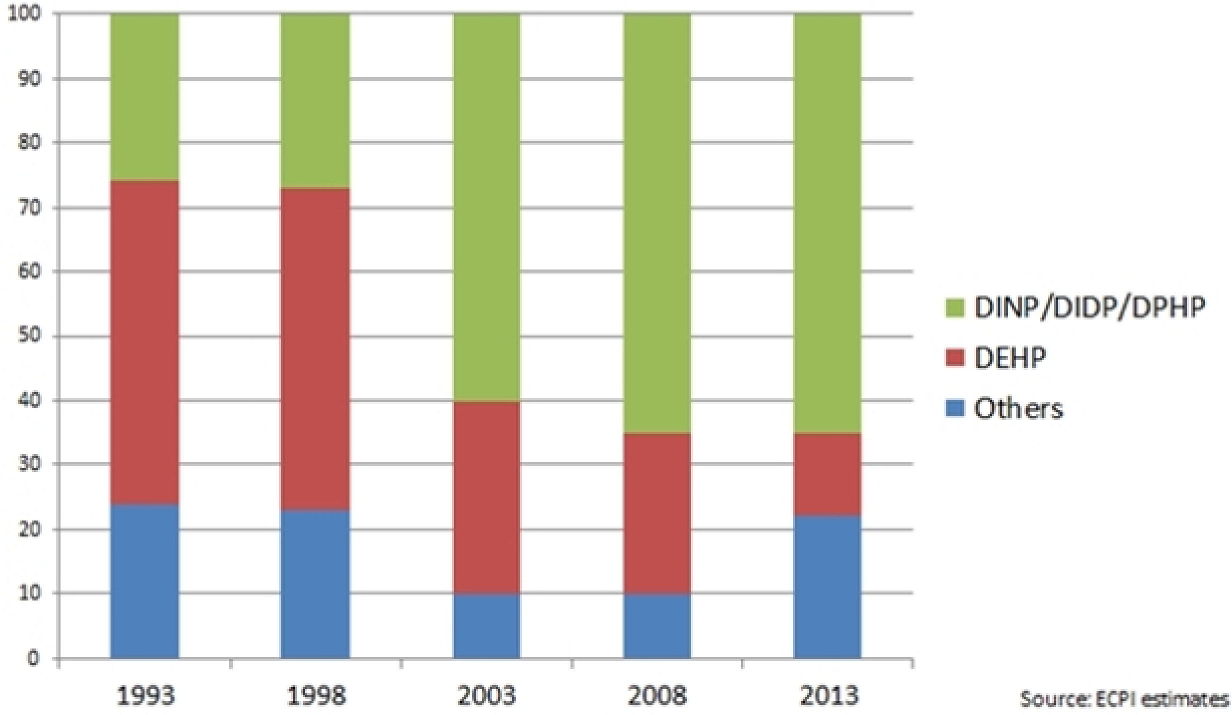


Figure3. Plasticizers consumption in Europe
Source: The European Council for Plasticisers and Intermediates (ECPI). (2014).

One has to note that Europe differentiates from the rest of the world in having almost completely substituted low molecular weight phthalates by other plasticizers through market and regulatory pressure (see section3 on the analysis of regulations and policies). The only market where DEHP remains used largely is medical applications.

2.2 End use Markets for plasticized PVC

According to ECPI (European Council for Plasticisers and Intermediates):

- 96% of plasticisers are used in soft PVC production for durable goods (cable, film, roofing, flooring or wall coverings, etc.).
- Only 4% are used in sensitive applications (medical devices, food packaging, toys), and these applications are all covered by specific European legislation to ensure optimal consumer and environmental safety.
- High molecular weight phthalates account for around 85% of the European market for phthalates.
- Low molecular weight phthalates represent less than 11% of the phthalates used in Europe, and this figure has been falling steadily for more than 10 years.

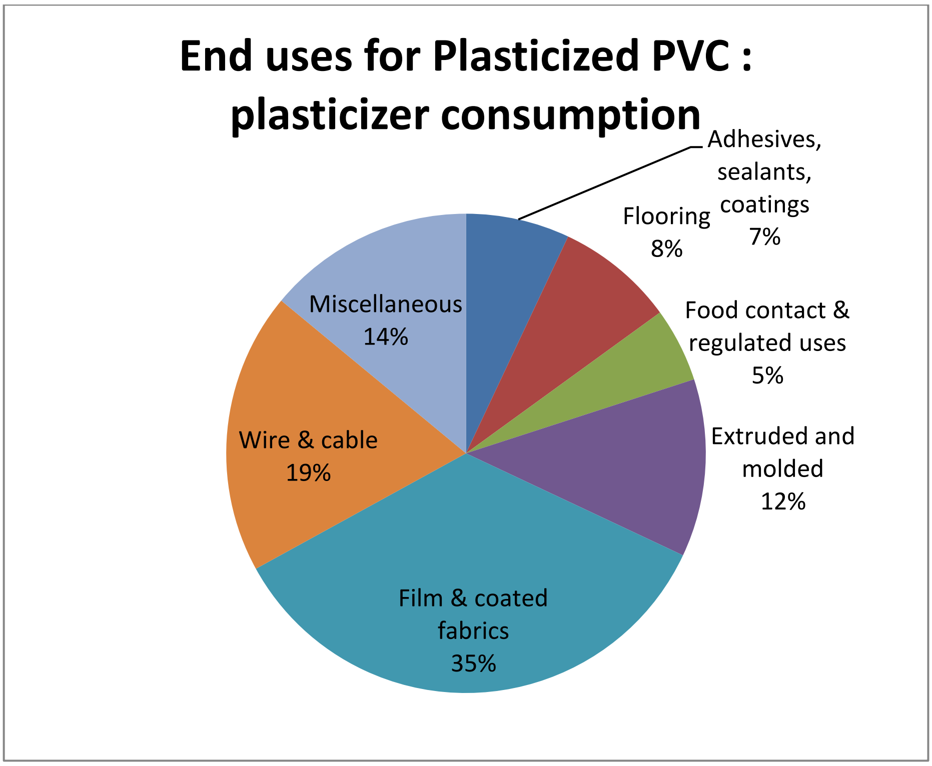


Figure 4: End uses for Plasticized PVC: plasticizer consumption
Source: Wilkes, C., Summers J., & Daniel, C. (2005). *PVC Handbook*, Krauskopf, L. G. & Godwin, A *Plasticizers* (Fig 5.2 p.193). Munich: Hanser Publishers.

3 Analysis of legislation, policies and investigated risks

Over the last decades, PVC plasticizers and more particularly phthalate plasticizers have been under much regulatory scrutiny. This section summarizes first the regulatory constraints applicable today. A second section shall then analyses potential upcoming restrictions and reclassifications. Finally, we remind important obligations a substance in development has.

3.1 Regulatory frame in force

3.1.1 Classified substances and the regulations applicable to them

The first step for a chemical to be considered by regulators is its classification and labelling. Classification of a chemical imposes obligations to label it[1], to foresee special appropriate packaging[2], to provide a safety data sheet to the customer[3].

Low molecular weight phthalates plasticizers and some alkyl esters (between 3 and 6 Carbons) are classified dangerous.

They are furthermore subject to authorization or proposed to be made subject to authorization (REACH Regulation). When the substances are subject to authorization the latest application date and sunset date are indicated[4]. Other plasticizers are not. Please note that from industry knowledge the use of several of those plasticizers is not known in Europe. Several phthalates were not even registered in Europe.

[1] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on the Classification, Labelling & Packaging of substances and mixtures (2008, December 16). Title III. Retrieved from http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008R1272&from=EN (on 2015, July 3)

[2] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on the Classification, Labelling & Packaging of substances and mixtures. (2008, December 16). Title IV. Retrieved from http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008R1272&from=EN (on 2015, July 3)

[3] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 on concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). (2006, December 18). Art. 31. Retrieved from http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R1907-20140410&from=EN (on 2015, July 3)

[4] Sunset date: latest date by which a manufacture may place a substance on the European market without an authorization. Please note exception: latest application date.

Latest application date: latest date at which an Application for Authorization must be introduced to the European Chemicals Agency enabling the substance to continue to be placed on the market pending decision by the European Commission, even after the sunset date.

Chemical name	CAS number	Classification	Registered	Subject to authorization?	Sunset date	Latest Application date
BenzylButyl Phthalate (BBP)	85-68-7	Toxic for Reproduction IB	Yes	Yes	21/02/2015	21/08/2013
DEHP	117-81-7	Toxic for Reproduction IB	Yes	Yes	21/02/2015	21/08/2013
DBP	84-74-2	Toxic for Reproduction IB	Yes	Yes	21/02/2015	21/08/2013
DiBP	84-69-5	Toxic for Reproduction IB	Yes	Yes	21/02/2015	21/08/2013
1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich	71888-89-6	Toxic for Reproduction, Category 1B, H360D	No	Tbc	Tbc	Tbc
Bis(2-methoxyethyl) phthalate	117-82-8	Toxic for Reproduction, Category 1B, H360D	No	Tbc	Tbc	Tbc
1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters	68515-42-4	Toxic for Reproduction, Category 1B, H360D	No	Tbc	Tbc	Tbc
Dipentyl phthalate (DPP)	131-18-0	Toxic for Reproduction, Category 1B, H360D	No	Tbc	Tbc	Tbc
N-pentyl-isopentylphthalate	776297-69-9	Toxic for Reproduction, Category 1B,	No	Tbc	Tbc	Tbc

		H360D				
Diisopentylphthalate	605-50-5	Toxic for Reproduction, Category 1B, H360D	Yes	Tbc	Tbc	Tbc
1,2-Benzenedicarboxylic acid, dipentylester, branched and linear	8477-06-0	Toxic for Reproduction, Category 1B, H360D	No	Tbc	Tbc	Tbc

Table 1: Phthalates subject to or being proposed for authorisation

On 12 December 2014, the European Chemicals Agency (ECHA) Member State Committee has concluded that DEHP is an endocrine disruptor of equivalent level of concern for its environmental properties. This classification is contested by the European Council of Plasticizers and Intermediates[5] based on the following main elements:

- ECPI considers that the science on DEHP does not support such a conclusion as the weight of evidence shows that DEHP does not cause adverse endocrine effects in fish and other aquatic organisms. Moreover, DEHP does not bio accumulate and therefore DEHP cannot pose a hazard to higher mammals in the environment.
- ECPI does not agree with the Member State Committee that the WHO/IPCS definition of adverse effects consequent to an endocrine mode of action, for the environment, has been met and demonstrated in the dossiers submitted

As can be seen in the table above applications have been submitted for the use of DEHP and DBP. So far only one application of DEHP has been granted to Rolls Royce plc for "the processing of a stop-off formulation containing DEHP during the diffusion bonding and manufacture of aero engine fan blade"[6]. More implementing decisions are in the pipeline however.

First, ECHA recommended to grant authorisation as the risk is adequately controlled for the following application:

For 12 years:

- Use of DBP as an absorption solvent in a closed system in the manufacture of maleic anhydride (Deza a.s, Sasol-Huntsman GmbH.)

[5] The European Council for Plasticisers and Intermediates (ECPI). (2014, December 17). *ECHA conclusion to list DEHP as an Endocrine Disruptor for the environment*. Retrieved from: http://www.plasticisers.org/mediaroom/38/57/ECHA-conclusion-to-list-DEHP-as-an-Endocrine-Disruptor-for-the-environment (on 2015, July 3)

[6] Commission implementing decision of 7 August 2014 granting an authorisation for a use of bis(2-ethylhexyl) phthalate (DEHP) under Regulation (EC) No 1907/2006 of the European Parliament and of the Council, C(2014) 5551 final.(2014, August 7). Retrieved from: http://ec.europa.eu/environment/chemicals/reach/pdf/c_2014_5557_en.pdf (on 2015, July 3)

- Use of DBP in propellants Formulation (ammunition for civil and military use, ejection seats etc…) (Deza a.s.)

For 4 years:
- Industrial use of DEHP and DBP in the manufacture of solid propellants and motor charges for rockets and tactical missiles (Roxel (UK Rocket Motors) Ltd)
- Industrial use of DBP within a specialty paint in manufacture of motors for rockets and tactical missiles (Roxel (UK Rocket Motors) Ltd)

To continue the European Chemicals agency recommended to grant authorization for socio-economic reasons for the following applications:
For 4 years:
- DEHP use in Formulation of DEHP in compounds, dry-blends and Plastisol formulations (Arkema, Grupa Azoty and Deza a.s.)
- DEHP Industrial use in polymer processing by calendering, spread coating, extrusion, injection moulding to produce PVC articles [except erasers, sex toys, small household items (<10cm) that can be swallowed by children, clothing intended to be worn against the bare skin; also toys, cosmetics and food contact material (restricted under other EU regulation)] (Arkema, Grupa Azoty and Deza)

For 7 years:
- Formulation of recycled soft PVC containing DEHP in compounds and dry-blends (Vinyloop Ferrara SPA, Stena Recycling AB, Plastic Planet srl)
- Industrial use of recycled soft PVC containing DEHP in polymer processing by calendering, extrusion, compression and injection moulding to produce PVC articles (Vinyloop Ferrara SPA, Stena Recycling AB, Plastic Planet srl)

After 21 February 2015 only those companies having submitted the application for authorization shall be allowed to place DEHP on the market and only in the above mentioned uses pending the implementing decision of the Commission which should in principle follow those recommendations.

In food contact, only the following uses of DEHP would continue:
(a) Plasticiser in repeated use materials and articles contacting non-fatty foods;
(b) Technical support agent in concentrations up to 0,1 % in the final product

Since no application was made for BBP, the still allowed uses in food contact will be discontinued.

Other plasticizers are not classified. This includes the following families:
- High Molecular Weight orthophthalates such as DINP and DIDP (>7C)
- DINCH (Cyclohexanoate)
- Adipates

- Benzoates
- Citrates
- Phosphate esters
- Sebacates
- Azelates
- Trimellitates (TOTM)
- Terephtalates (DOTP and DBT)
- Oil based plasticizers (ESBO, ELO, Castor oil based)

3.1.2 Other restrictions

Due to historical reasons, the high molecular weight phthalates DINP and DIDP have been subject to use restrictions in toys and childcare articles[7] and food contact[8] at times when the distinction on properties within the phthalate family based on molecular weight was not so clearly made. Recently the Commission decided that no further restrictions are necessary for the above mentioned phthalates[9].

3.2 Upcoming reclassification/restrictions?

3.2.1 Reclassification of DINP?

On 10 November 2014, Denmark announced its intention to require a new harmonized classification for DINP as toxic to reproduction Repr. 1B, H360DRepr. 2, H361f[10].
This intention was actually made public by the Agency only later (early February). To date the classification dossier (annex XV report) has not been submitted yet and a public

[7] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 on concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). (2006, December 18). Annex XVII entry 52. Retrieved from http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R1907-20140410&from=EN (on 2015, July 3)

[8] Commission Regulation (EU) No 10/2011of 14 January 2011on plastic materials and articles intended to come into contact with food. (2011, January 14). Annex I, table 1, entries 728 & 729. Retrieved from http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011R0010&from=EN (on 2015, July 3)

[9] European Commission, Environmental Directorate-General & Enterprise and Industry Directorate-General. (2014, January 15). *Phthalates entry 52, Commission conclusions on the review clause and next steps*, p.4. Retrieved from: http://ec.europa.eu/enterprise/sectors/chemicals/files/reach/entry-52_en.pdf (on 2015, July 3)

[10] The European Chemical Agency (ECHA). (n.d.) *Current CLH intentions*. Retrieved from http://echa.europa.eu/registry-current-classification-and-labelling-intentions/-/substance-rev/4917/term?_viewsubstances_WAR_echarevsubstanceportlet_SEARCH_CRITERIA_NAME=1%2C2-Benzenedicarboxylic+acid%2C%20di-C8-10-branched+alkyl+esters%2C%20C9-rich&_viewsubstances_WAR_echarevsubstanceportlet_SEARCH_CRITERIA_EC_NUMBER=271-090-9 (on 2015, July 3)

consultation has not begun. The relevance of this new classification proposal is questioned by the plasticizer industry[11].

3.2.2 ECHA evaluation of potential additional restrictions concerning DEHP, BBP, DBP and DiBP

According to Article 69(2), ECHA shall after 21 February 2015 consider whether the use of these phthalates in articles poses a risk to human health or the environment that is not adequately controlled. If ECHA considers that the risk is not adequately controlled, it shall prepare an Annex XV dossier, in order to initiate the restriction procedure. The compilation of the Annex XV dossier is carried out as a joint project between ECHA and the Danish CA[12].
The articles falling in the categories below might be subject to restriction:

- Articles that may lead to prolonged contact with skin or mucus membranes
- Articles for indoor use, including articles in vehicle interiors
- Articles that may come in contact with food or other fluids or solids intended for ingestion or transfusion to humans (e.g., medical devices or supplies)

The Agency is expected to issue a report by 8 January 2016[13]. A restriction would then probably be implemented by the end of the year.

3.3 Regulatory obligation for substance subject to R&D

Beyond the duty to notify the agency in order to identify the substance under development, the project should also apply for an R&D exemption according to article 9 of REACH (regulation 1907/2006/EC). Otherwise a registration dossier would have to be submitted to

[11] The European Council for Plasticisers and Intermediates (ECPI). (2015, February 16). *Questions scientific basis of surprising proposal by Denmark for harmonised classification and labelling of DINP*. Retrieved from http://www.plasticisers.org/mediaroom/70/57/ECPI-questions-scientific-basis-of-surprising-proposal-by-Denmark-for-harmonised-classification-and-labelling-of-DINP (on 2015, July 3)
[12] The European Chemicals Agency (ECHA). (n.d.). *Previous calls for comments and evidence.* (DEHP, DBP, BBP and DiBP). Retrieved from : http://www.echa.europa.eu/web/guest/addressing-chemicals-of-concern/restriction/previous-calls-for-comments-and-evidence/-/substance-rev/8721/term (on 2015, July 3)
[13] The European Chemicals Agency (ECHA). (n.d.). *Current Restriction Intentions*. (DEHP, DBP, BBP and DiBP). Retrieved from : : http://www.echa.europa.eu/web/guest/registry-of-current-restriction-proposal-intentions/-/substance-rev/6301/term (on 2015, July 3)

the European chemicals agency before 1 tonne of product is put on the market in line with article 6 of REACH.

4 Plasticisers Key Performance Indicators

Plasticisers are responsible for the physical properties of the plasticised product, its processing performance, and its cost. In selecting a plasticiser, the downstream user must consider a number of technical parameters, such as compatibility, efficiency, permanence, and economy, which depend on specific technical criteria before the ultimate goals of the production and final product (article) can be achieved.

Clasification of plasticisers

- Phthalates
  - Diisononyl phthalate (DINP)
  - Diisodecyl phthalate (DIDP)
  - Di(2-propylheptyl) phthalate (DPHP)
  - Di(2-ethylhexyl) phthalate (DEHP, DOP, dioctyl phthalate)
  - n-Butyl benzyl phthalate (BBP)
  - Linear phthalates
  - Diundecyl phthalate (DUP)
  - Ditridecyl (DTDP) phthalate
  - Dimethyl phthalate (DMP)
  - Di-n-butyl phthalate (DBP)
  - Diethyl phthalate (DEP)
  - Other

- Aliphatics
  - Adipates
    - **DOA**
  - Triethylene glycol di-2-ethylhexanoate
  - **Alkane sulfonic esters of phenol (ASEPs**)
  - Azelates and sebacates
  - Citrates
  - Other

- Terephthalates
  - Dioctyl terephthalate (DOTP)
  - Di-n-butyl terephthalate (DBT)

- Epoxy Plasticizers

- Benzoates

- **Dibenzoates**
- Other

➢ Trimellitates

- **Trioctyl trimellitate (TOTM)**
- Triisononyl trimellitate (TINTM)
- Other

➢ Phosphate Plasticizers

- Aryl phosphates
- Alkyl phosphates

➢ Polymeric Plasticizers

The objective of this section is to define a set of performance indicators for general and specific plasticizers in order to achieve the desired business results for PLACARD. These indicators are the objectives to be targeted and represent the most valuable properties for the plasticizers in the converting industry.
The success of the project will be determined if Placard plasticizer is finally seen as a technically and economically feasible product in the market.

The most used families of plasticizers used for soft PVC in building and construction applications are summarized in Table 2.

Name	Main use	Key performance
Phthalates		
DEHP	General purpose	
High Molecular Weight Phthalates (DINP, DIDP,DPHP)	General purpose, durable goods	Improved permanency
Specialty plasticizers		
Adipates	Cable	Cold flexibility
Di-benzoates	Sealants and flooring	
Alkyl sulfonic esters of phenol	Saponification resistance, sealants	Fast fusing processability
Trimellitates	Cable, High temperature	Good performance at high temperature

Table 2: Plasticizer families and properties

4.1 Main Performances

The table here below provides yet another classification of plasticizers according to their performance into 3 families: general purpose, performance plasticizers and specialty plasticizer. It shows both the primary and secondary performance functions.

Family	General Purpose	Performance plasticizers			Specialty plasticizers		
		Strong solvent	Low temp	Low volatility	Low diffusion	Stability	Flame resistance
Phthataltes	X	√	√	√	√		√
Trimellitates			√	X	√		
Aliphatic dibasic esters			X				
Polyesters				X	X		
Epoxides			√	√		X	
Phosphates		√	√				X
Extenders	X						
Miscellaneous		X		X	X		

X = Primary Performance Function; √ = Secondary Performance Function

Table 3: Key plasticisers families and associated performance characteristics
Source: Wilkes, C., Summers J., & Daniel, C. (2005). *PVC Handbook*, Krauskopf, L. G. & Godwin, A *Plasticizers* (p.177). Munich: Hanser Publishers.

4.2 Selected performance parameters

Plasticizing efficiency

The primary function of a plasticizer is to give a certain hardness to PVC. Plasticizers have different plasticizing efficiency, meaning that one will have to use more or less of the plasticizer to get the desired plasticizing effect. The more a plasticizer is plasticizing, the less material will be necessary to reach the required hardness. This has an effect on the price of a formulation (see section 7). In order to compare plasticizers, it is therefore necessary to determine a substitution factor which is calculated as per the Equation below:

$$Substitution\ Factor\ (SF) = \frac{phr\ plasticizer\ at\ hardness\ x}{phr\ benchmark\ plasticizer\ at\ hardness\ x}$$

Mechanical behaviour: tensile strength, the force required to pull a material to the point of breaking. In principle, for the same hardness and temperature, the tensile strength should be similar. It is therefore another way to measure the plasticizing efficiency. There could however be some variation between plasticizers.
It is also known that epoxydized structures contribute to a better stability to heat and to UV. One would therefore expect both better processability and better ageing properties.

Gelation and fusion will be used to determine the **processability** of the plasticizer.
The lower the gelation temperature, the less energy is required to process the plasticizer.

A key parameter to control as well is the **volatility** of the plasticizer. Due to the high processing temperature (between 160 and 170°C) fumes may be formed and appropriate risk management measures must be installed. Less volatile substances are therefore of interest. This will also be true for certain end uses such as indoor applications where volatility should be minimized where restriction of Volatile Organic compounds content are in place as is the case in Germany[14], France[15] or Belgium[16].
To continue, we decided to measure the performance of the plasticizer after **ageing** through measuring the **variation of its tensile modulus**.

For the time being, the **performance of the plasticizer at low temperature** has not been measured but this is a property we would like to investigate in order to determine if a price premium could be claimed for such properties. Indeed it is known that other epoxydized products have a good performance at low temperatures. Low temperature modulus values are determined by ASTM D 1043 (Clash-Berg T_f) and brittleness temperature is determined by ASTM D 746 (T_B).

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[14] Umwelt Bundesamt (UBA). (2015, April 1). *AgBB: Health-related Evaluation of Emissions of Volatile Organic Compounds (VVOC, VOC and SVOC) from Building Products.* Retrieved from http://www.umweltbundesamt.de/en/topics/health/commissions-working-groups/committee-for-health-related-evaluation-of-building (on 2015, July 3)
[15] Gouvernement français [French Government]. (2011, March 23). *Décret n° 2011-321 du 23 mars 2011 relatif à l'étiquetage des produits de construction ou de revêtement de mur ou de sol et des peintures et vernis sur leurs émissions de polluants volatils.* [Decree No. 2011-321 of 23 March 2011 on the labeling of construction products or wall cladding or floor and paints and varnishes on their emissions of volatile pollutants]. Retrieved from http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000023759679&categorieLien=id (on 2015, July 3).
[16] Service public fédéral sante publique, sécurité de la chaine alimentaire et environnement, Belgique [Federal public health public service, food chain safety and environment, Belgium]. (2014, August 18). *Arrêté royal du 8 mai 2014 établissant les niveaux seuils pour les émissions dans l'environnement intérieur de produits de construction pour certains usages prévus.[* Royal Decree of 8 May 2014 establishing the threshold levels for emissions into the indoor environment of building products for certain intended uses]. *Retrieved from* http://www.ejustice.just.fgov.be/cgi/article_body.pl?language=fr&caller=summary&pub_date=14-08-18&numac=2014024239 (on 2015, July 3). (M.B. effective from 2015, January 1)

Compatibility
Compatibility of product with PVC both in liquid and ry blend form is a key performance parameter to be determined.[17]

4.3 Comparison of technical properties of Placard plasticizer with benchmark plasticizers

In the following paragraphs we compare Placard plasticizer with the following benchmarks. For general purpose plasticizers, the benchmarks are DEHP, DINP and DOTP. Indeed DEHP use whilt almost discontinued in Europe remains the main plasticizer globally. Change to high molecular weight phthalate or non phthalates such as DOTP as however taken place to a great extent in Europe. Those are therefore better benchmarks for the European market.

We have also selected two other plasticizers as reference.
Epoxydized soybean oil is a well-established plasticizer in the same epoxidized family as Placard.
Grindsted soft-N-safe is on competing "green plasticizer".

4.3.1 Hardness

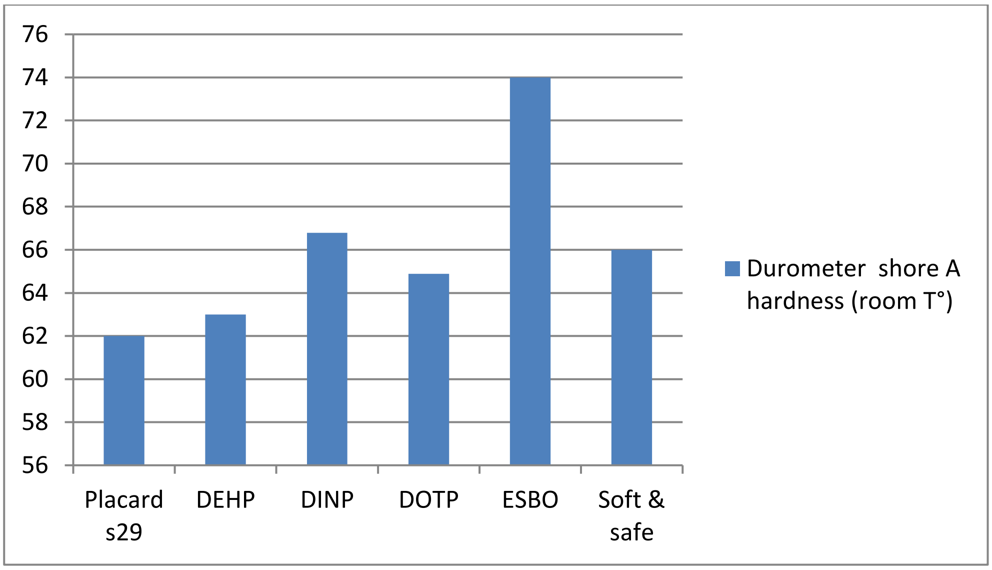


Figure 5: PVC hardness with 70 phr plasticizer, 6 phr stabilizer and 3 phr co-stabilizer
Source: Placard Consortium

[17] Feedback European Council of Plasticizer manufacturers and Intermediate (ERFMI) held on 8/06/2015.

The graph above shows the very good performance of Placard plasticizer which has a slightly better plasticizing effect than DEHP and a clear advantage compared to its European competitors.

4.3.2 Mechanical properties:

Tensile strength of PVC plasticized by DINP is similar to that of PVC plasticized by DEHP, as reported in **Figure 6 a**), extracted from [1]. In this case, Placard, which lowers the strength by a higher amount (**Figure 6 b)**), is more efficient than DEHP and DINP (a plasticizer, softening the polymer, is expected to decrease the tensile strength).
In **Figure 6 a)**, the tensile strength of PVC plasticized by 70 phr of DEHP can be estimated to be, by the linear fitting,

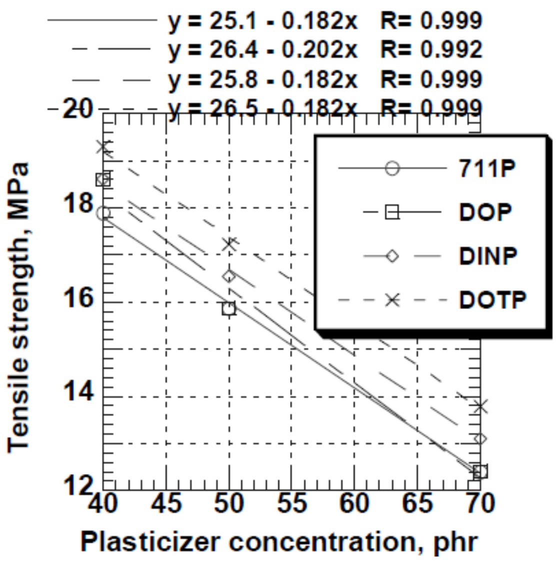
$$\sigma_T(DEHP) = 26.4 - 0.202phr = 12.3\ MPa$$

And the tensile strength of PVC plasticized by DINP:

$$\sigma_T(DINP) = 25.8 - 0.182phr = 13.6\ MPa$$

Therefore almost the same value of strength. Instead, by **Figure 6 b)** the tensile strength of PVC with Placard S29 is 20% lower than that of PVC plasticized with DEHP, and the tensile strength of soft PVC with placard S32 is 15% lower than that of soft PVC with DEHP. Addition of Placard involves a decrease of the strength by a factor of 20% (for S29) and 15% (for S32) compared to DEHP and DINP.

a)



b)

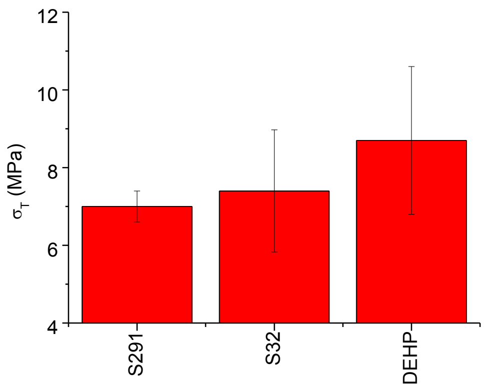


Figure 6: Tensile strength comparison a) between DEHP and DINP plasticised PVC and b) between soft PVC samples with DEHP and Placard.
Source: Placard Consortium

4.3.3 Gelation and fusion

Gelation of PVC plastisols with DINP occurs at higher temperatures (about 15°C) compared to PVC plastisols with DEHP, as reported in Figure **7** a), whereas gelation is faster (about 10 °C) in the case of Placard, as reported in Figure **7**b). **Addition of Placard therefore involves a decrease of the gelation temperature by 10°C compared to DEHP and by 25°C compared to DINP.**

a) b)

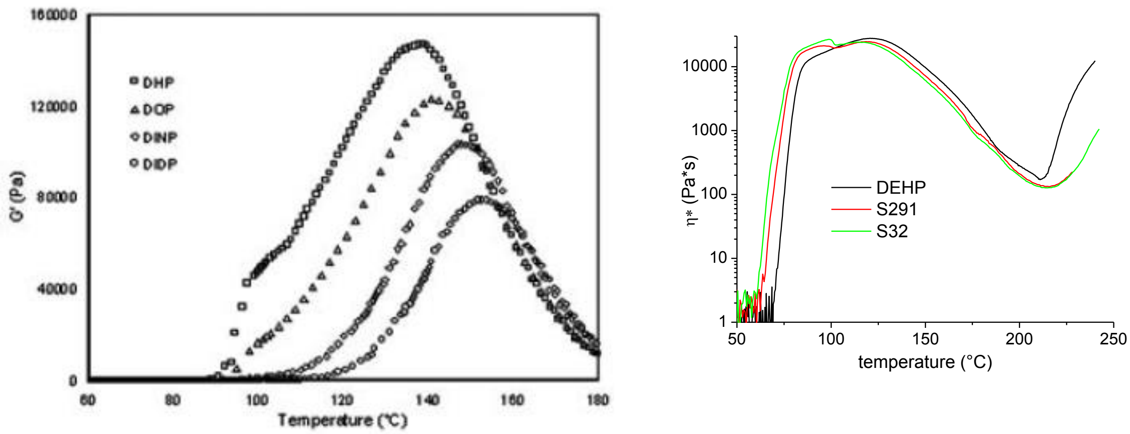


Figure 7: Viscosity evolution comparison a) between DEHP and DINP plasticized PVC and b) between soft PVC samples with DEHP and Placard
Source: Placard Consortium

4.3.4 Volatility

Placard plasticizer S29 is characterized by a diffusivity 1.94 times lower than that of DEHP, and therefore 1.3 times higher than that of DINP. Its diffusivity is slightly higher that of ESBO or Grindstead Soft-N- Safe.

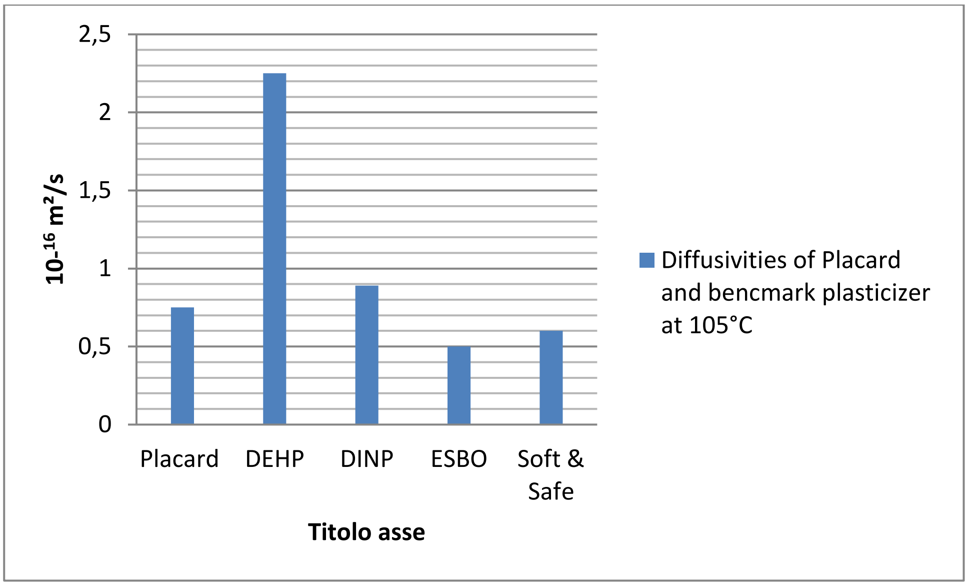


Figure 8: Diffusivity comparison between soft PVC samples with Placard and benchmark plasticizers
Source: Placard Consortium

4.3.5 Performance after ageing

Placard plasticizer keeps good performances after ageing performed at 105°C for 15 days. It is comparable to ESBO but better than DEHP and much more stable than Grinstead soft and safe.

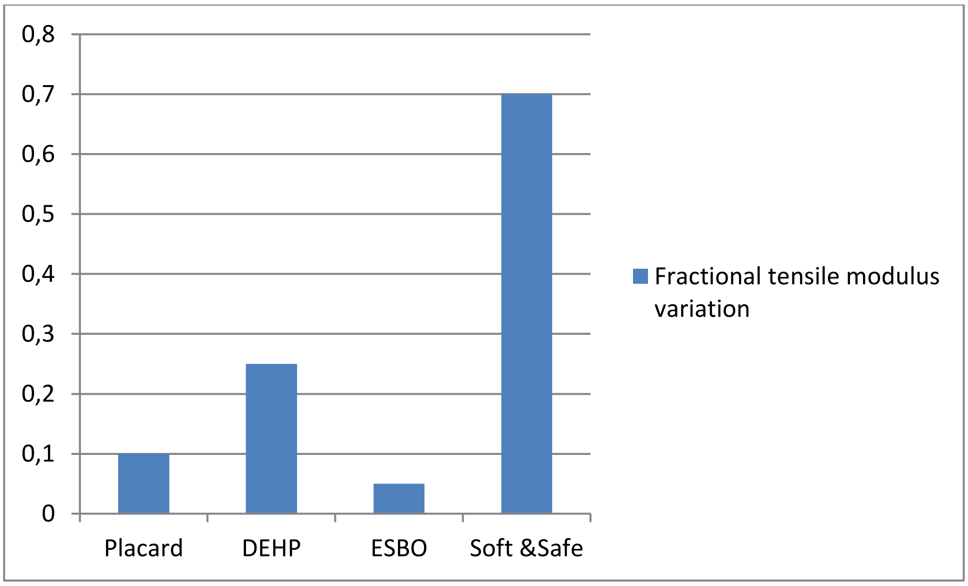


Figure 9: Comparing ageing behaviour of Placard plasticizer and plasticizers benchmarks
Source: Placard Consortium

4.3.6 Thermal stability

At the moment we do not have values for Placard plasticizer , this will be part of further research activity.

4.3.7 Compatibility

This key performance shall be evaluated later in the project both for liquid plasticizer and dry blends. This is an important market requirement.

5 Green PVC Plastizicers

PVC is a very versatile thermoplastic because of its ability to solve a broad range of different concentrations of plasticizer. The most commonly used plasticizers in PVC are phthalates. However, there is an increasing pressure from both public authorities and customers to shift towards the use of phthalate-free alternatives. Since the last years the plasticizer suppliers have been constantly developing alternatives to phthalates DEHP and DINP, which are produced using phthalic anhydrides.

According to Lanxess, the global market for phthalate-free plasticizers is currently estimated in 2013 EUR1.3bn ($1.7bn) with annual growth rate of 7%.

The desired properties of "Green" Plasticizers suppliers are:

- Reduction of greenhouse gas emissions and carbon footprint.
- Flame resistance
- Safe end-of-life disposal
- Direct one-to-one replacement for DEHP, DINP and DPHP
- Cost competitive alternative
- Safe toxicological profile, suitable for sensitive applications
- Low temperature flexibility and good oil resistance
- Designed for demanding high temperature applications
- Excellent low Volatile Organic Compounds (VOC) characteristics
- Good resin compatibility, especially for PVC-rubber copolymers
- Provides increased hydrocarbon resistance
- Very low mixing viscosity
- Easy processing
- Low migration values
- Excellent thermal and UV stability

5.1 Non phthalates general purpose plasticizers

Hexamol DINCH (BASF) and DOTP fall within this family and are clearly marketed as an alternative to phthalates. Those and especially DOTP are gaining growing market share.

Which selling points?

DINCH[18]

- Non phthalate
- Balanced set of properties
- Thoroughly studied and excellent toxicological profile
- Excellent cold flexibility
- Support user to make material available

DOTP[19]

- Safe
- High performing
- Affordable
- Phthalate free
- Non VOC

[18] BASF, (n.d.) *Hexamol® DINCH® brochure*. Retrieved from : http://www.plasticizers.basf.com/portal/load/fid255202/Hexamoll%C2%AE%20DINCH%C2%AE%20-%20the%20trusted%20non-phthalate%20plasticizer.pdf (on 2015, July 3)

[19] Oxea. (n.d.). *Oxsoft® go phthalate free brochure*. Retrieved from : http://ox-rch.by.nf/fileadmin/phthalate/OXSOFT/OXSOFT_OXBLUE-Bruchure.pdf (on 2015, July 3)

5.2 Bio-based plasticizers

A huge variety of products are investigated to determine their suitability as plasticizers. Actually on the market it can be found the following bio-based/” plasticizers.

Company	Product	
Lanxess	Mesamoll	based on alkanesulfonic acid esters
UNITEX	BioAmber	bio-succinic acid-derived plasticizers
Eastman	Scandiflex	based on bio-butanol
Oxea	Oxblue	
Dow	Dow Ecolibrium	
Galata Chemicals	Drapex® Alpha	epoxidized soybean oil
PolyOne	reFlex 100	bioplasticizer pipeline
Myriant	Myriflex	biosuccinic acid-based plasticizers
Roquette	Polysorb ID 37	100% bio-based isosorbide diester
DuPont’s	Soft-N-Safe	vegetable oil-based plasticizer
Proviron	Proviplast	

Table 4: Bio-based plasticizers on the market.
Source: ICIS Green Chemicals. (2013)

Another natural plasticizers tested are epoxidized oils of soybean (ESBO), canola (ECO), sunflower (ESFO) and safflower (ESAO). ESBO, ESFO and ESAO are good replacements for DINP for indoor applications. However, crosslinking takes place during thermal ageing of suspension PVC plasticized with ESBO, ECO and ESFO {6}.

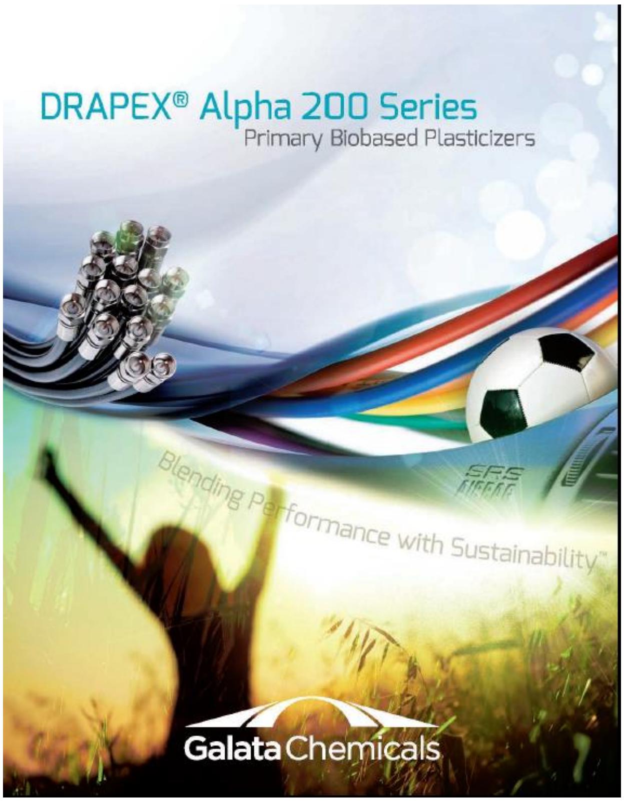
5.2.1 Which selling points? Some examples

Dow Ecolibrium[20]

- Phthalate and lead free
- Biobased and hence sustainable
- Reduction of greenhouse gases
- Outstanding performance at low and high temperature

[20] Dow (n.d.). *Dow Ecolibrium, Bio-based plasticiser*. Retrieved from http://www.dow.com/ecolibrium/ (on 2015, July 3)

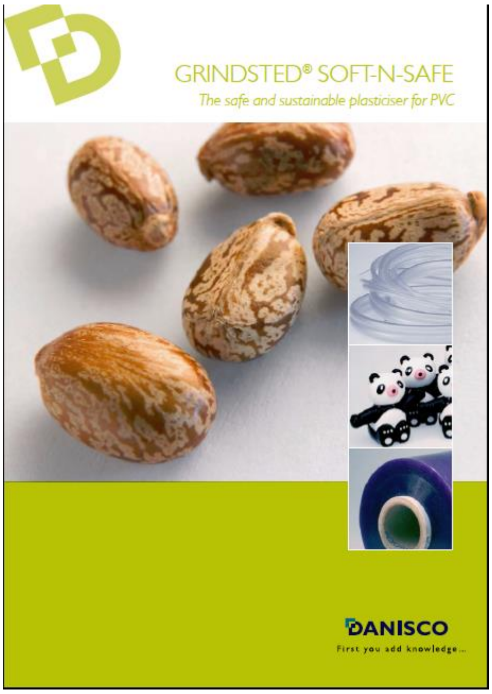
Drapex Alpha[21]



- Natural oil based primary plasticizer
- Replacement of petroleum based plasticizer
- Improved extraction resistance
- Reduced amount of volatile organic compounds
- Enhanced processability
- Excellent low temperature flexiblity
- Excellent UV light stability
- Wide range of application
- Price competitive relative to conventional plasticizers[22]
- Compares performance with DINP, DOTP and DINCH, DEHP is not even quoted anymore

[21] Galata (n.d.). *Drapech Alpha200 series. Primary bio-based plasticizers brochure*. Recuperated from : http://www.galatachemicals.com/pdf/Galata_DrapexAlpha1.pdf (on 2015, July 3)
[22] Claim is true, quoted price 1,4 EUR/kg

Dupont/Danisco Grindsted® Soft-N-Safe[23]



- Safe and sustainable alternative to phthalates
- Fully biodegradable
- Fully digestible, metabolisism like vegetable oils
- No negative influence on the environment, e.g. no indication of acute aquatic toxicity
- No sign of hormone-disrupting effects or mutagenic/ chromosome aberration
- No indication of dermal absorption/irritation or ocular irritants
- Based on sustainable, non-GM resources, grown and harvested under controlled conditions
- Suited for food contact and medical applications
- Positive public image compared to traditional plasticisers sus as phthalates
- Similar properties to DEHP but less volatile and les migration

[23] Danisco. (n.d.) *GRINDSTED® SOFT-N-SAFE The safe and sustainable plasticiser for PVC*. Retrieved from : http://www.danisco.com/softnsafe/doc/snsbrochure.pdf (on 2015, July 3)

Myriant's Miriflex DOSX[24]

- Mechanical properties similar to those produced by DOA
- Phthalate-free
- Bio-based
- Lower carbon footprint
- Non-food based
- Low temperature flexibility and migration similar to DOA
- DOSX is priced and performance equal to DOA and useful as a secondary plasticizer with DOP
- Applications: general purpose offset, flooring, low temperature flexibilization and food film

[24] Myriant. (n.d.) *Succinate Esters for Renewable Plasticisers*. Retrieved from : http://www.myriant.com/pdf/succinate-based-plasticizers.pdf (on 2015, July 3)

5.3 Claiming the green premium marketing: conclusions

- Phthalate free and sustainable (positive image, children, green colour)
- Full toxicological profile identified
- Bio-based
- Low volatility and migration
- Reduction of CO_2
- Reference point remains general purpose plasticizers
- Sometime improved performance for specific application (food contact, medical, low temperatures)
- The differentiating “green” arguments are not strong because not substantiated
- **Availability is key**

6 Sustainable use of additives in PVC

The PVC value chain (resin, plasticizer and stabilizer producers, converters) has embarked in a 10 year (2011-2020) sustainability programme called VinylPlus[25]. This programme follows a first successful 10 years commitment called Vinyl2010 This Programme has 5 main challenges

1) Controlled loop management : mainly focusing on recycling (800 kT/year PVC waste to be recycled by 2020)
2) Organochlorine emissions
3) Sustainable use of additives (more see below)
4) Sustainable energy & climate stability : focusing on reducing energy use in production
5) Sustainability awareness

A Task force of VinylPlus further developed concept to make the objective “sustainable use of additives a reality. A tool to reach this aim is the so called EPD+ (Environmental Product Declaration Plus) system. This system relies on existing building blocks such as environmental product declaration or information from REACH, but goes beyond so as to match the sustainability criteria developed by the Non-Governmental Organization “The Natural Step”.

In a sustainable society nature is no subject to systematically increasing:

1. Concentration of substances extracted from the earth crust (hence renewable energy, renewable raw materials or recycled, controlled loop)
2. Concentration of substance produced by society (hence minimize emission, controlled loop, emitted products biodegradable)
3. Nature must not be systematically degraded by physical means (sourcing and production must come from well managed ecosystems)
4. People must not be subject to conditions that systematically undermine their capacity and means (functionality supporting human needs, no negative impact to humans or the environment, must enable recycling and compatibility with other PVC waste streams)

In essence, the plasticizer producer will have to produce new data on the sustainable performance of its additive before marketing it:

- Full Toxicological dataset in line with REACH regulation 1907/2006
- Risk assessment in line with « ICCA Guidance on Chemical Risk Assessment, Product Stewardship in action: Sound chemicals management is a global responsibility, 2011. (http://www.icca-chem.org/ICCADocs/ICCA_GPS%20July2011_LowResWEB.pdf)

[25] Information on VinylPlus can be obtained on www.vinylplus.eu

- Life Cycle Analysis, impact assessment and interpretation of the additive according to ISO 14040 to 14044 standards
- Environmental Product Declarations indicators calculated from the above data for the use in products in line with EN 14025:2011, Environmental labels and declarations – Type III environmental declarations – principles and procedures or more specific product standards such as EN 15804 Sustainability of construction works. Environmental product declarations. Core rules for the product category of construction products
- Product Environmental Footprint (PEF) indicators currently under development (http://ec.europa.eu/environment/eussd/smgp/product_footprint.htm)

For reference the currently considered sustainability indicators that may be relevant for PVC can be found below:

Climate change	Photochemical ozone formation
Ozone depletion	Acidification
Ecotoxicity for aquatic fresh water	Eutrophisation terrestrial
Human toxicity cancer effects	Eutrophisation water
Human toxicity non cancer effects	Resource depletion water
Particulate Matter-Respiratory inorganic	Resource depletion mineral/fossil
Ionizing radiation human health effect	Land transformation

Table 5: Indicators considered in EN 15804 (in green) and in PEF (all)

Additional requirements related to TNS boundary conditions will be added in time.

The main PVC additives producers will support this process. On 16 April 2015, a fully revised LCA of DINP was released[26]. A new LCA of Ca Zn stabilizer is expected soon.

[26] The European Council for Plasticisers and Intermediates (ECPI). (2015, April 16) *ECPI concludes LCA study on DINP*. Retrieved from : http://www.plasticisers.org/mediaroom/73/57/ECPI-concludes-LCA-study-on-DINP (on 2015, July 3)

For the LCA itself, PlasticsEurope, http://www.plasticseurope.org/plasticssustainability/eco-profiles.aspx (on 2015, July 3)

7 Market and price

7.1 Pricing

7.1.1 Background

The table here below provides an overview of Reference competing plasticizers to Placard plasticizer.
It shows prices in different regions (Europe, USA and Asia-Pacific) over a period running from July 2014 to June 2015.
Those prices show the variations across regions in the perspective of global sales. They may also be used in order to estimate corresponding pricess in another region when the pricie data were not available directly in one region, especially in Europe.

The following remarks should be taken into account:

To begin with, the prices have been converted to € to allow for comparison. One should however take into account that over the last 12 months the € depreciated by 22%. There could therefore be an overestimate of the prices in other regions.
Markets are also not directly comparable. Prices in Asia are consistently 20% lower than in Europe.

To continue, one should take into account the plasticizer performance for pricing. The substitution factor defined as the amount of plasticizer per hundred resin required to get the same 80 shore A hardness as 52phr of DEHP at room temperature. It is expressed as a ratio of PHR substitute plasticizer divided by 52 PHR DEHP.

Furthermore, gelation temperatures may vary across plasticizers requiring less energy to plasticize the PVC. This is a striking feature of Placard plasticizer as we have seen above.
The Energy saving factor was calculated as follows:

$$Energy\ saving\ factor\ = \frac{1 - 30\%\ \times (DOP\ processing\ T° - Plasticizer\ processing\ T°}{DOP\ processing\ T°}$$

Price comparison of different plasticizers										
Acronym Phtalates	Chemical structure	Molecular weight	Subst factor	Energy saving factor	min-max price/t		US min-max price/t (€)		min-maxprice/t Asia/Pacific (€) CFR	
DOP-DEHP	di(2-ethylhexyl)	390	1	1,00	1410-1540		1419	2040	1032	1358
DINP	di(isononyl)	418	1,06	1,03	1420-1550		1264	1885	996	1402
	Trimellitates									
TOTM	tri(2-ethylhexyl)	546	1,17	NA			2235	3130		
	Adipates									
DOA	di(2-ethylhexyl)	370	0,93	NA			1925	2682		
	epoxides									
ESBO	poxidized soybean o	1000	1,1	NA	1600?				1234	1411
	Others									
DOTP	-ethylhexyl)terephta	390	1,03		1420-1550		1452	1983	1023	1428
DINCH	di(isononyl) cyclohexane-1,2 dicarboxylate	422	NA	NA	1800	*	2061	2430		
Grindsted Soft-N-Safe			1,05	NA	3640	*				
Drapex Alpha			NA	NA	1400	*				
xydized Cardanol Acetate		ca 363	0,98	0,98	2300 €/T+ margin					
Substitution factor = PHR required for 80A Durometer hardness at room temperature vs required DOP level (52,0 phr)										
Energy saving factor : 1- 30%x (DOP processing T°-Plasticizer processing T°)/DOP processing T°										
NA : not available										
* : direct quotations										
? : estimate										
All other prices : source ICIS international (July 2014 to July 2015)										
Exchange rate $/€ = 0,88173										

Table 6: Price comparison of different plasticizers

7.1.2 Discussion

To begin, one can see that general purpose plasticizers DEHP, DINP and DOTP are found within similar price ranges between 1410 and 1550 €/T in Europe. The same tendency can be observed in other regions with DEHP actually priced higher than substitutes in America. There is little correlation between prices and substitution factors for those general purpose plasticizers except marginally in the US, but prices seem to be much more dictated by manufacturing capacity than actual performance. It should also be noted that there is no difference in price for the non-phthalate DOTP despite as we have seen earlier increasing regulatory pressure on phthalate plasticizers.

The bio-based plasticizer epoxidized soybean oil fares better than general purpose plasticizers but not by a big margin (100 €/T price premium). This plasticizer has the advantage to be approved for food contact applications.

DINCH price could range between 1800 (EU) and 2000 €/t (US) but it has applications in niche markets such as food contact or medical applications, which is not for the time being the case for Placard plasticizer. It is interesting to note that DINCH is only reported in pricing tools in the US where the demand seems to be higher for this type of plasticizer.

At current forecasted production prices, Placard plasticizer would rather be in the price range of speciality plasticizers such as DOA (average 2300 €/T) or TOTM (average 2700 €/T). This is why it would be important to further investigate Placard properties in cold conditions which due to its structure should be good.
Placard is moreover like TOTM of low volatility and has distinct advantages in plasticizing performance and processability. This alone would justify a price premium of 15% over DINP and 5% over DEHP (combining the substitution factor and the energy saving factor).

To continue, it is very difficult to ascertain whether the market is ready to pay a green premium for bio-based materials. True, the price of Grindsted soft-N-Safe reaches 3640 €/T but it is far from being a commercial success and the volumes available are in relatively low quantities.
Other bio-based plasticizers hardly show a green premium (100€/T for ESBO due to specific properties such as applicability for food contact or the fact it is bio-based?). Drapex another bio-based plasticizer is priced in the same range as general purpose plasticizers.

In conclusion, although an adequate marketing could enable to claim for a green premium, it will be important that the Placard plasticizer shows other distinctive properties, one of which could be a good performance in cold and to temperature variations enabling to reach markets in the construction field such as cables, membranes for civil engineering and water retention that could also be used in cold climates, landfills etc.

7.2 Availability

Next to pricing, the availability of the material is a key parameter for access to market. With the availability of Cardanol oil in reasonable quantities (300,000 T/year), Placard plasticizer clearly has a basis for allowing a stable supply to PVC converters in construction. This availability could potentially be translated in higher price to be required. The premium will not be big though as there are available alternatives, but companies might be interested to guarantee themselves from the increasing regulatory pressure on phthalates and the recent price volatility.

8 Conclusions

Before concluding on market aspects we want to remind the obligation for the project to notify the agency in line with article 9 of the REACH regulation in order to get an exemption from registration for R&D purposes. Failing this no more than 1 tonne of product may be placed on the market and further development would not be possible.

DINP and DIDP have become the major alternatives to DEHP for general purpose plasticizer applications due to their technical performance close to DEHP and superior to most alternatives, their availability and their comparable costs. Recently DOTP has been gaining market share as an alternative general purpose non phthalate plasticizers. The unabated regulatory pressure on phthalate based plasticizer gives an opportunity for non-phthalate alternatives to develop. However as could be seen above, there doesn't seem to be a price premium granted to non-phthalate general purpose plasticizers. The fact of being bio-based doesn't seem to give a better price premium when properties are similar to general purpose plasticizers.

All other plasticizers which can claim a price premium have specific properties such as food contact useability (ESBO), medical applications (DINCH) or the ability to perform in low or high temperature (e.g. TOTM).
A review of the current green and bio-based plasticizers marketing materials showed however that positioning and marketing was not particularly focused and that the products competed more on typical performance claiming to be green or bio-based without substantiation.

We have also seen that it is to be expected that main plasticizers will provide more extended sustainability data (toxicology, ecotoxicology, risk assessment, full life cycle analysis). It will therefore be a must to generate this data in order to compete with those. On the other hand the development of industry standards should enable those products for which the necessary data have been collected to differentiate from so called "green plasticizers" based on their actual sustainability performance. The bio-based sourcing of Placard plasticizer. Its use of non-food sources and its ability to facilitate recycling should therefore position the plasticizer as bringing additional sustainability value provided this can be adequately documented.

Further to establishing the product sustainability credentials, we have seen its improved performances compared with competitors. Indeed one needs 8% less Placard plasticizer than DINP to obtain the same plasticizing effect. The material shows a good processeability and an energy cost reduced by 5%. The material moreover displays a low volatility and excellent resistance to ageing. To continue its raw materials are relatively abundant.

The plasticizers on the market are however quite price driven. Despite the above advantages, Placard plasticizer will need to exhibit properties enabling it to compete with other specialty plasticizers. Due to its chemical structure we think it would be worthwhile to investigate into the plasticizer performance at low temperature. If its performance can be proven to be comparable to TOTM, it will definitely become an alternative on demanding construction markets such as cabling or civil engineering.

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10 Tables and Figures

10.1 Tables

10.2 Figures