# **RIVM ZZS-2-BIO** project

# The biobased replacement potential of hazardous substances.

Dr. D. S. van Es

Report 1506

Colophon

TitleRIVM ZZS-2-BIO project; The biobased replacement potential of hazardous substances.Author(s)Dr. D. S. van EsNumber1506ISBN-number978-94-6257-352-9Date of publication10-11-2014ConfidentialityNoOPD code-Approved byIr. C. Bolck, Dr. J. van Haveren

Wageningen UR Food & Biobased Research P.O. Box 17 NL-6700 AA Wageningen Tel: +31 (0)317 480 084 E-mail: info.fbr@wur.nl Internet: www.wur.nl

© Wageningen UR Food & Biobased Research, institute within the legal entity Stichting Dienst Landbouwkundig Onderzoek

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system of any nature, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publisher. The publisher does not accept any liability for inaccuracies in this report.

# Abstract

A quick scan of the ZZS (zeer zorgwekkende stoffen) list of 371 substances of very high concern shows that there is significant potential in biobased replacement of part of the list. Most inorganic (i.e. metal based or metal containing) substances on the list cannot be replaced by biobased (or fossil based) alternatives due to their specific physical/chemical properties or applications; e.g. the use of arsenic in solar cells or the use of lead oxide in glass manufacturing.

Some ZZS substance categories are very complex, requiring more time and effort to analyse; such as the petroleum products, but also the coal tar products. Since these categories deal with very large volumes, changes in particular components of integrated chains have impact on the total chain, and hence should be treated with care. A detailed analysis of these complex substance categories thus falls outside of the scope of this quick scan. They could, however, be the subject of a new, dedicated study.

For the remaining part of the substances of very high concern it is shown that in many cases easily implementable biobased alternatives are already available or in advanced stages of development. However, in some cases safe, biobased alternatives are still in early development. This in spite of a growing need for replacement, as is the case for e.g. high polarity aprotic solvents such as DMF, or NMP. Since solvents like NMP enable the manufacturing of environmentally friendly water borne coatings and paints, as well as the development of various carbohydrate based materials, finding effective substitutes should be given high priority. Unfortunately, currently there are no Dutch national science programs that could support or initiate this.

Also more advanced, indirect type of replacement appears feasible. An example of possible short term implementation is the partial replacement of toxic ethylene oxide for the production of ethylene glycol by the hydrogenolysis of glucose to ethylene glycol and propylene glycol. Other advanced level replacements require more time, and deeper analysis in order to assess the impact on product/value chains.

A shortlist of nine substances that could be replaced by biobased alternatives on short term is also presented in this quick scan report. The suggested biobased alternatives for this shortlist are either already commercially available or close to commercialisation.

Overall, this quick scan results in a number of recommendations

- A dedicated follow-up study into the biobased replacement potential for the petroleum products and coal tar products categories.
- Investigate the possibilities for a program on alternative, preferentially biobased, high polarity solvents that can involve the whole value chain, from production to specific applications.
- Specific follow-up studies on ZZS substances for which advanced level replacements have been identified (mid to long term replacements)
- Start a discussion between end-users of the substances on the shortlist, and (potential) producers of biobased alternatives, in order to evaluate the practical feasibility of biobased substitution.

С	Content	
A	bstract	3
1	Introduction	5
2	Methods	7
3	Results & Discussion	8
4	Conclusions & Shortlist	36
R	leferences	41
A	cknowledgements	42
A	ppendix	43

# 1 Introduction

Given the transnational scope of the subject (inventory of chemical substances of very high concern in the EU), combined with the fact that most information on these substances can be found in non-Dutch databases, the language of this report is English. Nevertheless, various terms and descriptions will remain in Dutch.

The policy on chemical substances by the Dutch Ministry of Infrastructure and Environment (Min. I&M) sets targets for reducing the exposure of both man and environment to dangerous chemical substances, particularly for substances called 'zeer zorgwekkende stoffen' (ZZS). These substances are defined by criteria stated in article 57 of the European REACH Regulation and taken up in the respective REACH and CLP Annexes as Substances of Very High Concern (SVHC). In addition, the Ministry considers substances that are listed as 'priority hazardous' in the European Water Framework Directive, the European POP Regulation or within the OSPAR convention as ZZS as well, as these fulfill the criteria stated in article 57.f for substances with an 'equivalent level of concern'. So SVHCs as taken up in the annexes of REACH and CLP as well as (other) substances that fulfill the criteria of article 57.f are referred to as ZZS.

These substances are identified at European level and depending on the nature, application and use volumes, measures are being taken to achieve a gradual phase-out. This phase-out has already begun for certain substances, such as certain types of phthalate plasticisers that have been put on the annex XIV list of the REACH regulation. The use of these substances is prohibited from a certain date, unless companies request an authorisation for use. From a policy perspective it is not only desirable to support the ongoing processes at European level, but also, where possible, to stimulate Dutch enterprises to replace substances of very high concern pro-actively.

Substitution can be achieved in various ways. In the search for functional substitutes to substances of very high concern, increasingly the potential of biobased alternatives is included. The development of a renewable feedstock based chemical industry is an ongoing process. The transition of a fossil resource to a biobased chemical industry offers opportunities for an accelerated phase-out of substances of very high concern. In order to effectively exploit these opportunities supply of biobased alternatives and demand for safe substitutes for substances of very high concern need to be matched, i.e. companies from the supply and demand side need to be brought into contact. The goal of this project is to perform a quick scan matching initiatives from the biobased chemical industry with (groups of) substances of very high concern, whose substitution is highly desirable. The outcome of this quick scan will list the most important examples of substitution of substances of very high concern by biobased products or processes as well as chances for developments in the Netherlands.

In 2013 the RIVM published a report named "Biobased alternativen voor prioritaire stoffen: Een verkennende studie".[1] This study is a basic inventory of biobased alternatives for existing chemicals in the Netherlands which are currently available or being developed. Although several dozen substances were identified in this report, the list is not exhaustive. The report furthermore gives an overview of available methodologies to assess health and safety risks as well as the sustainability of (new) biobased substances, since biogenic substances are not necessarily safer or more

sustainable than fossil derived ones. The current quick scan report is a continuation, in higher detail, of the aforementioned 2013 study.

# 2 Methods

The information on usage/application of the chemicals of high concern is obtained from internet searches using Google, Wikipedia and specific websites of companies, either producers or end-users of the chemicals. Also public information retrievable from e.g. the European Chemicals Agency (ECHA) and the US Environmental Protection Agency (EPA) website has been used. Information on tonnage is based on the data supplied by the RIVM as available from publically disseminated REACH registrations.

The use of patent literature for this study is limited due to several factors. Patent (applications) can be an indication that the assignees (companies or institutes) are active in a certain field of innovation, but can also be used defensively, e.g. to generate freedom to operate, or to divert attention from actual developments. Furthermore, often commercially important developments are not patented in early stages in order to prevent premature public dissemination of knowledge. While for some specific developments patent searches can be done with relative ease, more generic searches or searches involving broadly applicable chemicals can be highly time consuming. E.g. the subject ethylene oxide (oxirane) already gives 1.528 hits in the Espacenet database over the period 2000-2014. Hence, finding <u>relevant</u> patent literature for the 371 substances under consideration in this report falls outside of the scope of the current project.

In this study the chemicals under investigation are part of a list of 371 substances of very high concern as given by the RIVM.

In order to structure the information the data are presented as follows in table form:

- the name (as given in the RIVM list), as well as other, more commonly recognised names
- the CAS# number
- the type of compound:
  - o Intermediate for substances that are commonly transformed into other products, and are not significantly applied in end-products
  - oSolvents
  - oAdditives
  - 0 Minerals
  - oOres
  - oPesticides
  - oCatalysts
- Classification as either organic (Org) or inorganic (Inorg)
- BR-level: biobased replacement level (see below)
- When applicable/desirable the chemical structure is given
- Major applications/markets
- Biobased options/(potential) Suppliers/Stakeholders
  - oCompany names are anonymised, designated as CMP#, while trade/product names are anonymised as TP#.

### 3 Results & Discussion

For most of the substances on the ZZS list (see table 1), only those that are registered in the scope of the REACH Regulation with a reported tonnage of > 100 ton per year are discussed. The reported tonnages are the total annual European registration volumes, i.e. production and import into the EU.

In this report a biobased replacement level (or BR-level) is introduced, which serves as an indication for the potential for replacement of a substance of high concern by biobased alternatives.

The four different BR-levels used in this report are defined as:

- Level 0: no known possibilities either at the current state of technological development or due to the inherent chemical/physical properties/requirements.
- Level 1: drop-in replacement
  - odrop-in is useful only in case the toxicity of the substance of high concern is due to (a) contaminant(s) (e.g. benzene) in the product that arise from the currently used feedstocks and/or conversion technologies, which can be eliminated by using an alternative feedstock.
- Level 2: direct replacement of the substance of high concern by a biobased alternative, based on comparable functionality.
  - o Example: replacement of phthalate plasticisers by biobased non-phthalate plasticisers.
- Level 3: indirect replacement of substance of high concern.

oMore complex, probably longer term process, as it involves biobased replacement of the material that the substance of high concern is used in.

Since most biobased materials are by definition organic substances (apart from minerals like e.g. silica that can be obtained from agroresidues), the focus is on these type of substances on the ZZS list.

On short term (1-5 years) only level 1 and level 2 replacements are feasible as they will have the smallest impact on the whole product/value chain. Level 1 replacement will require minimal changes in the production chain, as the drop-in substance will be practically similar to the original substance. Level 2 replacement will require investments in redesigning chemical processes or processing conditions, re-formulating, and end-product testing (e.g. quality, durability, functionality, toxicity, stability, flammability, etc.). Of course care must be taken that a biobased level 2 replacement is inherently safe.

Level 3 replacement is even more complex since it involves redesigning the product/value chain. Care must be taken to exclude unwanted side effects, like overall reduction of efficiency or increase of unwanted emissions over the whole chain. These prerequisites of course also apply to level 1 and 2 replacements.

In this chapter only those substances that have a potential for biobased replacement (BR levels 1-3) will be discussed. The remaining substances, identified with BR level 0, are listed in the appendix. These substances have no biobased replacement options due to inherent properties. In case of the inorganic substances, the inherent/required chemical or physical properties fall outside of the scope of organic substances (e.g. mercury, cadmium salts, etc). In case of BR

level 0 organic substances, the current applications are too specific (inherent chemical properties) to allow for (biobased) replacement.

Entry	Substance group	# ZZS	# on Annex XIV	Org/Inorg	# Biobased
		registered	candidate list		replacement
		Substances			options
1	Petroleum products	219	-	Org	nd
2	Other	33	15	Org	12
3	Lead/lead compounds	26	26	Org/Inorg	4
4	Nickel/nickel compounds	15	-	Inorg	0
5	Coal products	13	2	Org	>1
6	Boron/boron compounds	10	5	Inorg	0
7	Cadmium/cadmium compounds	6	4	Inorg	0
8	Br/Cl hydrocarbons	6	3	Org	1
9	Oxiranes	5	1	Org	3
10	Chromium/chromium	4	4	Inorg	0
	compounds				
11	Cobalt/cobalt compounds	4	4	Inorg	0
12	Phthalates	3	3	Org	3
13	Azo dyes	3	3	Org	0
14	Hydrazines	3	2	Inorg	0
15	Butadiene(s)	3	-	Org	1
16	Beryllium	2	-	Inorg	0
17	Brominated flame retardants	2	1	Org	0
18	Chlorinated aromatics	2	1	Org	1
19	Glycol ethers	2	2	Org	2
20	Organo mercury	2	-	Inorg	0
21	Non-approved PPP	2	1	Org	0
22	Phenols	1	1	Org	0
23	Arsenic compounds	1	-	Inorg	0
24	Organotin	1	1	Org	1
25	Acrylamide	1	1	Org	0
26	Dimethylformamide	1	1	Org	1
27	Formamide	1	1	Org	0
	Total	371	82		>29

Table 1: overview of the substances/substance groups discussed in this report.

# Petroleum and coal products; entry 1 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
1	Petroleum and coal products	219	-	

The extensive group of ZZS registered petroleum and coal-based products is too complicated to be discussed in detail in this quick scan. Most, if not all of these substances are part of the crude oil and coal distillation/fractionation process as applied by various oil companies or petrochemical processors. Crude oil distillation produces a large number of fractions/products, which form an integrated/interdependent family of substances. Changes in the production or use of certain fractions/product groups has direct impact on the whole system making this rather complex. Furthermore, due to the very large scale of operations, even small changes can have dramatic impact. The overall economy of the distillation process depends on complete valorisation of the feedstock. Taking out fractions will hence also have significant impact on the economic viability of the whole process. An investigation into potential biobased replacement of substances in the petroleum/coal products group therefore requires dedicated attention, and warrants a separate specific project.

# Other; entry 2 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
2	Other	33	15

The category "other" contains a list of 33 substances of various types (in the original ZZS list order), with widely differing applications and tonnages. Out of this category 12 substances have been selected as having BR level 2, or 3 and are discussed below.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
bis(2-methoxyethyl)	111-96-6	Solvent		100-1,000	Org	2
ether, diglyme						

~<sup>0</sup>~~<sup>0</sup>~

# Applications/Markets

High boiling, high polarity solvent.

# Biobased options/(potential) Suppliers/Stakeholders

Several biobased ethers and esters are possible: isosorbidedimethyl ether (CMP1), lactic acid esters (CMP2, CMP3), glycerol ethers, γ-valerolactone (CMP4), methyl levulinate (ML, CMP4), 2-methyl-THF.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1,2-dimethoxyethane;	110-71-4	Solvent		100-1,000	Org	2
ethylene glycol dimethyl						
ether; glyme (EGDME)						

\_0\_\_\_\_\_

# Applications/Markets

Together with a high-permittivity solvents (e.g. propylene carbonate), dimethoxyethane is used as the low-viscosity component of the solvent for electrolytes of lithium batteries. Dimethoxyethane is also a good solvent for oligo- and polysaccharides.

11

### Biobased options/(potential) Suppliers/Stakeholders

Glymes are amongst others produced by CMP5.

Several biobased ether are possible: isosorbidedimethyl ether (CMP1), lactic acid esters (CMP2, CMP3), glycerol ethers, γ-valerolactone (CMP4), methyl levulinate (CMP4), 2-methyl-THF.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
2-nitropropane	79-46-9	Intermediate		1,000-10,000	Org	2
		Solvent				



### Applications/Markets

Chemical intermediate, solvent, inks, coatings, adhesives, polymers

### Biobased options/(potential) Suppliers/Stakeholders

In its role as high polarity solvent 2-nitropropane could be replaced by high polarity biobased solvents like isosorbidedimethyl ether (CMP1), lactic acid esters (CMP2, CMP3), γ-valerolactone (CMP4), methyl levulinate (CMP4).

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
ethyleneimine; aziridine	151-56-4	Intermediate		100+	Org	3

### H N ∠⊃

### Applications/Markets

Ethyleneimine is used in polymerization products; as a monomer for polyethyleneimine (PEI); as a comonomer for polymers (e.g., with ethylenediamine); and in paper and textile chemicals, adhesives, binders, petroleum refining chemicals, fuels and lubricants, coating resins, varnishes, lacquers, agricultural chemicals, cosmetics, ion exchange resins, photographic chemicals, and surfactants. PEI finds many applications in products like: detergents, adhesives, water treatment agents and cosmetics. Thanks to the ability to modify the surface of cellulose fibres, PEI is employed as a wet-strength agent in the paper-making process.

# Biobased options/(potential) Suppliers/Stakeholders

Biobased alternatives for PEI are under development and could reduce the need for ethyleneimine. The scope is too broad to give specific examples.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Formaldehyde,	25214-70-4	Intermediate		100-1,000	Org	2
oligomeric reaction						
products with aniline						
(technical MDA)						

# Applications/Markets

Technical MDA is registered as intermediate, mainly for the manufacture of methylene diphenyl diisocyanate (MDI). In addition to the use in the manufacture of MDI, the Annex XV report indicates the following uses for technical MDA:

- as curing agent for epoxy resins in
- in the production of high performance polymers

- as a starting point for the synthesis of 4,4'-methylenebis (cyclohexaneamine)

# Biobased options/(potential) Suppliers/Stakeholders

Biobased diamines. However, most of these are aliphatic (other reactivity) and/or less rigid, giving different properties of the final product. Potential suppliers are CMP6, CMP7, CMP8.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
4-tert-butylbenzoic acid (PTBBA)	98-73-7	Intermediate		100-1,000	Org	2

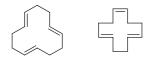
ОН

PTBBA is mainly used in the EU for the manufacture of thermal stabilisers in PVC. For this purpose, PTBBA is first converted into its metal salts (Metal-p-tert-butylbenzoate, Me-PTBB). According to ESPA (European Stabiliser Producers Association) six plants are using PTBBA for the production of liquid mixed metal stabilisers.[3] The second most important use of PTBBA in the EU is the use as process regulator (chain stop agent) in polymers industry for producing alkyd and polyester resins.

# Biobased options/(potential) Suppliers/Stakeholders

Potentially, lignin derived benzoic acid derivatives; these are however not yet commercial, while the eco-toxicological impact is still mostly unknown.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Cyclododecatriene	676-22-2,	Intermediate		Conf.	Org	3
(CDT)	706-31-0					



# Applications/Markets

Chemical intermediate (butadiene trimerisation), precursor for dodecanedioic acid (antiseptics, coatings, corrosion inhibitor, surfactant, engineering plastics; PA12X), laurolactam (precursor to the polyamide PA12).

# Biobased options/(potential) Suppliers/Stakeholders

For the end-application, high performance polyamides for e.g. automotive applications several biobased alternatives are already commercially available: PA1010, PA1012 (CMP6, TP1), CMP9, castor oil based (sebacic C10). Also long-chain biobased diacids are available from companies like CMP1 and CMP8.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Dimethylacetamide	127-19-5	Solvent		10,000-	Org	2
(DMAc)				100,000		

Dimethylacetamide is commonly used as a solvent for fibers (e.g., polyacrylonitrile, spandex) or in the adhesive industry. It is also employed in the production of pharmaceuticals and plasticizers as a reaction medium.

### Biobased options/(potential) Suppliers/Stakeholders

There is a broadly recognised need for alternatives to polar aprotic solvents, like DMAc, DMF, and NMP. Significant efforts are being undertaken to develop effective, safe biobased alternatives. None are currently commercially available on large scale. Furthermore, no "one-size fits all" solutions have been found yet.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
N-Methyl-2-pyrrolidone	872-50-4	Solvent,		10,000-	Org	2
(NMP)		Intermediate		100,000		

### Applications/Markets

NMP is used to recover pure hydrocarbons while processing petrochemicals (such as the recovery of 1,3-butadiene using NMP as an extractive distillation solvent) and in the desulfurization of gases. Due to its good solvency properties N-methyl-2-pyrrolidone is used to dissolve a wide range of chemicals, especially in the polymers field. It also used as a solvent for surface treatment of textiles, resins and metal coated plastics or as a paint stripper. It is utilized as a solvent in the commercial preparation of polyphenylene sulfide. In the pharmaceutical industry, Nmethyl-2-pyrrolidone is used in the formulation for drugs by both oral and transdermal delivery routes. NMP and its derivatives are used as intermediates for the synthesis of agrochemicals, pharmaceuticals, textile auxiliaries, plasticizers, stabilizers and specialty inks. It is also employed as a nylon precursor. The rubber industry uses it for SBR latex production and the electronics industry for printed circuit board manufacturing.

### Biobased options/(potential) Suppliers/Stakeholders

There is a broadly recognised need for alternatives to polar aprotic solvents, like DMAc, DMF, and NMP. Significant efforts are being undertaken to develop effective, safe biobased alternatives. None are currently commercially available on large scale. Furthermore, no "one-size fits all" solutions have been found yet. The paints and coatings industry is very interested in developing sustainable alternatives for NMP as dispersing agent in the production of water borne high solids coatings. These products have been developed as alternative to organic solvent borne coatings systems and the related problem of VOC emissions. The development of biobased water borne high solids coatings also strongly depends on the use of dispersing agents like NMP, since many of the biobased coatings systems currently under development, like non-isocyanate polyurethanes (NIPU's), are chemically and structurally different from their petrochemical analogues (i.e. more polar) requiring high polarity solvents.

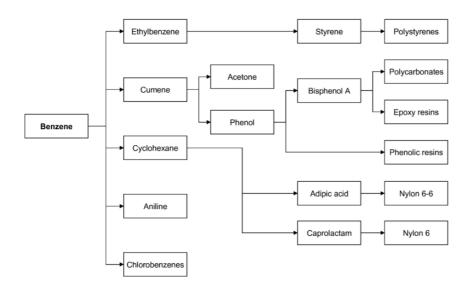
Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Benzene	71-43-2	Intermediate		1,000-10,000	Org	3



# Applications/Markets

Benzene is used mainly as an intermediate to make other chemicals. About 80% of benzene is consumed in the production of three chemicals, ethylbenzene, cumene, and cyclohexane. Its most widely produced derivative is ethylbenzene, precursor to styrene, which is used to make polymers and plastics. Cumene is converted to phenol for resins and adhesives. Cyclohexane is used in the manufacture of Nylon. Smaller amounts of benzene are used to make some types of rubbers, lubricants, dyes, detergents, drugs, explosives, and pesticides.

In both the US and Europe, 50% of benzene is used in the production of ethylbenzene/styrene, 20% is used in the production of cumene, and about 15% of benzene is used in the production of cyclohexane (eventually to nylon).



# Biobased options/(potential) Suppliers/Stakeholders

Phenol and cyclohexane can be obtained from lignin, although these processes are still mainly at an academic stage.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Isoprene, 2-methyl-1,3-	78-79-5	Intermediate		10,000-	Org	3
butadiene				100,000		

It is most readily available industrially as a by-product of the thermal cracking of naphtha or oil, as a side product in the production of ethylene. About 800,000 tonnes are produced annually. About 95% of isoprene production is used to produce cis-1,4-polyisoprene, a synthetic version of natural rubber.[2]

### Biobased options/(potential) Suppliers/Stakeholders

Synthetic natural rubber is highly similar to natural rubber from *Hevea brasiliensis* (the rubber tree), but does not lead to allergic reactions due to the absence of residual proteins. Alternative sources of natural rubber like Russian Dandelion and Guayule could be an option in order to prevent *Hevea* specific latex allergies.

Acrylonitrile 107-13-1 Intermed	XIV			
	liate	1,000,000- 10,000,000	0	3

# CN

### Applications/Markets

Most industrial acrylonitrile is produced by catalytic ammoxidation of propylene, also known as the Sohio process. Acrylonitrile is used principally as a monomer to prepare polyacrylonitrile (PAN) or several important copolymers, such as styrene-acrylonitrile (SAN), acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA), and other synthetic rubbers such as acrylonitrile butadiene rubber (NBR). PAN is the precursor for high strength carbon fiber. Dimerization of acrylonitrile affords adiponitrile, used in the synthesis of certain polyamides (PA66). Acrylonitrile is also a precursor in the industrial manufacture of acrylamide and acrylic acid. Acrylamide is prepared on an industrial scale by the hydrolysis of acrylonitrile by nitrile hydratase. Most acrylamide is used to synthesize polyacrylamides(PAM), which find many uses as water-soluble thickeners. These include use in wastewater treatment, papermaking, ore processing, tertiary oil recovery, and the manufacture of permanent press fabrics.

### Biobased options/(potential) Suppliers/Stakeholders

Biobased options are only partially feasible at level 3 replacement, which are long term developments, e.g. in the area of biobased carbon fibers, or polysaccharide based thickeners (CMP10, CMP11, CMP12).

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Cyclohexane	85-42-7	Intermediate		10,000-	Org	2
dicarboxylic anhydride,				100,000		
Hexahydrophthalic						
anhydride, HHPA						



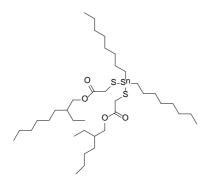
# Applications/Markets

Anhydride curing agent for aliphatic epoxy resins. Intermediate for expoxy resins. Low viscosity reactive diluents. The low viscosity and high latency of anhydride hardeners makes them suitable for processing systems which require addition of mineral fillers prior to curing, e.g. for high voltage electrical insulators. Intermediate for PVC plasticisers. Unsaturated polyester resin co-monomer, intermediate for alkyd resins and rust inhibitors.

### Biobased options/(potential) Suppliers/Stakeholders

Several level 2 biobased alternatives can be thought of, such as itaconic anhydride, (methyl)succinic anhydride (CMP13) and Diels-Alder adducts from furan and maleic anhydride.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
di-n-Octyltin-bis-2-	15571-58-1	Additive		1,000-10,000	Inorg/Org	2
ethylhexyl-						
mercaptoacetate						



Liquid tin PVC stabilizer.

# Biobased options/(potential) Suppliers/Stakeholders

Level 2 replacement involves development of organic, biobased PVC heat stabilisers, such as dihydropyridines or uracils. Stakeholders are e.g. CMP14, CMP15, CMP16, CMP17, CMP18, CMP19.

# Lead/lead compounds; entry 3 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
3	Lead/lead compounds	26	26	

The list of lead compounds contains many inorganic substances that serve as intermediate for glass and ceramics production and lead battery production (see appendices). Those lead compounds that are eligible for biobased replacement fall under the category PVC heat stabilisers. Lead stabiliser phase out is to be finalised in the EU by 2015. Whereas most lead based stabilisers are being replaced by calcium/zinc stabilisers, development of organic biobased stabilisers is still interesting from a sustainability perspective.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Dioxobis(stearato)trilead,	12578-12-0	Additive		100,000-	Inorg/Org	2
Dibasic lead stearate				1,000,000		
(DBLS)						

Di Basic Lead Stearate finds application in cable manufacturing, PVC processing, calandering operations and extrusions. Due to toxicity, Di Basic Lead Stearate is not used in articles that are likely to come in contact with foodstuff. Normally, Di Basic Lead Stearate is used along with Lead Stearate and Tri Basic Lead Sulphate.

# Biobased options/(potential) Suppliers/Stakeholders

Level 2 replacement involves development of organic, biobased PVC heat stabilisers, such as dihydropyridines or uracils. Stakeholders are e.g. CMP14, CMP15, CMP16, CMP17, CMP18, CMP19.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Fatty acids, C16-18,	91031-62-8	Additive		10,000-	Inorg/Org	2
lead salts				100,000		

# Applications/Markets

PVC stabiliser, lubricants.

# Biobased options/(potential) Suppliers/Stakeholders

Level 2 replacement involves development of organic, biobased PVC heat stabilisers, such as dihydropyridines or uracils.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Sulfurous acid, lead salt,	62229-08-7	Intermediate		100-1,000	Inorg	2
dibasic						

# Applications/Markets

Intermediate for PVC stabilisers.

# Biobased options/(potential) Suppliers/Stakeholders

Level 2 replacement involves development of organic, biobased PVC heat stabilisers, such as dihydropyridines or uracils. Stakeholders are e.g. CMP14, CMP15, CMP16, CMP17, CMP18, CMP19.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Trilead dioxide	12141-20-7	Additive		100,000-	Inorg	2
phosphonate (Dibasic				1,000,000		
Lead Phosphite)						

PVC stabilizer.

# Biobased options/(potential) Suppliers/Stakeholders

Level 2 replacement involves development of organic, biobased PVC heat stabilisers, such as dihydropyridines or uracils. Stakeholders are e.g. CMP14, CMP15, CMP16, CMP17, CMP18, CMP19.

# Nickel/nickel compounds; entry 4 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
4	Nickel/nickel compounds	15	-

None of the nickel compounds mentioned on the ZZS list is eligible for biobased replacement due to very specific intrinsic properties of these metal containing substances.

# Coal products; entry 5 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
5	Coal products	13	2

The terms tar and pitch are often used interchangeably. However, pitch is considered more solid while tar is more liquid. Coal tar is a brown or black liquid of extremely high viscosity. Coal tar is among the by-products when coal is carbonized to make coke or gasified to make coal gas. Coal tars are complex and variable mixtures of phenols, polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds. When used for many industrial processes, bituminous coal must first be "coked" to remove volatile components. Coking is achieved by heating the coal in the absence of oxygen, which drives off volatile hydrocarbons such as propane, benzene and other aromatic hydrocarbons, and some sulphur gases. This also drives off a considerable amount of the contained water of the bituminous coal. Coking coal is used in the manufacture of steel, where carbon must be as volatile-free and ash-free as possible.[2,4]

21

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Extract residues	101316-	Intermediate	-	10,000-	Org	?
(coal), light oil alk.,	62-5			100,000		
acid ext., indene						
fraction						
Tar acids,	84989-04-	Intermediate	-	1,000-10,000	Org	5
methylphenol rich	8					
in 3- and 4-						
methylphenol						
Tar, brown-coal,	101316-	Intermediate	-	10,000-	Org	5
low-temp.;	84-1			100,000		
aliphatic,						
naphthenic and						
cyclic aromatic						
hydrocarbons,						
heteroaromatic						
hydrocarbons and						
cyclic phenols.						
Pitch, coal tar,	121575-	Intermediate	-	10,000-	Org	?
high-temp., a	60-8			100,000		
complex mixture						
of three or more						
membered						
condensed ring						
aromatic						
hydrocarbons.						
Tar acids, xylenol	84989-06-	Intermediate	-	1,000-10,000	Org	?
fraction; rich in	0					
2,4- and 2,5-						
dimethylphenol						
Solvent naphtha	85536-20-	Intermediate	-	10,000-	Org	?
(coal), xylene-	5			100,000		
styrene cut						
Solvent naphtha	65996-79-	Intermediate	-	1,000-10,000	Org	?
(coal); indene and	4					
other polycyclic						
ring systems						
containing a single						
aromatic ring.						
Anthracene oil;	90640-80-	Intermediate	-	100,000-	Org	?

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
complex	5			1,000,000		
combination of						
phenanthrene,						
anthracene and						
carbazole.						
Creosote oil,	90640-84-	Intermediate	-	100,000-	Org	5
acenaphthene	9			1,000,000		
fraction;						
acenaphthene,						
naphthalene and						
alkyl naphthalene.						
Distillates (coal	90640-86-	Intermediate	-	100,000-	Org	?
tar), heavy oils;	1			1,000,000		
tri- and						
polynuclear						
hydrocarbons and						
heterocyclic						
compounds.						
Pitch, coal tar,	65996-93-	Intermediate	-	1,000,000-	Org	5
high-temp.;	2			10,000,000		
complex mixture						
of three or more						
membered						
condensed ring						
aromatic						
hydrocarbons.						
Pyridine, alkyl	68391-11-	Intermediate	-	Conf.	Org	?
derivs.;	7					
complex						
combination of						
polyalkylated						
pyridines derived						
from coal tar						
distillation.						

A Dutch based coal tar processor, CMP20, produces predominantly naphthalene, creosote, carbon black and pitch. The latter is used for the production of carbon electrodes, and also bitumen emulsions for road construction. The primary source of raw material is coal tar from steel mill cokes plants. As of 2012 the plant had a capacity to process 140,000 ton of tar per year.

A large part of the binders used in the graphite industry for making "green blocks" are coke oven volatiles (COV). A considerable portion of these COV used as binders is coal tar. During the baking process of the green blocks as a part of commercial graphite production [ e.g. electrodes for aluminium production], most of the coal tar binders are vaporised and are generally burned in an incinerator to prevent release into the atmosphere, as COV and coal tar can be injurious to health. Creosote was originally used as wood preservative. Coal tar is also used to manufacture paints, synthetic dyes, and photographic materials. Furthermore, coal tar distillates are a prime source of polyaromatic and heteroaromatic platform chemicals for fine chemical production. [2,4]

### Biobased options/(potential) Suppliers/Stakeholders

Tar products can also be obtained from wood (wood-tar); which has a different composition. Various efforts are already being undertaken to replace creosote by biobased wood preservatives. Currently, there are no large scale commercial biobased alternatives.

Since coal tar distillates are complex mixtures of substances with various areas of applications it is difficult to assess the biobased replacement potential without detailed analyses of the value chains.

Biobased replacement levels could span from level 1, if drop-in replacement is free from e.g. PAHC contamination, to level 2 for e.g. creosote and level 3 for wood tar and activated carbon/graphite.

# Boron/boron compounds; entry 6 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
6	Boron/boron compounds	10	5

None of the boron compounds mentioned in the ZZS list are eligible for biobased replacement due to the very specific intrinsic properties of these substances.

# Cadmium/cadmium compounds; entry 7 (>100 ton/annum)

I	Entry	Substance group	# ZZS registered	# on Annex XIV candidate
			Substances	list
7	7	Cadmium/cadmium compounds	6	4

None of the cadmium compounds mentioned in the ZZS list are eligible for biobased replacement due to the very specific intrinsic properties of these metal containing substances.

# Bt/Cl hydrocarbons; entry 8 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
8	Br/Cl hydrocarbons	7	3	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Alkanes, C10-13,	85535-84-	Additive		1,000-10,000	Org	2
chloro (Short Chain	8					
Chlorinated Paraffins)						

# Applications/Markets

Chlorinated paraffins are used as extreme-pressure-lubricant additives in metalworking fluids; as flame retardants in plastics, rubber, and paints; to improve water resistance of paints and fabrics; and as a secondary plasticizer in polyvinyl chloride.[2,5,6]

# Biobased options/(potential) Suppliers/Stakeholders

For application as plasticiser several biobased alternatives are available or under development, e.g. isosorbide esters (CMP21), TP2(CMP22), citrate esters (CMP23). The suggested alternatives are only feasible in the role of plasticisers for PVC.

# Oxyranes; entry 9 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
9	Oxyranes	5	1	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Epichlorohydrine,	106-89-8	Intermediate		100,000-	Org	3
ECH				1,000,000		

# Applications/Markets

Epichlorohydrin is mainly converted to bisphenol A diglycidyl ether, a building block in the manufacture of epoxy resins. It is also a precursor to monomers for other resins and polymers.

### Biobased options/(potential) Suppliers/Stakeholders

Biobased epoxides (non-BPA based) can be prepared via synthetic routes not involving ECH. There are currently no commercial products known. CMP9 and CMP24 produce biobased ECH from glycerol on small scale.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Propylene oxide	75-56-9	Intermediate		1,000,000 +	Org	3



### Applications/Markets

Between 60 and 70% of all propylene oxide is converted to polyether polyols for the production of polyurethane plastics. About 20% of propylene oxide is hydrolyzed into propylene glycol (unsaturated PE resins, de-icing), via a process which is accelerated by acid or base catalysis. Other major products are polypropylene glycol, propylene glycol ethers, and propylene carbonate.[10]

# Biobased options/(potential) Suppliers/Stakeholders

Propylene glycol (PG), together with ethylene glycol (EG) can be prepared from biomass via hydrogenolysis of glucose (1<sup>st</sup> gen. from starch, 2<sup>nd</sup> gen. from cellulose) or glycerol. Various agro and chemical companies (e.g. CMP25, CMP3, CMP24) already produce bio EG and PG.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Ethylene oxide	75-21-8	Intermediate		1,000,000 +	Org	3

### 0 △

### Applications/Markets

Ethylene oxide is one of the most important raw materials used in the large-scale chemical production. Most ethylene oxide is used for synthesis of ethylene glycols, including diethylene glycol and triethylene glycol, that accounts for up to 75% of global consumption. Other important products include ethylene glycol ethers, ethanolamines and ethoxylates. Among glycols, ethylene glycol is used as antifreeze, in the production of polyester and polyethylene terephthalate (PET – raw material for plastic bottles), liquid coolants and solvents. Biobased options/(potential) Suppliers/Stakeholders

The world's largest producers of ethylene oxide are CMP24 (3–3.5 million tonnes in 2006), CMP26 (1.328 million tonnes in 2008–2009) and CMP8 (1.175 million tonnes in 2008–2009).[12]

Propylene glycol (PG), together with ethylene glycol (EG) can be prepared from biomass via hydrogenolysis of glucose (1<sup>st</sup> gen. from starch, 2<sup>nd</sup> gen. from cellulose). Various agro and chemical companies (e.g. CMP25, CMP3, CMP27) already produce bio EG and PG. CMP27 and others however use a route via fermentation of sugar to bioethanol, dehydration to ethylene, and subsequently petrochemical methodology via ethylene oxide. So care must be taken to exclude bio EG obtained via this route since it still involves EO, and is energetically unfavourable.

# Chromium/chromium compounds; entry 10 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
10	Chromium/chromium compounds	4	4
	compounds		

None of the chromium compounds on the ZZS list have potential for biobased replacement due to the very specific intrinsic properties of these metal containing substances.

# Cobalt/cobalt compounds; entry 11 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
11	Cobalt/cobalt compounds	4	4

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Cobalt(II) diacetate	71-48-7	Catalyst		1,000 -	Inorg	2
				10,000		

# Applications/Markets

Cobalt acetate is a precursor to various oil drying agents, catalysts that allow paints and varnishes to harden.

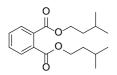
# Biobased options/(potential) Suppliers/Stakeholders

Cobalt acetate could be replaced by Iron/ascorbic acid (vitamin C) catalysts in some applications (still under development).

# Phthalates; entry 12 (>100 ton/annum)

Entry	Substance group	Substance group		# ZZS registered		# on Annex XIV candidate	
			Substanc	ces	list		
12	Phthalates		3		3		
Substance	CAS#	Type	Annex	Tonnage	Org/Inorg	BR-Level	

Substance	CAS#	Type	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Diisopentylphthalate,	605-50-5	Additive,		10-100	Org	2
isoamylphthalate		solvent				



# Applications/Markets

Not found.

# Biobased options/(potential) Suppliers/Stakeholders

Could be e.g. replaced by isoamyl esters of furandicarboxylic acid (FDCA); not currently commercially available (CMP6, CMP3).

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Hexahydromethylphthalic	25550-	Intermediate		1,000-10,000	Org	2
anhydride	51-0					
Hexahydro-4-	19438-	Intermediate		1,000-10,000	Org	2
methylphthalic anhydride	60-9					

# Applications/Markets

Meythylhexahydrophthalic Anhydride (MHHPA) is produced by hydrogenation of Methyltetrahydrophthalic Anhydride (MTHPA), obtained by reacting isoprene with maleic anhydride. MHHPA is a thermo-setting epoxy resin

curing agent mainly used in electric and electronic field. MHHPA has several advantages: Low melting point, low viscosity of the mixtures with alicyclic epoxy resins, long applicable period, high heat-resistance of the cured material and excellent electrical properties at high temperature. MHHPA is widely used for impregnating electrical coils, casting electricity components and sealing semiconductors, outdoor insulators, capacitors, light emitting diodes and digital displays.[2]

# Biobased options/(potential) Suppliers/Stakeholders

Various possibilities exist for replacing these anhydrides by biobased aliphatic anhydrides; e.g. (methyl)succinic anhydride, itaconic anhydride, hexahydro-3-methylphthalic anhydride, etc. Some of these substances are commercially available on small scale, some are under development.

# Azo dyes; entry 13 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
13	Azo dyes	3	3

These substances are low volume, very specific.

# Hydrazines; entry 14 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
14	Hydrazines	3	2

There are currently no biobased biobased alternatives for hydrazine due to very specific intrinsic properties of this substance.

# Butadiene(s); entry 15 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
15	Butadiene(s)	3	-

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1,3-butadiene	106-99-0	Intermediate		10,000- 100,000	Org	3

 $\sim$ 

# Applications/Markets

Most butadiene is polymerized to produce synthetic rubber. While polybutadiene itself is a very soft, almost liquid material, copolymers prepared from mixtures of butadiene with styrene and/or acrylonitrile, such as acrylonitrile butadiene (NBR) and styrene-butadiene (SBR) are tough and/or elastic. SBR is the material most commonly used for the production of automobile tires.

Smaller amounts of butadiene are used to make the nylon intermediate, adiponitrile, by the addition of a molecule of hydrogen cyanide to each of the double bonds in a process called hydrocyanation developed by DuPont. Other synthetic rubber materials such as chloroprene, and the solvent sulfolane are also manufactured from butadiene. Cyclooctadiene and cyclododecatriene are produced via nickel- or titanium-catalyzed dimerization and trimerization reactions, respectively.

# Biobased options/(potential) Suppliers/Stakeholders

Biobased replacement of cyclooctadiene and cyclododecatriene (see those specific entries) could reduce the need for butadiene for those applications

# Beryllium; entry 16 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
16	Beryllium	2	-

No possibilities for biobased due to the very specific intrinsic properties of metallic substance.

# Brominated flame retardants; entry 17 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
17	Brominated flame retardants	2	1

No possibilities for biobased due to the very specific intrinsic chemical properties i.e. the possibility to release bromine radicals under combustion conditions.

# Chlorinated aromatics; entry 18 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
18	Chlorinated aromatics	2	1

No possibilities for biobased, due to the very specific chemical functionality of these products. Functional biobased alternatives will probably have a comparably negative toxicological profile.

# Glycol ethers; entry 19 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
19	Glycol ethers	2	2	

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
2-ethoxyethanol;	110-80-5	Solvent		1,000-	Org	2
ethylene glycol				10,000		
monoethyl ether						

HOVO

# Applications/Markets

2-Ethoxyethanol, also known by the trademark Cellosolve or ethyl cellosolve, is a solvent used widely in commercial and industrial applications. 2-ethoxyethanol is used in products, such as varnish removers and degreasing solutions.[2,8]

# Biobased options/(potential) Suppliers/Stakeholders

Methyl and Ethyl Cellosolve could be replaced by partially alkylated biobased di/triols, like trimethyl glycerol, tertiary butyl glycerol, monomethylisosorbide, etc. One of the few currently commercially available biobased alternatives are lactic acid esters (CMP2, CMP3, CMP3).

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
2-methoxyethanol;	109-86-4	Solvent		1,000-	Org	2
ethylene glycol				10,000		
monomethyl ether						

HOVO

# Applications/Markets

2-Methoxyethanol is used as a solvent for many different purposes such as varnishes, dyes, and resins. It is also used as an additive in airplane de-icing solutions.[2,8]

# Biobased options/(potential) Suppliers/Stakeholders

Methyl and Ethyl Cellosolve could be replaced by partially alkylated biobased di/triols, like trimethyl glycerol, tertiary butyl glycerol, monomethylisosorbide, etc. One of the few currently commercially available biobased alternatives are lactic acid esters (CMP2, CMP3, CMP3).

# Organo mercury; entry 20 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
20	Organo mercury	2	-

No possibilities for biobased.

# Non-approved PPP; entry 21 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
21	Non-approved PPP	2	1	

No possibilities for biobased due to very specific property requirements.

# Phenols; entry 22 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
22	Phenols	1	1

No possibilities for biobased due to very specific property requirements.

# Organotin; entry 24 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
24	Organotin	1	1	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
dibutyltin dichloride;	683-18-1	Mineral		1,000-	Inorg	2
DBTC				10,000		

Cl < CI

# Applications/Markets

As the raw material for the manufacture of other organotin compounds, Dibutyltin Dichloride is invaluable as an intermediate for the manufacture of butyltin based catalysts and PVC stabilizers.

# Biobased options/(potential) Suppliers/Stakeholders

In case of PVC stabilisers, biobased (co-)stabilisers could be used/developed as alternatives to tin based stabilisers. Stakeholders are e.g. CMP14, CMP15, CMP16, CMP17, CMP18, CMP19.[7]

# Acrylamide; entry 25 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
25	Acrylamide	1	1	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Acrylamide	79-06-1	Intermediate		100,000- 1,000,000	Org	3

O NH<sub>2</sub>

Acrylamide is prepared on an industrial scale by the hydrolysis of acrylonitrile by nitrile hydratase. Most acrylamide is used to synthesize polyacrylamides (PAM), which find many uses as water-soluble thickeners. These include use in wastewater treatment, papermaking, ore processing, tertiary oil recovery, soil conditioner and the manufacture of permanent press fabrics. Some acrylamide is used in the manufacture of dyes and the manufacture of other monomers.

### Biobased options/(potential) Suppliers/Stakeholders

Biobased, non-acrylate water soluble thickeners. Some types are already available, various are under development (CMP10, CMP11, CMP12, CMP3). Successful implementation will depend on price and technical performance.

# N,N-dimethylformamide; entry 26 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
26	N,N-dimethylformamide	1	1

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
N,N-	68-12-2	Solvent		10,000-	Org	2
dimethylformamide				100,000		
(DMF)						

0 H⊥\_N\_

### Applications/Markets

The primary use of dimethylformamide is as a solvent with low evaporation rate. DMF is used in the production of acrylic fibers and plastics. It is also used in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings.

### Biobased options/(potential) Suppliers/Stakeholders

There is a broadly recognised need for alternatives to polar aprotic solvents, like DMAc, DMF, and NMP. Significant efforts are being undertaken to develop effective, safe biobased alternatives. None are currently commercially available on large scale. Furthermore, no "one-size fits all" solutions have been found yet.

### 4 Conclusions & Shortlist

A quick scan of a selection of the ZZS shows that there is significant potential in biobased replacement of part of the 371 substances considered. As expected, currently many inorganic substances cannot be replaced by biobased alternatives due to their specific physico/chemical properties or requirements; e.g. the use of arsenic in photovoltaic cells or the use of lead oxide in glass manufacturing. Long term developments like e.g. organic solar cells could however open up possibilities in the future.

Some categories are very complex, requiring more time and effort to analyse; such as the petroleum products, but also the coal tar products. Since these categories deal with very large volumes, changes in particular components of integrated chains have impact on the total chain, and hence should be treated with care.

Whereas for some ZZS substances biobased alternatives (level 2 replacement) are already available or in advanced stages of development (e.g. glyme or diglyme alternatives), safe, biobased alternatives for high polarity aprotic solvents such as DMF, DMAc or NMP are still in early development, despite a growing need for replacement. Nevertheless, also here biobased alternatives are possible, yet on longer term (5-10 years). Given the industrial and environmental importance of these solvents, the development of alternatives should be treated with high priority, e.g. by government initiated R&D programmes. For example, a ban on the use of NMP as a dispersing agent could be detrimental to the further development/implementation of (biobased) high solids coatings that serve to reduce VOC emissions.

Also level 3 replacement appears feasible. An example of possible short term implementation is the partial replacement of ethylene oxide for the production of ethylene glycol by the hydrogenolysis of glucose to ethylene glycol and propylene glycol. Other level 3 replacements require more time, and deeper analysis in order to assess the impact on product/value chains.

Overall, this quick scan results in a number of recommendations

- A dedicated follow-up study into the biobased replacement potential for the petroleum products and coal tar products categories.
- Investigate the possibilities for a program on alternative, preferentially biobased, high polarity solvents that can involve the whole value chain, from production to specific applications.
- Specific follow-up studies on ZZS substances for which advanced level replacements have been identified (mid to long term replacements)
- Start a discussion between end-users of the substances on the shortlist, and (potential) producers of biobased alternatives, in order to evaluate the practical feasibility of biobased substitution.

The following table contains a shortlist of nine substances of high concern, for which short-term biobased alternatives have been identified. These alternatives are either already commercially available or close to commercialisation. Hence, the table includes a list of known (potential) suppliers and stakeholders that can be contacted by the RIVM and the ministry for further information. The regulatory status of the substances of very high concern on this shortlist is given in appendix 2.

#### Biobased replacement shortlist

Substance	CAS#	Туре	Tonnage	BR-Level	(potential) Alternatives	CAS#	(potential) Suppliers
bis(2-	111-96-6	Solvent	100-1,000	2	Dimethylisosorbide	5306-85-4	CMP1
methoxyethyl)							
ether, diglyme							
					GVL, gamma-valerolactone	108-29-2	CMP4
					ML, methyl levulinate	624-45-3	CMP4
					Lactic acid esters,	97-64-3	CMP2, CMP3
Stakeholders <sup>A</sup>	e.g. ethyl lactate CMP8, CMP5, CMP24 (Glymes producers). Glymes are too widely used to pinpoint specific areas of application or specific user groups. Glymes are amongst other used in electrolytes for (lithium batteries), inkjet cartridges, brake fluid, paints and carpet cleaners and active pharmaceutical intermediates (APIs). They are also widely used in the production of printed circuit boards and microchips. Furthermore, glymes are good solvents for oligo- and polysaccharides.[8]						
1,2-	110-71-4	Solvent	100-1,000	2	Dimethylisosorbide	5306-85-4	CMP1
dimethoxyethane;							
ethylene glycol							
dimethyl ether;							
glyme (EGDME)							
					GVL, gamma-valerolactone	108-29-2	CMP4

<sup>A</sup> Patent search gives 96 hits on glymes from 2000-2014, yet none related to alternatives.

Substance	CAS#	Туре	Tonnage	BR-Level	(potential) Alternatives	CAS#	(potential) Suppliers
					ML, methyl levulinate	624-45-3	CMP4
					Lactic acid esters,	97-64-3	CMP2, CMP3
					e.g. ethyl lactate		
Stakeholders <sup>A</sup>	CMP8, CM	MP5, CMP24. Gly	rmes are too wid	ely used to p	inpoint specific areas of applica	tion or specific	user groups. Glymes are amongst other
	used in ele	ectrolytes for (lith	ium batteries), in	ıkjet cartridge	es, brake fluid, paints and carpe	t cleaners and ac	tive pharmaceutical intermediates (APIs).
	They are a	llso widely used in	the production	of printed ci	rcuit boards and microchips. Fu	urthermore, glyn	nes are good solvents for oligo- and
	polysaccha	arides.[2,9]					
2-nitropropane	79-46-9	Intermediate,	1,000-10,000	2	Lactic acid esters,	97-64-3	CMP2, CMP3, CMP3
		Solvent			e.g. ethyllactate		
					ML, methyl levulinate	624-45-3	CMP4
Stakeholders <sup>B</sup>	CMP24 wa	as found as a pro	ducer. The main	application a	as solvent is in coatings (not spe	cified further).[2	2,9] The majority of 2-nitropropane is used
	internally a	as a chemical inte	rmediate. The re	maining proc	duct is sold for use primarily as	a taggant in the	production of C-4 explosives. A very small
	amount is	used for research	and developme	nt. The role o	of chemical intermediate cannot	t be substituted l	by biobased alternatives.
Cyclododecatriene	4904-61-	Intermediate	Conf.	3	TP1; PA 1010		CMP6
(CDT) <sup>C</sup>	4				(= polymer, will fall under		
					REACH polymer		
					exemption)		
					Castor oil based C10 diacid,	111-20-6	CMP9
					sebacic acid		
					Fatty acid diacids;	71-70-5	CMP1, CMP8
					octadecanedioic acid		
Stakeholders	CMP6 (Ma	ain CDT produce	r). Applications	are very dive	rse and include the automotive	and wire & cabl	e sectors.[2] No specific markets or

<sup>&</sup>lt;sup>A</sup> Patent search gives 96 hits on glymes from 2000-2014, yet none related to alternatives.

<sup>&</sup>lt;sup>B</sup> Patent search gives 59 hits on nitro and propane from 2000-2014, yet none related to alternatives to 2-nitro-propane.

<sup>&</sup>lt;sup>C</sup> Patent search gives 51 hits on CDT from 2000-2014, all are related to production or purification.

Substance	CAS#	Туре	Tonnage	BR-Level	(potential) Alternatives	CAS#	(potential) Suppliers	
	application	ns are given.						
Alkanes, C10-13,	85535-	Additive	1,000-10,000	2	Isosorbide esters	REACH	CMP21	
chloro (Short	84-8				TP3	registration		
Chain Chlorinated						pending		
Paraffins)								
					TP2, Fully acetylated	736150-63-3	CMP22	
					glycerol monoester of 12-			
					hydroxystearic acid			
					Citrate esters; e.g. Acetyl	77-90-7	CMP23	
					Tributyl Citrate (ATBC)			
Stakeholders <sup>A</sup>	In 2009, c	hlorinated paraf	fins were produce	ed by 78 man	ufacturers worldwide, includir	ng 2 in the United S	States, 40 in China, and 22 in India [5,6]	
	Chlorinate	ed paraffins are u	used as extreme-p	ressure-lubri	cant additives in metalworking	g fluids; as flame re	tardants in plastics, rubber, and paints; to	
	improve v	vater resistance of	of paints and fabr	ics; and as a s	econdary plasticizer in polyvir	nyl chloride. The su	aggested alternatives are only feasible in	
	the role of	f plasticisers for	PVC.					
Propylene oxide	75-56-9	Intermediate	1,000,000 +	3	Propylene glycol	57-55-6	CMP25, CMP3, CMP24	
Stakeholders <sup>B</sup>	CMP28, C	CMP29, CMP26,	СМР24, СМР8 (	PO and PG 1	producers).[10] Between 60 an	nd 70% of all propy	lene oxide is converted to polyether	
	polyols fo	r the production	of polyurethane	plastics. [less	efficient from propylene glyco	ol] About 20% of p	propylene oxide is hydrolyzed into	
	propylene	glycol [2]; 45%	of propylene glyc	ol produced	is used as chemical feedstock	for the production	of unsaturated polyester resins (UPR).[11]	
	UPR have	e a wide variety o	of applications (us	ually glass fib	ore reinforced). The major ind	ustries for UPR are	e Building & Constructions,	
	Automoti	ve/Transportatio	on, Pipes & Tank	s, Marine, Wi	ind energy, and Electrical & Electronics. Major players in European and North American			
	regions in	clude CMP30, C	MP31, CMP13, C	CMP32, and O	CMP33. Like ethylene glycol, p	propylene glycol is	able to lower the freezing point of water,	
	and so it i	s used as aircraft	de-icing fluid.					
Ethylene oxide	75-21-8	Intermediate	1,000,000 +	3	Ethylene glycol directly	107-21-1	CMP25, CMP3	

<sup>A</sup> No relevant patent found. <sup>B</sup> Subject too broad for efficient patent search.

Substance	CAS#	Туре	Tonnage	BR-Level	(potential) Alternatives	CAS#	(potential) Suppliers
					from sugars		
Stakeholders <sup>B</sup>	of polyeste	er fibers and fa		polyethylene	terephthalate resins (PET) us		ly used as a raw material in the manufacture kaging.[2] CMP37, CMP38, CMP39,
2-ethoxyethanol; ethylene glycol monoethyl ether	110-80-5	Solvent	1,000- 10,000	2	Lactic acid esters, e.g. ethyl lactate	97-64-3	CMP2, CMP3
					ML, methyl levulinate	624-45-3	CMP4
Stakeholders <sup>A</sup>	intermedia various for of 2-ethox behind the concern al expected t	ites, hydraulic rmulations, suc syethanol are n e growth of the bout the toxicc hat these subs	and brake fluids, pla ch as paints, inks an ot mentioned. The e entire glycol ether plogical effects of so	asticizers, and ad cleaning fl growth of warket. [14] ome ethylene ced by other,	ti-icing agents and cosmetic/ uids accounts for over half o ater-based coatings that use g The growth in propylene gly oxide-based glycol ethers. N	personal care prod of all glycol ether co glycol ethers as coa col (P-series) glyco Methyl- and ethyl e	aning products, pharmaceuticals, chemical lucts. The use of glycol ethers as solvents in onsumption.[8] Specific producers or users lescing agents has been the major factor l ethers has been due primarily to increased thylene glycols are in decline. It is to be ethylene glycol monopropyl ether is useful
2-methoxyethanol; ethylene glycol monomethyl ether	109-86-4	Solvent	1,000- 10,000	2	Lactic acid esters, e.g. ethyl lactate	97-64-3	CMP2, CMP3
					ML, methyl levulinate	624-45-3	CMP4
Stakeholders <sup>A</sup>	See 2-etho	oxyethanol					

<sup>&</sup>lt;sup>A</sup> Patent search gives 96 hits on glymes from 2000-2014, yet none related to alternatives.

### References

- [1] Biobased alternatieven voor prioritaire stoffen : Een verkennende studie. Van Helmond et al. 2013:
- http://www.rivm.nl/Documenten en publicaties/Wetenschappelijk/Rapporten/2013/februari/Biobased alternatieven voor prioritaire stoffen Een verkennende studie.
- [2] Source: Wikipedia
- [3] Source: ESPA (European Stabiliser Producers Association)
- [4] Source: www.petrochemistry.eu; Coal Chemicals Sector Group (CCSG)
- [5]Source: <u>http://www.doverchem.com</u>.
- [6] Source: http://ntp.niehs.nih.gov/go/roc12.
- [7] Source: http://www.stabilisers.org.
- [8] Source: <u>http://www.glycol-ethers.eu</u>
- [9] Source: EPA
- [10] Source: http://www.propylene-glycol.com
- [11] Source: http://www.marketsandmarkets.com/PressReleases/unsaturated-polyester-resin-upr.asp;

www.cefic.org.

- [12] Source: <u>www.petrochemistry.eu</u>.
- [13] Source: http://www.cpme-pet.org/members.
- [14] Source: http://www.ihs.com/products/chemical/planning/ceh/glycol-ethers.aspx?pu=1&rd=chemihs.

### Acknowledgements

Several people and organisations contributed to this report

### WUR-FBR

Ir. C. Bolck Dr. J. van Haveren Drs. L. Thissen

# RIVM

Dr. C. W. M. Bodar Dr. E. H. W. Heugens Ir. R. J. Luit

### Ministry of I&M

H. B. Lindeijer-Schoof Dr. J. F. M. van der Waals

# Appendix 1

Overview of EU Regulatory measures in REACH and CLP applicable to the substances included in the shortlist.

Substance	CAS	Inclusion in	Inclusion in	Inclusion in CLP	Remarks
	Number	REACH	REACH	(Regulation EC	
		(Regulation EC	(Regulation EC	1272/2008)	
		1907/2006) Annex	1907/2006) Annex	Annex VI	
		XIV	XVII (restriction)	(harmonised	
		(authorisation)		classification)	
bis(2-	111-96-6	Authorisation	Restriction on the	Repro Cat 1B	
methoxyethyl)		applies per 22-08-	placing on the		
ether, diglyme		2017; Latest	market and use for		
		application date: 22-	supply to the general		
		02-2016	public (substance,		
			mixture)		
1,2-	110-71-4	Not included	Restriction on the	Repro Cat 1B	
dimethoxyethan		(on candidate list	placing on the		
e; ethylene		based on SVHC)	market and use for		
glycol dimethyl			supply to the general		
ether; glyme			public (substance,		
(EGDME)			mixture)		
2-nitropropane	79-46-9	Not included	Restriction on the	Carc. Cat 1B	
			placing on the		
			market and use for		
			supply to the general		
			public (substance,		
			mixture)		
Cyclododecatrie	4904-61-4	Not included	Not included	Not included	REACH
ne (CDT)					registrations
					for
					intermediate
					and non-
					intermediate
					uses
Alkanes, C10-13,	855-35-84-	Not included		Not included	
chloro (Short	8	(on candidate list			
Chain		based on SVHC)			
Chlorinated		(PBT)			
Paraffins)					

Propylene oxide	75-56-9	Not included	Restriction on the	Carc. Cat 1B
		(on candidate list	placing on the	Muta. Cat 1B
		based on SVHC)	market and use for	
			supply to the general	
			public (substance,	
			mixture)	
Ethylene oxide	75-21-8	Not included	Restriction on the	Carc. Cat 1B
			placing on the	Muta. Cat 1B
			market and use for	
			supply to the general	
			public (substance,	
			mixture)	
2-	110-80-5	Not included	Restriction on the	Repro Cat 1B
ethoxyethanol;		(on candidate list	placing on the	
ethylene glycol		based on SVHC)	market and use for	
monoethyl			supply to the general	
ether			public (substance,	
			mixture)	
2-	109-86-4	Not included	Restriction on the	Repro Cat 1B
methoxyethanol		(on candidate list	placing on the	
; ethylene glycol		based on SVHC)	market and use for	
monomethyl			supply to the general	
ether			public (substance,	
			mixture)	

### Appendix 2

Remaining list of ZZS list substances. BR-Level 0 substances, limited to >100 ton/annum use.

# Other; entry 2 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
2	Other	33	15	

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
1,3-propanesultone;	1120-71-4	Intermediate		100-1,000	Org	0
1,2-oxathiolane 2,2-						
dioxide						

#### Applications/Markets

1,3-Propane sultone is a reactive intermediate for the mild and defined incorporation of sulfonate-groups into organic molecules. The resulting propane sulfonates serves as additives in organic baths, as monomers, colours and wetting agents.

#### Biobased options/(potential) Suppliers/Stakeholders

None; outdated, phased out substance.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
N-methylacetamide	79-16-3	Intermediate		Conf.	Org	0

### Applications/Markets

#### Chemical intermediate

#### Biobased options/(potential) Suppliers/Stakeholders

None identified. Difficult to assess replacement options.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1,3,5-	2451-62-9	Intermediate		100-1,000	Org	0
tris(oxiranylmethyl)-						
1,3,5-triazine-						
2,4,6(1H,3H,5H)-trione;						
Triglycidyl isocyanurate						
(TGIC)						

### Applications/Markets

The main use of triglycidyl isocyanurate is as a three-dimensional cross-linking or curing agent in polyester powder coatings (paints).

### Biobased options/(potential) Suppliers/Stakeholders

The high reactivity of TGIC is the reason for its toxicity, yet it also makes it very convenient for application in environmentally friendly powder coating resins that make products more durable and reduce the emissions of coating related VOC's. Replacement by biobased epoxides is possible, but will not significantly alter the toxicity due to the inherent reactivity of low molecular weight epoxides.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
ethylene thiourea; imidazolidine-2-thione;	96-45-7	Intermediate		100-1,000	Org	0
2-imidazoline-2-thiol						

Ethylene thiourea is used primarily as an accelerator for vulcanizing polychloroprene (neoprene) and polyacrylate rubbers.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
quinoline	91-22-5	Intermediate		100-1,000	Org	0

#### Applications/Markets

Quinoline is used in the manufacture of dyes, the preparation of hydroxyquinoline sulfate and niacin. It has also used as a solvent for resins and terpenes. Quinoline is mainly used as a feedstock in the production of other specialty chemicals. Its principal use is as a precursor to 8-hydroxyquinoline, which is a versatile chelating agent and precursor to pesticides. Its 2- and 4-methyl derivatives are precursors to cyanine dyes. Oxidation of quinoline affords quinolinic acid (pyridine-2,3-dicarboxylic acid), a precursor to the herbicide sold under the name "Assert".

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
styrene oxide; (epoxyethyl)benzene;	96-09-3	Intermediate		100-1,000	Org	0
phenyloxirane						

© Wageningen UR Food & Biobased Research, institute within the legal entity Stichting Dienst Landbouwkundig Onderzoek

47

Styrene oxide is used as a reactive plasticizer or diluent for epoxy resins; in the production of styrene glycol and its derivatives; as a raw material for the production of phenethyl alcohol used in perfumes; as a chemical intermediate for cosmetics, surface coatings, and agricultural and biological chemicals; and in the treatment of fibers and textiles.

### Biobased options/(potential) Suppliers/Stakeholders

Biobased alternative epoxides will probably have similar toxicological effects as styrene oxide.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
2-nitrotoluene	88-72-2	Intermediate		10,000- 100,000	Org	0



### Applications/Markets

Chemical intermediate for *o*-toluidine.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
o-toluidine	95-53-4	Intermediate		10,000-	Org	0
				100,000		

NH<sub>2</sub>

### Applications/Markets

Chemical intermediate for the production of dyes. They are a component of accelerators for cyanoacrylate glues.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Neodecanoic acid vinyl	51000-52-3	Intermediate		10,000-	Org	0
ester				100,000		

Vinyl ester of mixture of carboxylic acids with the common structural formula  $C_{10}H_{20}O_2$ 

#### Applications/Markets

VeoVa 10 Monomer (Momentive Specialty Chemicals) is widely used as a modifying co-monomer in the manufacture of vinyl acetate based polymer latices. VeoVa 10 Monomer is also used for the production of VeoVa 10/(meth)acrylic latices and solution polymers.

#### Biobased options/(potential) Suppliers/Stakeholders

None. Toxicological effects probably inherently related to vinyl ester functionality.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
N-(1,3-dimethylbutyl)-	793-24-8	Additive		10,000-	Org	0
N'-phenyl-p-phenylene				100,000		
diamine (6PPD)						

Applications/Markets

6PPD functions as a powerful antioxidant and antiozonant for natural and synthetic elastomer compounds (e.g. tire components) and as a synthetic polymer stabilizer. Santoflex<sup>TM</sup> 6PPD (Eastman Chemical) provides protection against fatigue degradation in both static and dynamic operating conditions

49

#### Biobased options/(potential) Suppliers/Stakeholders

None. Too specific.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Azodicarbonamide	123-77-3	Intermediate		10,000-	Org	0
				100,000		

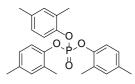
#### Applications/Markets

The principal use of azodicarbonamide is in the production of foamed plastics as a blowing agent. The thermal decomposition of azodicarbonamide results in the evolution of nitrogen, carbon monoxide, carbon dioxide, and ammonia gases, which are trapped in the polymer as bubbles to form a foamed article.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Trixylyl phosphate	25155-23-1	Additive		1,000-10,000	Org	0
(TXP)						



#### Applications/Markets

Hydraulic Fluids; Industrial uses but not in consumer articles .

#### Biobased options/(potential) Suppliers/Stakeholders

# Lead/lead compounds; entry 3 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
3	Lead/lead compounds	26	26

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Lead (II) oxide (PbO)	1317-36-8	Intermediate		100,000- 1,000,000	Inorg	0

### Applications/Markets

Modern applications for PbO are mostly in lead-based industrial glass and industrial ceramics, including computer components. The consumption of lead, and hence the processing of PbO, correlates with the number of automobiles because it remains the key component of automotive lead-acid batteries.<sup>1</sup>

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Lead oxide sulfate	12036-76-9	Intermediate		100-1,000	Inorg	0

### Applications/Markets

A number of lead basic sulfates are known: PbSO4·PbO; PbSO4·2PbO; PbSO4·3PbO; PbSO4·4PbO. They are used in manufacturing of active paste for lead acid batteries.

#### Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Lead titanium	12626-81-2	Intermediate		100-1,000	Inorg	0
zirconium oxide, Lead						
zirconate titanate (PZT)						

PZT is a ceramic perovskite material that shows a marked piezoelectric effect, which finds practical applications in the area of electroceramics. Being pyroelectric, this material develops a voltage difference across two of its faces when it experiences a temperature change. As a result, it can be used as a heat sensor. PZT is used to make ultrasound transducers and other sensors and actuators, as well as high-value ceramic capacitors and FRAM chips.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Orange lead (lead	1314-41-6	Intermediate		10.000	T.,	0
Ofalige lead (lead	1314-41-0	Intermediate		10,000-	Inorg	0

### Applications/Markets

Lead(II,IV) oxide is used in the manufacture of batteries, lead glass and rust-proof primer paints.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Pentalead tetraoxide	12065-90-6	Intermediate		100,000-	Inorg	0

### Applications/Markets

A number of lead basic sulfates are known: PbSO<sub>4</sub>·PbO; PbSO<sub>4</sub>·2PbO; PbSO<sub>4</sub>·3PbO; PbSO<sub>4</sub>·4PbO. They are used in manufacturing of active paste for lead acid batteries.

## Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Silicic acid, lead salt	11120-22-2	Intermediate		100-1,000	Inorg	0

Ceramic flux.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Tetraethyllead (TEL)	78-00-2	Additive		1,000-10,000	Inorg/Org	0

#### Applications/Markets

TEL is still used as an additive in some grades of aviation gasoline, and in some developing countries.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Tetralead trioxide	12202-17-4	Additive		1,000,000-	Inorg	0
sulphate (Tribasic Lead				10,000,000		
Sulphate)						

### Applications/Markets

A number of lead basic sulfates are known: PbSO4·PbO; PbSO4·2PbO; PbSO4·3PbO; PbSO4·4PbO. They are used in manufacturing of active paste for lead acid batteries.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

# Nickel/nickel compounds; entry 4 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
4	Nickel/nickel compounds	15	-

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Nickel Sulfide (NiS)	79-16-3	Ore		10,000- 100,000	Inorg	0

Nickel Ore

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Nickel(II) chloride	7718-54-9	Ore		10,000-	Inorg	0
(NiCl <sub>2</sub> )				100,000		

### Applications/Markets

In general nickel(II) chloride, in various forms, is the most important source of nickel for chemical synthesis. Nickel chloride solutions are used for electroplating nickel onto other metal items.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Nickel(II) hydroxide (NiOH <sub>2</sub> )	12054-48-7	Intermediate		1,000-10,000	Inorg	0

#### Applications/Markets

Due to reactivity in redox processes nickel (II) hydroxide is frequently used in electrochemical cells. In particular, as a good capacitor, it is frequently used for the storage of electrochemical energy. For example, it has been proposed as a useful electrode for use in electrical car batteries.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Nickel(II) dinitrate	13138-45-9	Intermediate		1,000-10,000	Inorg	0
$(Ni(NO_3)_2)$						

#### Applications/Markets

Precursor for industrial nickel hydrogenation catalysts.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Nickel(II) sulphate	7786-81-4	Intermediate		10,000-	Inorg	0
(NiSO <sub>4</sub> )				100,000		

### Applications/Markets

The salt is usually obtained as a by-product of copper refining. It is also produced by dissolution of nickel metal or nickel oxides in sulfuric acid. It is mainly used for electroplating of nickel.<sup>[</sup>

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
[carbonato(2-)]	9863-10-3	Intermediate		1,000-10,000	Inorg	0
tetrahydroxytrinickel,						
basic nickel carbonate						

### Applications/Markets

From the industrial perspective, the most important nickel carbonate is basic nickel carbonate with the formula  $Ni_4CO_3(OH)_6(H_2O)_4$ . The basic carbonate is an intermediate in the hydrometallurgical purification of nickel from its

ores and is used in electroplating of nickel. Nickel carbonates are used in some ceramic applications and as precursors to catalysts.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
nickel di(acetate)	373-02-4	Intermediate		100-1,000	Inorg	0

### Applications/Markets

Nickel(II) acetate is used for electroplating.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
dialuminium nickel	12004-35-2	Intermediate		100-1,000	Inorg	0
tetraoxide, Nickel						
aluminate						

### Applications/Markets

Component of hydrotreating catalysts.

#### Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
nickel bis(sulfamidate); nickel sulfamate	13770-89-3	Intermediate		100-1,000	Inorg	0

Sulfamate nickel plating is used for many engineering applications. It is deposited for dimensional corrections, abrasion and wear resistance, and corrosion protection. It is also used as an undercoat for chromium.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
nickel difluoride	10028-18-9	Intermediate		100-1,000	Inorg	0

#### Applications/Markets

Nickel(II) fluoride is the chemical compound with the formula NiF2. Unlike many fluorides, NiF2 is stable in air. NiF2 comprises the passivating surface that forms on nickel alloys, e.g. monel, which is why such materials are good to store or transport hydrogen fluoride or elemental fluorine. Nickel is one of the few materials that can be used to store fluorine because it forms this coating.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
trinickel disulfide;	12035-72-2	Intermediate		100-1,000	Inorg	0
nickel subsulfide						

### Applications/Markets

Nickel subsulfide is produced in nickel refineries and used in the manufacture of lithium batteries.

#### Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
nickel bis(dihydrogen phosphate)	18718-11-1	Intermediate		100-1,000	Inorg	0

None found.

### Biobased options/(potential) Suppliers/Stakeholders

None.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
nickel bis(2-	4454-16-4	Catalysts		100-1,000	Org/Inorg	0
ethylhexanoate), nickel						
octaoate						

### Applications/Markets

Homogeneous catalysts.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

# Boron/boron compounds; entry 6 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
6	Boron/boron compounds	10	5

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
diboron trioxide;	1303-86-2	Intermediate		1,000-10,000	Inorg	0
boric oxide						

### Applications/Markets

Diboron trioxideis a fluxing agent for glass and enamels, a starting material for synthesizing other boron compounds such as boron carbide. It is also used in the production of borosilicate glass

#### Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
perboric acid	11138-47-	Additive		10,000-	Inorg	0
sodium salt	9			100,000		
perboric acid,	12040-72-	Additive		10,000-	Inorg	0
sodium salt,	1			100,000		
monohydrate						
perboric acid,	37244-98-	Additive		10,000-	Inorg	0
sodium salt,	7			100,000	_	
tetrahydrate						

None, this substance has too specific chemical properties to allow for (biobased) substitution.

#### Applications/Markets

It serves as a source of active oxygen in many detergents, laundry detergents, cleaning products, and laundry bleaches. It has antiseptic properties and can act as a disinfectant.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
boric acid	10043-35-			100,000-	Inorg	0
	3			1,000,000		

#### Applications/Markets

The primary industrial use of boric acid is in the manufacture of monofilament fiberglass usually referred to as textile fiberglass. Textile fiberglass is used to reinforce plastics in applications that range from boats, to industrial piping to computer circuit boards. Boric acid is used in the production of the glass in LCD flat panel displays. Boric acid, mixed with borax (sodium tetraborate decahydrate) at the weight ratio of 4:5, is highly soluble in water, though they are not so soluble separately. The solution is used for fire retarding agent of wood by impregnation. Boric acid, in combination with silicone oil, is used to manufacture Silly Putty. Boric acid, in combination with eighty other chemicals, is used in Marcellus Shale hydraulic fracturing.

#### Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
disodium	1330-43-4	Mineral		100,000-	Inorg	0
tetraborate,				1,000,000		
anhydrous						
disodium	1303-96-4	Mineral		100,000-	Inorg	0
tetraborate				1,000,000		
decahydrate						
borax decahydrate	1330-43-4	Mineral		100,000-	Inorg	0
				1,000,000		
disodium	12179-04-	Mineral		100,000-	Inorg	0
tetraborate	3			1,000,000		
pentahydrate						

Borax: The term borax is often used for a number of closely related minerals or chemical compounds that differ in their crystal water content.

### Applications/Markets

Borax is used in various household laundry and cleaning products. It is a precursor for sodium perborate monohydrate that is used in detergents, as well as for boric acid and other borates. Ingredient in enamel glazes. Component of glass, pottery, and ceramics. Fire retardant

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

## Cadmium/cadmium compounds; entry 7 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
7	Cadmium/cadmium compounds	6	4

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
cadmium oxide	1306-19-0	Mineral		1,000 - 10,000	Inorg	0
(non-pyrophoric)						
cadmium (non-	7440-43-9	Mineral		1,000 - 10,000	Inorg	0
pyrophoric)						
cadmium	7440-43-9	Mineral		1,000 - 10,000	Inorg	0
(pyrophoric)						
Cadmium and	7440-43-9	Mineral		1,000 - 10,000	Inorg	0
cadmium						

#### compounds

#### Applications/Markets

Cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. Cadmium oxide is one of the main precursors to other cadmium compounds. Cadmium oxide is used in cadmium plating baths, electrodes for storage batteries, cadmium salts, catalyst, ceramic glazes, phosphors, and nematocide. Major uses for cadmium oxide are as an ingredient for electroplating baths, and in pigments. One of its few new uses is in cadmium telluride solar panels. Cadmium electroplating, consuming 6% of the global production, can be found in the aircraft industry due to the ability to resist corrosion when applied to steel components. This coating is passivated by the usage of chromate salts. In paint pigments, cadmium forms various salts, with CdS being the most common. This sulfide is used as a yellow pigment.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

## Bt/Cl hydrocarbons; entry 8 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
8	Br/Cl hydrocarbons	7	3	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1,2-dibromoethane	106-93-4	Pesticide		1,000-10,000	Org	0
(EDB)						



### Applications/Markets

EDB continues to be used as a fumigant for treatment of logs for termites and beetles, for control of moths in beehives.

### Biobased options/(potential) Suppliers/Stakeholders

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1,2,3-	96-18-4	Intermediate		1,000-10,000	Org	0
Trichloropropane						
(TCP)						

CI CI\_\_\_\_CI

### Applications/Markets

1,2,3-TCP had been used in the past primarily as a solvent for paint and varnish removal, as a cleaning and degreasing agent, and as a cleaning and maintenance solvent. No current information is available to indicate that it continues to be used for these purposes. 1,2,3-TCP is currently used as an intermediate in the production of polysulfone liquid polymers, the synthesis of hexafluoropropylene, and as a cross-linking agent in the synthesis of polysulfides. Polysulfone liquid polymers are used in the following industries: aerospace, automotive, consumer goods, electrical and electronic, health care, and in industrial equipment, such as compressor and pump valve components. Hexafluoropropylene is a fluorointermediate that is a key building block required to produce Teflon fluoropolymers. Polysulfides are used as catalyst sulfidation agents and in the formulation of lubricant additives created for use in high-pressure environments or applications.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1-bromopropane; n-	106-94-5	Solvent		1,000-10,000	Org	0
propyl bromide (NPB)						



#### Applications/Markets

Like other halocarbons, n-propyl bromide finds use as a solvent. It is used for the cleaning of metal surfaces, removal of soldering residues from electronic circuit boards. It is also a solvent for adhesives. It has been deployed as a replacement for perchloroethylene as a dry cleaning solvent. It is also used in the hole transport layer (HTL) of multi-layered OLEDs. The chemical's increasing use in the 21st century resulted from need for a substitute for chlorofluorocarbons and perchloroethylene (tetrachloroethylene). It has been approved for use under the U.S. EPA's Significant New Alternatives Policy (SNAP) as a suitable replacement for ozone depleting chemicals.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Chloroprene, 2-	126-99-8			10,000-	Org	0
chlorobuta-1,3-diene				100,000		

#### Applications/Markets

This colorless liquid is the monomer for the production of the polymer polychloroprene, a type of synthetic rubber. Polychloroprene is better known to the public as Neoprene, the trade name given by DuPont.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
1,2-dichloroethane;	107-06-2	Intermediate		1,000,000-	Org	0
ethylene dichloride				10,000,000		
(EDC)						

CI

#### Applications/Markets

Ethylene dichloride (EDC), is a chlorinated hydrocarbon, mainly used to produce vinyl chloride monomer (VCM, chloroethene), the major precursor for PVC production. As a useful 'building block' reagent, it is used as an intermediate in the production of various organic compounds such as ethylenediamine.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution. Although one could envision level 3 replacement by replacing PVC by biobased polymers, this option is highly challenging due to various specific advantages of PVC over other polymers, and the fact that EDC is one of the main outlets for chorine, which is produced during the production of the base chemical sodium hydroxide by electrolysis of brine.

# Chromium/chromium compounds; entry 10 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
10	Chromium/chromium	4	4
	compounds		

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
strontium chromate	7789-06-2	Additive		1,000 -	Inorg	0
				10,000		

### Applications/Markets

Corrosion inhibitor in pigments, as colorant in polyvinyl chloride resins, and as an anti-corrosive primer for zinc, magnesium, aluminum, and alloys used in aircraft manufacture.

### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
Potassium	11103-	Additive		100 - 1000	Inorg	0
hydroxyoctaoxodizincatedichromate	86-9					

### Applications/Markets

Used in industrial sealants and coatings in the aerospace sector and vehicle sector (fleet and commercial vehicles, heavy duty vehicles and trucks, military vehicles and agricultural equipment).

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

# Cobalt/cobalt compounds; entry 11 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
11	Cobalt/cobalt compounds	4	4	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Cobalt(II) dinitrate	10141-05-	Intermediate		1,000 -	Inorg	0
	6			10,000		

It is commonly reduced to metallic cobalt or precipitated on various substrates for Fischer-Tropsch catalysis.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Cobalt(II) sulphate	10124-43-	Intermediate		1,000 -	Inorg	0
	3			10,000		

#### Applications/Markets

Cobalt(II) sulfate is used in the preparation of pigments, as well as in the manufacture of other cobalt salts. Cobalt pigment is used in porcelains and glass. Cobalt(II) sulfate is used in storage batteries and electroplating baths, sympathetic inks, and as an additive to soils and animal feeds.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Cobalt(II) carbonate	513-79-1			1,000 -	Inorg	0
				10,000		

#### Applications/Markets

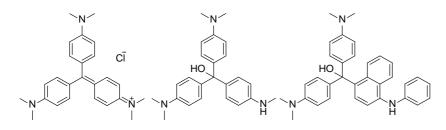
Cobalt carbonate is a precursor to cobalt carbonyl and various cobalt salts. It is a component of dietary supplements since cobalt is an essential element. It is a precursor to blue pottery glazes, famously in the case of Delftware.

#### Biobased options/(potential) Suppliers/Stakeholders

# Azo dyes; entry 13 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
13	Azo dyes	3	3

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
C.I. Basic Violet 3, Crystal violet or gentian violet	548-62-9	Additive		1-10	Org	0
4,4'-bis(dimethylamino)-4"- (methylamino)trityl alcohol	561-41-1	Additive		1-10	Org	0
α,α-Bis[4- (dimethylamino)phenyl]-4 (phenylamino)naphthalene- 1-methanol (C.I. Solvent Blue 4)	6786-83- 0	Additive		10-100 t	Org	0



All below 100 ton

Too specific.

# Hydrazines; entry 14 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
14	Hydrazines	3	2

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Hydrazine	302-01-2	Intermediate	111 (	10,000-	Inorg	0

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
				100,000		
hydrate(s) of hydrazine	7803-57-	Intermediate		10,000-	Inorg	0
	8			100,000		

 $H_2N-NH_2$ 

#### Applications/Markets

Hydrazine is mainly used as a foaming agent in preparing polymer foams, but significant applications also include its uses as a precursor to polymerization catalysts and pharmaceuticals. Additionally, hydrazine is used in various rocket fuels and to prepare the gas precursors used in air bags. Hydrazine is used within both nuclear and conventional electrical power plant steam cycles as an oxygen scavenger to control concentrations of dissolved oxygen in an effort to reduce corrosion. The majority use of hydrazine is as a precursor to blowing agents. Specific compounds include azodicarbonamide and azobisisobutyronitrile, which yield 100-200 mL of gas per gram of precursor. In a related application, sodium azide, the gas-forming agent in air bags, is produced from hydrazine by reaction with sodium nitrite.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

# Butadiene(s); entry 15 (>100 ton/annum)

Entry	Substance group		# ZZS re	# ZZS registered		# on Annex XIV candidate	
			Substance	es	list		
15	Butadiene(s)		3		-		
Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level	
			XIV				
isobutane	75-28-5	Propellant		1,000,000-	Org	0	
				10,000,000			

# $\downarrow$

### Applications/Markets

Isobutane is used as a refrigerant. Isobutane is also used as a propellant for aerosol cans and foam products. Biobased options/(potential) Suppliers/Stakeholders

67

None, this substance has too specific physical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
n-butane	106-97-8	Intermediate		1,000,000-	Org	0
				10,000,000		

 $\searrow$ 

#### Applications/Markets

Normal butane is mainly used for gasoline blending, as a fuel gas, either alone or in a mixture with propane, and as a feedstock for the manufacture of ethylene and butadiene.

### Biobased options/(potential) Suppliers/Stakeholders

7440-41-

7

Mineral

None, this substance has too specific physical and chemical properties to allow for (biobased) substitution.

# Beryllium; entry 16 (>100 ton/annum)

Entry	Substance group		# ZZS re	# ZZS registered		# on Annex XIV candidate	
			Substance	Substances			
16	Beryllium		2		-		
Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level	
			XIV				
beryllium oxide	1304-56-	Mineral		1-10	Inorg	0	
	9						

10-100

0

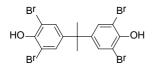
Inorg

All below 1000 tons

beryllium

## Brominated flame retardants; entry 17 (>100 ton/annum)

Entry	Substance group		# ZZS re	# ZZS registered		# on Annex XIV candidate	
			Substances		list		
17	Brominated flan	ne retard.	2		1		
Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level	
			XIV				
Tetrabromobisphenol	79-94-7	Additive		1,000-	Org	0	
A; TBBP-A				10,000	_		



### Applications/Markets

TBBPA can be used as reactive and additive flame retardant. In the reactive application, TBBPA is bound chemically to the polymers. The main use are epoxy resins of printed circuit boards. As an additive flame retardant it is used in acrylonitrile butadiene styrene, which are used e.g. in TVs.

### Biobased options/(potential) Suppliers/Stakeholders

Too specific: brominated flame retardants are highly efficient, and work synergistically with Sb<sub>2</sub>O<sub>3</sub>. Brominated biobased substances can be developed, yet these can have the same detrimental toxicological effects.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Decabromodiphenyl	1163-19-5	Additive		10,000-	Org	0
ether; DecaBDE				100,000		

### Applications/Markets

DecaBDE is a flame retardant. The chemical "is always used in conjunction with antimony trioxide" in polymers, mainly in "high impact polystyrene (HIPS) which is used in the television industry for cabinet backs." DecaBDE is

also used for "polypropylene drapery and upholstery fabric" by means of backcoating and "may also be used in some synthetic carpets."

#### Biobased options/(potential) Suppliers/Stakeholders

Too specific: brominated flame retardants are highly efficient, and work synergistically with Sb<sub>2</sub>O<sub>3</sub>. Brominated biobased substances can be developed, yet these can have the same detrimental toxicological effects.

### Chlorinated aromatics; entry 18 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate	
		Substances	list	
18	Chlorinated aromatics	2	1	

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
2,2'-dichloro-4,4'-	101-14-4	Intermediate		1,000-	Org	0
methylenedianiline; 4,4'- methylene bis(2-				10,000		
chloroaniline) (MOCA)						

#### Applications/Markets

The main use of MOCA is as a curing agent in the manufacture of polyurethane. This use is within the scope of authorisation (ECHA, 2011). MOCA is here not used to manufacture a substance, polyurethane for instance, but to provide specific properties, such as high abrasion resistance, heat, fuel and solvent resistance, high load-bearing and good mechanical and dynamic properties to the already existing substance (ECHA, 2011).

#### Biobased options/(potential) Suppliers/Stakeholders

Too specific.

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
α-chlorotoluene; benzyl	100-44-7	Intermediate		10,000-	Org	0
chloride				100,000		



Industrially, benzyl chloride is the precursor to benzyl esters which are used as plasticizer, flavorants, and perfumes. Phenylacetic acid, a precursor to pharmaceuticals, arises via benzyl cyanide, which is generated by treatment of benzyl chloride with sodium cyanide. Quaternary ammonium salts, used as surfactants, are readily formed by alkylation of tertiary amines with benzyl chloride.[1]

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific inherent chemical properties to allow for (biobased) substitution.

### Organo mercury; entry 20 (>100 ton/annum)

Substanceslist20Organo mercury2-	Entry	Substance group	# ZZS registered	# on Annex XIV candidate
20 Organo mercury 2 -			Substances	list
	20	Organo mercury	2	-

Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level
			XIV			
mercury	7439-97-6	Mineral		100- 1,000	Inorg	0
mercury and organic	7439-97-6	Mineral		100- 1,000	Inorg	0
mercury compounds						

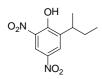
Less than 1000 tons

Mercury is used primarily for the manufacture of industrial chemicals or for electrical and electronic applications. It is used in some thermometers, especially ones which are used to measure high temperatures. A still increasing amount is used as gaseous mercury in fluorescent lamps, while most of the other applications are slowly phased out due to health and safety regulations. By far the largest use of mercury in the late 20th century was in the mercury cell process (also called the Castner-Kellner process) where metallic sodium is formed as an amalgam at a cathode made from mercury; this sodium is then reacted with water to produce sodium hydroxide.

### Biobased options/(potential) Suppliers/Stakeholders

# Non-approved PPP; entry 21 (>100 ton/annum)

Entry	Substance group	Substance group		# ZZS registered		# on Annex XIV candidate	
				es	list		
21	Non-approved I	Non-approved PPP			1		
Substance	CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level	
			XIV				
dinoseb	88-85-7	Herbicide		1000-	Org	0	
				10,000			



### Applications/Markets

Banned Herbicide

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Carbon monoxide, CO	630-08-0	Intermediate		100,000- 1,000,000	Org	0

### Applications/Markets

Carbon monoxide is an industrial gas that has many applications in bulk chemicals manufacturing. Large quantities of aldehydes are produced by the hydroformylation reaction of alkenes, carbon monoxide, and H2. Phosgene, useful for preparing isocyanates, polycarbonates, and polyurethanes, is produced by passing purified carbon monoxide and chlorine gas through a bed of porous activated carbon, which serves as a catalyst. Methanol is produced by the hydrogenation of carbon monoxide. In a related reaction, the hydrogenation of carbon monoxide is coupled to C-C bond formation, as in the Fischer-Tropsch process where carbon monoxide is hydrogenated to liquid hydrocarbon fuels. This technology allows coal or biomass to be converted to diesel. In the Monsanto process, carbon monoxide and methanol react in the presence of a homogeneous rhodium catalyst and hydroiodic acid to give acetic acid. This process is responsible for most of the industrial production of acetic acid.

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

# Phenols; entry 22 (>100 ton/annum)

Entry	Sub	Substance group		# ZZS re	# ZZS registered		# on Annex XIV candidate	
				Substance	es	list		
22	Phe	enols		1		1		
Substance		CAS#	Туре	Annex	Tonnage	Org/Inorg	BR-Level	
				XIV				
octylphenol; 4-(1,1	,3,3-	140-66-9	Intermediate		10,000-	Org	0	
tetramethylbutyl)p	henol;				100,000			
4-tert-Octylpheno	1							

#### Applications/Markets

Registration dossiers for 4-tert-octylphenol indicate that its ethoxylates are used in formulation of paints, industrial end-use of paints, consumer and professional end-use of paints and other products, in emulsion polymerisation, and as an intermediate in the production of ether sulphates. It seems that almost 50% of the 4-tert-OPnEO is used as emulsifiers in emulsion polymerisation (Annex XV report). In the public consultation industry (CEPAD/APERC) stated that 4-tert- OPnEOs "are used predominantly in the formulation of paint and coating products and are used at levels of generally 1% or less in those products" (RCOM, 2014).

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical properties to allow for (biobased) substitution.

### Arsenic compounds; entry 23 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
23	Arsenic compounds	1	-

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Gallium arsenide	140-66-9	Mineral		10- 100	Inorg	0
(GaAs)						

Semiconductors, PV cells, laser diodes, LEDs

#### Biobased options/(potential) Suppliers/Stakeholders

None, this substance has too specific chemical and physical properties to allow for (biobased) substitution.

# Formamide; entry 27 (>100 ton/annum)

Entry	Substance group	# ZZS registered	# on Annex XIV candidate
		Substances	list
27	Formamide	1	1

Substance	CAS#	Туре	Annex XIV	Tonnage	Org/Inorg	BR-Level
Formamide	75-12-7	Solvent		10- 100	Org	0

O H<sup>⊥⊥</sup>N-H H

### Applications/Markets

It is chemical feedstock for the manufacture of sulfa drugs, other pharmaceuticals, herbicides, pesticides and the manufacture of hydrocyanic acid.

### Biobased options/(potential) Suppliers/Stakeholders