Annex XV report

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR 1A OR 1B, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name: **Sodium peroxometaborate**

EC Numbers: 231-556-4

CAS numbers: 7632-04-4

Submitted by: **Denmark**

CONTENTS

PROPOSAL FOR IDENTIFICATION OF SODIUM PEROXOMETABORATE AS SVHC

Substance Name: **Sodium peroxometaborate**

EC Numbers: 231-556-4

CAS numbers: 7632-04-4

- The substance is proposed to be identified as a substance meeting the criteria of Article 57 (c) of Regulation (EC) 1907/2006 (REACH) owing to its classification as toxic for reproduction category 1B.

Summary of how the substance(s) meet(s) the criteria set out in Article 57 of the REACH Regulation

Sodium peroxometaborate is covered by Index numbers 005-017-00-7, 005-017-01-4, of Regulation (EC) No 1272/2008 in Annex VI, Part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) for reproductive toxicity, Rep. 1B (H360Df: "May damage the unborn child. Suspected of damaging fertility").

Therefore this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as toxic for reproduction in accordance with Article 57(c) of REACH.

Registration dossiers submitted for the substance?

No

PART I

JUSTIFICATION

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	231-556-4
EC name:	sodium peroxometaborate
CAS number (in the EC inventory):	7632-04-4
CAS numbers:	12040-72-1[a] 10332-33-9[b] 13517-20-9[c] 10486-00-7 [d] 37244-98-7[e]
CAS names:	Perboric acid (HBO(O2)), sodium salt (1:1)
IUPAC name:	sodium peroxometaborate
Index number in Annex VI of the CLP Regulation	005-017-00-7, 005-017-01-4,
Molecular formula:	BHO3.Na *
Molecular weight range:	81.80 *
Synonyms:	Perboric acid (HBO(O2)), sodium salt (9CI); Perboric acid (HBO3), sodium salt (8CI); Sodium perborate (NaBO3) (6CI,7CI); Perborn; Sodium borate (NaBO3); Sodium perborate; Sodium peroxoborate

* The molecular and structural information provided here is theoretical and the information in the literature indicates that the substance is not well-defined. It is supposed to consist of sodium borate and a boron oxygen radical. Note: Ullmann specifies that the substance can be produced by the "dehydration" of the dimeric salts commonly referred to as the sodium perborate monohydrate or tetrahydrate. This reference to "dehydration" may be confusing as chemical transformations other than crystalline water removal are involved.

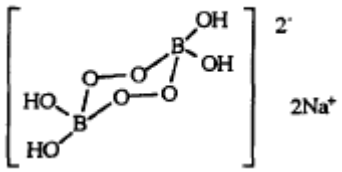
Structural formula (from EU RAR 2007a):

$O=B-O-O^- Na^+$

According to EU RAR (2007a) the peroxoboron anions have a dimeric structure, i.e. they exist either in anhydrous form or as hexahydrate.

This means that there may be in reality only 2 types of structures:

- The dimeric cyclic structure with 2 peroxy bridges:



  This structure has historically been referred to as the "sodium perborate monohydrate" (empirical formula NaBO3.1H2O). These old name and formula do however not take into account the dimeric cyclic nature of the substance. The same structure may also have been wrongly represented by the empirical formula NaBO2.H2O2.

  In reality, there would not be any crystalline water in "sodium perborate monohydrate". Hydrates of that dimeric structure also exist. For instance, what was historically known as "sodium perborate tetrahydrate" (empirical formula NaBO3.4H2O) is in fact the hexahydrate of the dimeric structure.

- The "dehydrated" form of sodium perborate. It is obtained from the "sodium perborate monohydrate" (which is not a true hydrate as explained above). The empirical formula is NaBO3. This structure is presented in the EU RAR (2007a) as not well-defined. It is supposed to consist of sodium borate and a boron oxygen radical.

However, it is still customary to use the "old" formulas and nomenclature of "sodium perborate monohydrate" and "sodium perborate tetrahydrate". Several other CAS numbers exist for e.g. disodium salt perborate compounds. These are, however, not described in this Annex XV dossier.

All perboric acids, sodium salt compounds are available in different forms divided into the following two types of compounds. The classification differs slightly for the two types of compounds:

- containing < 0.1 % (w/w) of particles with an aerodynamic diameter of below 50 µm

- containing ≥ 0.1 % (w/w) of particles with an aerodynamic diameter of below 50 µm

This Annex XV dossier also covers the remaining 5 CAS numbers, which all have the same harmonised classification as reproductive toxicant as the registered CAS number and a very similar structure. This is in line with the provisions of the Commission roadmap on substances of very high concern[1], which states that there might be cases in which non registered substances can still be considered relevant for identification. One example might be a substance that is currently not produced or used in Europe, but might be used as an alternative to another relevant SVHC. This exemption is particularly relevant when the most appropriate approach is the category approach (i.e., analogous substances).

1.2 Composition of the substance

UVCB

1.3 Physico-chemical properties

Not relevant for the identification of the substance as SVHC in accordance with Article 57(c).

[1] http://register.consilium.europa.eu/doc/srv?l=EN&t=PDF&gc=true&sc=false&f=ST%207664%202013%20INIT&r=http%3A%2F%2Fregister.consilium.europa.eu%2Fpd%2Fen%2F13%2Fst07%2Fst07664.en13.pdf

2 HARMONISED CLASSIFICATION AND LABELLING

Sodium peroxometaborate is subject to harmonised classification with Repr 1B, H360Df with various specific concentration limits

PBS are reactive oxidants and liberate hydrogen peroxide in aqueous solution under formation of sodium borate/ boric acid, which is considered to be the cause of the induction of the adverse effects on development and fertility.

The classification as Rep 1B and the specific concentration limits of PBS depend on the content of boron in the substances. This is similar to the classification of the borates and their hydrated forms, where the classification as Rep 1B, H360Df and the specific concentration limits, depending on the boron content of the substances. The specific concentration limits are listed below.

Table 2*:* Classification according to part 3 of Annex VI, Table 3.1 of Regulation (EC) No 1272/2008

005-017-00-7	sodium perborate; [1] sodium peroxometaborate; [2] sodium peroxoborate; [containing < 0,1 % (w/w) of particles with an aerodynamic diameter of below 50 µm]	239-172-9 [1] 231-556-4 [2]	15120-21-5 [1] 7632-04-4 [2]	Oxid. Sol. 2 Repr. 1B Acute Tox. 4 * STOT SE 3 Eye Dam. 1	H272 H360Df H302 H335 H318	GHS03 GHS05 GHS08 GHS07 Dgr	H272 H360Df H302 H335 H318		Repr. 1B; H360Df: C ≥ 9 % Repr. 1B; H360D: 6,5 % ≤ C < 9 % Eye Dam. 1; H318: C ≥ 22 % Eye Irrit. 2; H319: 14 % ≤ C < 22 %	
005-017-01-4	sodium perborate; [1] sodium peroxometaborate; [2] sodium peroxoborate; [containing ≥ 0,1 % (w/w) of particles with an aerodynamic diameter of below 50 µm]	239-172-9 [1] 231-556-4 [2]	15120-21-5 [1] 7632-04-4 [2]	Oxid. Sol. 2 Repr. 1B Acute Tox. 3 * Acute Tox. 4 * STOT SE 3 Eye Dam. 1	H272 H360Df H331 H302 H335 H318	GHS03 GHS06 GHS05 GHS08 Dgr	H272 H360Df H331 H302 H335 H318		Repr. 1B; H360Df: C ≥ 9 % Repr. 1B; H360D: 6,5 % ≤ C < 9 % Eye Dam. 1; H318: C ≥ 22 % Eye Irrit. 2; H319: 14 % ≤ C < 22 %	

3 ENVIRONMENTAL FATE PROPERTIES

Not relevant.

4 HUMAN HEALTH HAZARD ASSESSMENT

With respect to CMR effects sodium peroxometaborate is subject to harmonised classification with Repr 1B, H360Df with various specific concentration limits).

Sodium peroxometaborate is a reactive oxidant and liberates hydrogen peroxide in aqueous solution under formation of sodium borate/ boric acid which is considered to be the cause of the induction of the adverse effects on development and fertility.

The classification as Repr 1B and the specific concentration limits of PBS depend on the content of boron in the substances. This is similar to the classification of the borates and their hydrated forms, where the classification as Repr 1B, H360Df and the specific concentration limits, depend on the boron content of the substances (see chapter 2).

5 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant.

6.2 CMR assessment

Sodium peroxometaborate is classified with Repr 1B, H360Df.

6.3 Substances of equivalent level of concern assessment.

Not relevant.

PART II

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

7 INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES – CONCLUSIONS ON EXPOSURE

NOTE – As sodium peroxometaborate is not registered there is very little information available on the use, exposure, alternatives and risks of the substance. The following information relates to similar substances which are the subject of a separate proposal, namely sodium perborate; perboric acid sodium salt. The abbreviation PBS in the text below refers to all three substances.

Conclusions:
Based on the reported information below, the following conclusions can be drawn:

- PBS is mainly used as bleaching agent in laundry detergents and machine dishwashing products.
- PBS is (per mid 2013) only manufactured by two companies in Europe. Worldwide, no other production exists.
- Exposure at the workplace (production and formulation) is by far the most important source of human exposure to PBS. Consumer exposure concentrations to PBS are in all situations expected to be very low.

7.1 Manufacturing sites

According to the dissemination website, three companies have registered PBS. It is, however, only the collective CAS no. 11138-47-9 that has been registered, while none of the other perborate compounds have been registered under REACH. These three companies are:

- Belinka Perkemija d.o.o. (Slovenia)
- Evonik Treibacher GmbH (Austria)
- Solvay Chemicals GmbH (Germany)

For the preparation of the Risk Assessment Report of PBS in 2007 (EU RAR, 2007a), 12 production sites representing 7 producers were identified. However, at 4 of the identified sites the production was ceased recently (in 2007 when the RAR was prepared). When comparing the identified production companies from the EU RAR report (2007a) with the companies that have registered PBS within the REACH system, it can be seen that in 2010 (when the registrations were made) only 3 producing companies remained, and one of these has stated that they, per mid 2013, have ceased the production of PBS. Thus, only two European producers remain (in 2013). One of these producers (in Slovenia) is new compared to the listed producers in the EU RAR (2007a) report.

7.2 Manufacture, import and export

All information given on manufacture, import/export and uses below concerns the collective CAS number 11138-47-9 of PBS i.e. sodium perborate in general including the mono- and tetrahydrates.

7.2.1 Worldwide

Several older sources (RPA, 2008; EU RAR, 2007a; HERA 2002) report on the European production of PBS, and from these figures it can be seen that in 2007 EU exported a large amount to the rest of the world (72% of the production in the EU – see Table 2). According to CEFIC (European Chemical Industry Council) only 1% of the total production quantity in Europe was imported in 1997.

Information received (October 2013) from the European producers of PBS confirms that EU is exporting most of the European production to the rest of the world. By October 2013 only two producers are left worldwide, and these two producers are located in the EU.

7.2.2 EU

The annual production in Europe can be found in Table 2 below. The data from 1997 to 2007 is based on older information from a RPA report (2008), and the newest information from 2010 is based on REACH registration information from ECHA's dissemination website. It is clearly shown from the table below that the production in Europe has been declining over the past 10-15 years. Furthermore, information received (October 2013) through contact with the producing companies for preparation of this Annex XV dossier indicates that the production is still declining and will continue to decline in the future.

Table 2: Production, sales and export of PBS in Europe (1997 – 2010). Source: RPA, 2008; HERA, 2002; *ECHA (dissemination website); **An educated guess based on indications received from companies (October 2013).

Year	Production (tonnes/year)	Sales in Europe (tonnes/year)	Sales in Europe (%)	Exports (tonnes/year)	Exports (% of European production)
1997	569,900	421,600	74%	153,000	27%
2000	537,600	283,849	53%	223,375	41%
2003	318,750	188,000	59%	130,750	41%
2004	294,000	*no information*		*no information*	
2005	199,000	*no information*		*no information*	
2006	178,000	*no information*		*no information*	
2007	196,000	54,000	28%	142,000	72%
2010	10,000 - 100,000 *				
2013	*< 40,000***				*Most of the production*

7.3 General trends of manufacturing

Information on production volumes from the dissemination website illustrates a decline in manufacturing volumes from 2008 to 2010. According to the RPA report (2008), one of the producers contacted at that time indicated that the quantity of PBS being manufactured at their location had been constant during the last five years (i.e. 2002-2007). At that time, the company expected a similar trend in the future as they exported most of the PBS to markets outside of the EU. In these markets, the consumption of PBS in the detergent industry is increasing due to increasing production of detergents as there are no suitable substitutes for PBS in these regions.

7.4 Use

7.4.1 Function

During use, the PBS ($NaBO_2(OH_2) \cdot x\ H_2O$) is intended to be decomposed to hydrogen peroxide (H_2O_2) which is the acting agent in the bleaching and cleaning process. The decomposition also results in the formation of sodium metaborate ($NaBO_2$), which is mainly available as boric acid (H_3BO_3) in aquatic solutions.

$$NaBO_2(OH_2) \cdot x\ H_2O \leftrightarrows NaBO_2 + H_2O_2 + x\ H_2O$$

PBS is therefore mainly used as a bleaching agent in laundry detergents and machine dishwashing products, but is also used in cleaning products and in cosmetic preparations (Sodium Perborate REACH Consortium; HERA, 2002). In cosmetic products, PBS has according to the CosIng database[2] an oxidising function.

7.4.2 Sectors of use, types of preparations, articles and processes involved

PBSs are only used in chemical preparations such as bleaching agents, cleaning agents and cosmetic products. No use of PBSs in articles has been identified. PBSs are hence only used in the detergent industry and to some (smaller) degree in the cosmetic products industry.

According to AISE (International Association for Soaps, Detergents and Maintenance Products), 96% of the PBS used in detergent products in 1999 was used in heavy duty bleach-containing powders or tablets, and 3% in machine dishwashing detergents (powders or tablets). (HERA, 2002).

Types of preparations involved

The Nordic countries have a common database where chemical substances contained in chemical preparations are listed. According to this database (SPIN – Substances in Preparations in Nordic countries), the following uses of PBS are reported for 2011:

- Washing agents for textile (detergents) – CAS 10486-00-7 (sodium perborate tetrahydrate)
- Cleaning/washing agents – CAS 10332-33-9 (sodium perborate monohydrate)

[2] CosIng is the European Commission database with information on cosmetic substances and ingredients. http://ec.europa.eu/consumers/cosmetics/cosing/index.cfm?fuseaction=search.simple

Other uses that have been reported for both the mono- and tetrahydrates from previous years (but not any longer) are:

- Bleaching agents
- Washing-up detergents (machine)
- Non-agricultural pesticides and preservatives (minor use)
- Conductive agents (minor use)
- Cleaning/washing agents for dish washing (machines) (minor use)

In Denmark, the Danish EPA has, during the last 10 years, performed several surveys of cosmetic products in Denmark. In five of these projects, a database of all ingredients in different types of cosmetic products has been prepared. The five types of cosmetic products surveyed are hair styling products, cosmetic products for children, sun tan lotions and body lotions for children, non-preserved cosmetic products and hair dyes. PBS (CAS 11138-47-9) was found only in a few hair dyes (3 from one producer out of 365 investigated hair dyes) (Danish EPA, 2013). This illustrates that PBS may still be used in cosmetic products, but mainly in specific types of cosmetic products where oxidising properties are necessary.

Concentrations used in preparations

In the EU RAR report (2007a) on PBS, content concentrations of PBS are listed for consumer products. These are shown in Table 3 below. Typical concentrations in detergents range from 4-25% PBS and typical concentrations in bleaching agents range from 5-50%.

Table 3: Content of PBS in consumer products (EU RAR report (2007a)).

Type of product	**Sodium perborate content (%)**	**Substance specification**
Detergent products		
Heavy duty laundry detergents	15-25%	Mono- and tetrahydrate
Laundry additive	16-20%	Not given
Automatic dishwasher detergents	4-18%	Tetrahydrate
Bleaching agents		
Denture cleansers	5-25%	Mono- and tetrahydrate
Stain removers	5-50%	Monohydrate

7.4.3 Operational conditions of use – existing legislation

PBSs are restricted in cosmetic products. According to Regulation No. 1223 on cosmetic products (2009), borates and tetraborates are only allowed in certain types of cosmetic products and in the concentrations listed in Annex III: "List of substances which cosmetic products must not contain except subject to the restrictions laid down".

Table 4: Restrictions on borates and tetraborates according to Regulation No. 1223/2009 on cosmetic products – Annex III "List of substances which cosmetic products must not contain except subject to the restrictions laid down".

Annex III Ref. No.	Substance/ chemical name	Product type, body parts	Max conc. in ready for use preparation	Wording of conditions of use and warnings
1a	Boric acid, borates and tetraborates	Talc	5% (as boric acid)	Not to be used for children under 3 years of age. Not to be used on peeling or irritated skin.
		Oral products	0.1% (as boric acid)	Not to be swallowed. Not to be used for children under 3 years of age.
		Other products (excluding bath products and hair waving products)	3% (as boric acid)	Not to be used for children under 3 years of age. Not to be used on peeling or irritated skin.
1b	Tetraborates	Bath products	18% (as boric acid)	Not to be used for children under 3 years of age.
		Hair products	8% (as boric acid)	Rinse well.
12	Hydrogen peroxide and other compounds or mixtures that release hydrogen peroxide	Hair products	12% of H_2O_2 (40 volumes), present or released	Wear suitable gloves. Contains hydrogen peroxide. Avoid contact with eyes. Rinse immediately if product comes into contact with them.
		Skin products	4% of H_2O_2, present or released	Contains hydrogen peroxide. Avoid contact with eyes. Rinse immediately if product comes into contact with them.
		Nail hardening products	2% of H_2O_2, present or released	Contains hydrogen peroxide. Avoid contact with eyes. Rinse immediately if product comes into contact with them.
		Oral products, including mouth rinse, tooth paste and tooth whitening or bleaching products	$\leq 0.1\%$ of H_2O_2, present or released	Contains hydrogen peroxide. Avoid contact with eyes. Rinse immediately if product comes into contact with them.
		Tooth whitening or bleaching products	$> 0.1\ \% \leq 6\%$ of H_2O_2, present or released	Concentration of H_2O_2 present or released indicated in percentages. Not to be used on a person under 18 years of age. To be only sold to dental practitioners.

Furthermore, PBS is included in Group 30 of Annex XVII of REACH Regulation (inserted with Regulation (EC) No 109/2012) and is therefore not allowed as such and in mixtures for the general public. This applies to concentrations above the specific concentration limits according to the respective entries in Annex VI of the CLP Regulation (see Table 2). An exemption for detergents expired on 1st of June 2013.

7.4.4 General trends of use

According to the SPIN database (Substances in Preparations in Nordic countries), PBS is used in preparations in the Nordic countries, but its use is strongly decreasing. The following PBS compounds are found in the SPIN database:

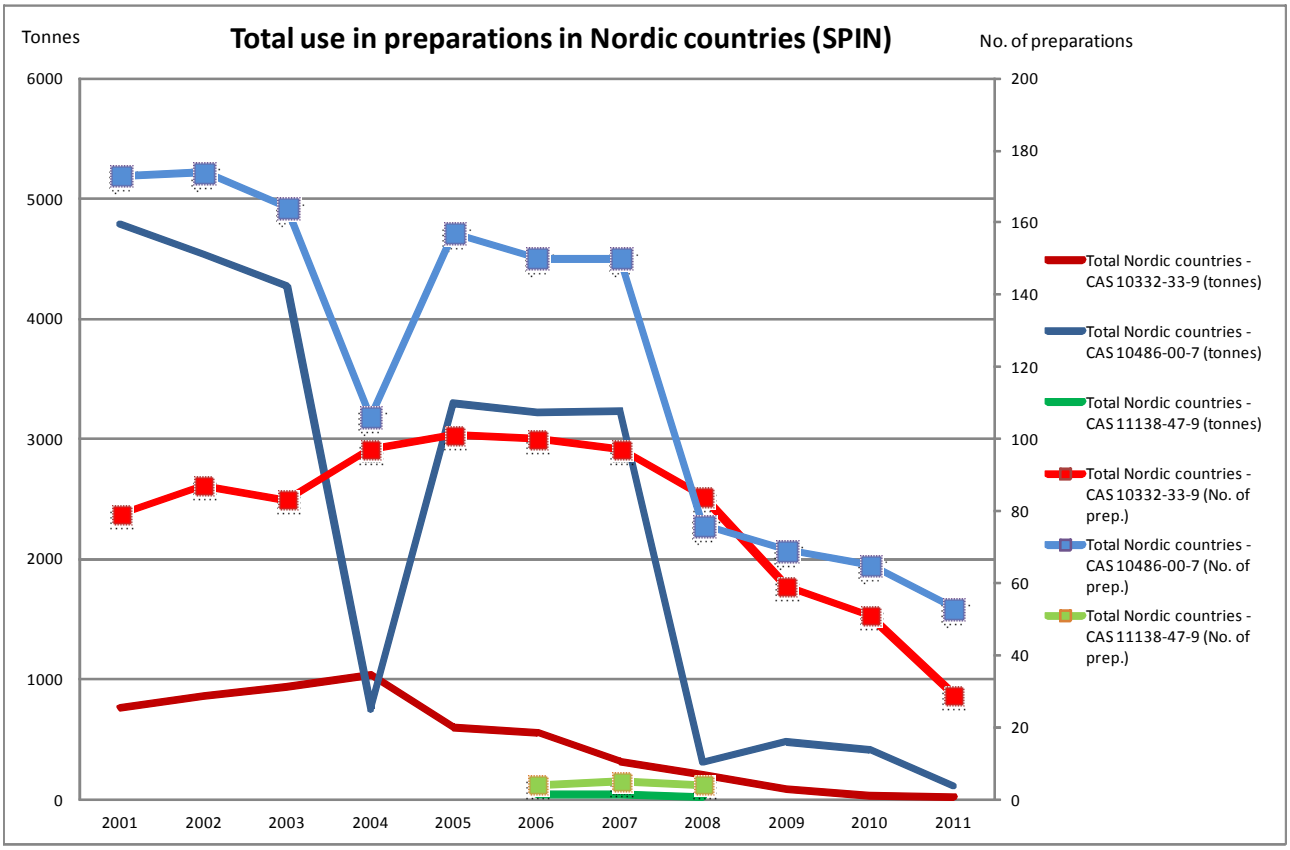
- CAS 11138-47-9 (collective CAS no. for the monohydrates and tetrahydrates)
- CAS 10332-33-9 (sodium perborate monohydrate)
- CAS 10486-00-7 (sodium perborate tetrahydrate)

The total use of these three sodium perborate compounds in the Nordic countries is illustrated in Figure 1 below. There are very few data on the collective CAS number 11138-47-9, as most of the data are confidential (typically when the number of preparations is below three). The green lines in Figure 1 representing the collective CAS number 11138-47-9 are therefore only a compilation of data from Finland for the years 2006 to 2008. All other data are confidential. The total use of CAS 11138-47-9 in the Nordic countries was 44.2 tonnes in 2006, which was reduced to 15.6 tonnes in 2008. These amounts cover Finland only as data for Sweden, Norway and Denmark are confidential. CAS 11138-47-9 was used only in 4 preparations in 2006 and 2008.

The total use of sodium perborate monohydrate (CAS 10332-33-9) in the Nordic countries is represented by the two red lines in Figure 1. The total use in the four Nordic countries peaked in 2004 with a total tonnage of 1,031.7 tonnes used in 97 different chemical preparations. Since then the total use of CAS 10332-33-9 has been decreasing in all four Nordic countries to a total use of 18.4 tonnes in 29 different chemical preparations in 2011.

The total use of sodium perborate tetrahydrate (CAS 10486-00-7) in the Nordic countries is represented by the two blue lines in Figure 1. The total use in the four Nordic countries peaked in 2001 with a total tonnage of 4,541.6 tonnes used in 172 different chemical preparations. Since then the total use of CAS 10486-00-7 has been decreasing in all four Nordic countries to a total use of 107.6 tonnes in 53 different chemical preparations in 2011.

Figure 1: Overview of the use of PBS in preparations in the Nordic countries (2001-2011). Left axis is the total amount of the different PBSs in tonnes used in preparations in the Nordic countries. Right axis is the total number of preparations where PBSs are used in the Nordic countries.



All in all the use of PBS in chemical preparations in the Nordic countries has been reduced drastically from 2001 to 2011. The reduction in the tonnage is 98%, from 2001 to 2011 for both the sodium perborate monohydrate and tetrahydrate CAS numbers. Similarly, the reduction in number of preparations has been decreased by about 70% in 2011, for both the sodium perborate monohydrate and tetrahydrate compared to the years where the substances were used in the highest number of preparations.

Some of the companies that have registered the use of PBS in chemical products in the Danish Product Register were contacted. All these companies gave the same statement that most, if not all, applications of PBS in chemical products have now been phased-out following the harmonised classification of PBS with Repr. 1B.

This confirms the general trend from the SPIN database and the picture from contact with the producers indicating that PBS is no longer used, or at least decreased considerably in the EU.

7.4.5 Actors in the supply chain

The following actors in the supply chain of PBSs exist:

- Manufacturers of PBSs

- Formulators of laundry detergents, machine dishwashing products, cleaning products and cosmetic products
- Distributors of the preparations containing PBSs
- Users – professional and consumers

7.5 Estimated releases and exposures

7.5.1 Exposure of humans

Exposure to PBS can take place at the workplace during the production and formulation of the detergent products and bleaching agents, and during use of bleaching agents and detergent products (during laundry washing and automatic dishwashing). Exposure to PBS will happen in the form of exposure to sodium perborate dust/powder or tablets, but may also happen at the workplace in the form of contact with chemical solutions (EU RAR, 2007a).

The expected exposure routes are mainly dermal exposure, but exposure in the form of inhalation of dusts/powders may also occur.

As described earlier, the concentration of PBS in the detergent products and in the bleaching agents lies between 4-25% and 5-50% respectively. Workers may be exposed to PBS in concentrated form, whereas consumers will only be exposed to PBS in the diluted forms in the final detergent and bleaching products.

In addition to the exposure to PBS, exposure to the degradation products, i.e. hydrogen peroxide and boric acid, may also occur and must be taken into account in the exposure scenarios. An indirect exposure of humans to PBS via the environment is unlikely as PBS is degraded in the sewage treatment plants. However, boron from PBS may be ingested with drinking water coming from fresh water containing boric acid from the use of detergent products and bleaching agents (EU RAR, 2007a).

In the EU RAR (2007a) report it is concluded that exposure at the workplace is by far the most important source of human exposure to PBS. Consumer exposure concentrations to PBS are in all situations expected to be very low.

7.5.2 Exposure of the environment

During the use of consumer products containing PBS for cleaning and bleaching purposes, the perborate is intended to be decomposed to hydrogen peroxide (which is the active agent in the bleaching and cleaning process) and to sodium metaborate, which is mainly available as boric acid under environmental conditions. From this it is concluded in the EU RAR (2007a) report that it can be assumed that apart from releases of PBS during the industrial production and the formulation of detergent products/bleaching agents, the aquatic environment will be mainly exposed to its degradation products.

The aquatic compartment is by far the main target compartment of PBS due to the physical-chemical properties and the use characteristics. From the degradation behaviour of PBS it is concluded that in most cases boric acid is the relevant compound in the aquatic environment. Only at production and formulation sites without standard temperature and pressure, hydrogen peroxide releases into surface water can occur (EU RAR, 2007a).

8 CURRENT KNOWLEDGE ON ALTERNATIVES

Conclusions:
Based on the reported information below, the following conclusions can be drawn:

- In the EU sodium perborates have almost exclusively been replaced by the alternative sodium percarbonate.
- It seems that sodium percarbonate directly can replace sodium perborate as bleaching agent in the formulation of detergents and cleaning agents. However, the shelf life may be decreased compared to using sodium perborate.

8.1 Current knowledge on alternatives

In the EU RAR (2007a) on sodium perborate the trends in the use of sodium perborate are discussed. Here it is concluded that there is some evidence that PBS during the last two years (i.e. 2005-2006) partly was substituted by sodium percarbonate and that the importance of sodium percarbonate as bleaching agent will increase further. In the RPA (2008) report carried out one year later, it is stated that the use of PBS as bleaching agent in detergents is rapidly declining as the substance is substituted by sodium percarbonate. Furthermore, it is stated that any reduction in the use of PBSs would expect to be counteracted by an increased use of sodium percarbonates.

This trend in substitution (described in these reports from 2007-2008) is reflected by the lower tonnage band reported in the dissemination website compared to the estimated use volume provided by RPA in 2008. Furthermore, this trend in substitution has been confirmed by contact to the REACH registrants in 2013. The production of PBS has drastically been decreased mainly due to PBS being substituted by sodium percarbonate as bleaching agent.

- Most of the remaining production is being exported from Europe to markets elsewhere in the world, where the substitution has not yet been carried out as effectively. However, according to a producer of sodium percarbonate[3], the alternative sodium percarbonate is now also being widely used in the developing areas of South America, the Middle East and Africa.

According to the EU RAR (2007a), PBS was earlier the favourite bleaching agent over sodium percarbonate as PBS could ensure a longer shelf life in the formulation of the detergent. In the RPA (2008) report, it is stated that sodium percarbonate is found to deliver a similar technical performance compared to PBS when used in a colder climate. In other words, alternatives to PBS (for colder climates (i.e. in Europe)) have been tested and found feasible. It is not directly stated in these reports, but it is assumed that sodium percarbonate directly can replace PBS as bleaching agent in the formulation of detergents and cleaning agents. As producers today report of a wide use of sodium percarbonate in the developing areas of South America, the Middle East and Africa, this could indicate that the problems of using sodium percarbonate in warmer climates have been overcome.

It can therefore be concluded that today PBS to a very large extent has already been substituted by sodium percarbonate as bleaching agent in detergents and cleaning products. This is also illustrated by the fact that the European 2010 production of PBS has been reduced to about 90% of the 1997

[3] http://www.ocichemical.com/index.php/sodium-percarbonate

production, and that the use of PBS in the Nordic countries in 2011 has been reduced with 98% compared to the use of PBS in 2001.

8.2 Information on the alternative: Sodium percarbonate CAS 15630-89-4

Sodium percarbonate is also called solid hydrogen peroxide and has the chemical formulation of $2Na_2CO_3 \cdot 3H_2O_2$.[4] Sodium percarbonate has a high content of oxygen. When placed in water, it releases H_2O_2 and Na_2CO_3.

Sodium percarbonate (disodium carbonate, compound with hydrogen peroxide (2:3), CAS no. 15630-89-4) has no harmonised classification, but has been notified to the ECHA C&L inventory database. The notified self-classification submitted by industry on sodium percarbonate is summarised in Table 5 below.

In total, 16 aggregated notifications with various classifications can be found in the ECHA C&L inventory database. The classifications shown in Table 5 are the most widely used classification notified by a total of 86 notifiers. A minority of the notifiers has applied other classifications such as Ox. Sol. 1, H271; Skin Irrit. 2, H315; STOT SE 3, H335; Aquatic Acute 2, H401.

Table 5: Self-classification of sodium percarbonate (ECHA C&L inventory database, 2013) according to the CLP Regulation (EC) no. 1272/2008 (CLP Regulation).

International chemical identification	CAS No	Classification	
		Hazard Class and Category Code(s)	Hazard statement Code(s)
Disodium carbonate, compound with hydrogen peroxide (2:3)	15630-89-4	Ox. Sol. 2 Acute Tox. 4 Eye Dam. 1	H272 H302 H318

Sodium percarbonate is not classified as reprotoxic (Repr. 1B, H360Df “May damage the unborn child. Suspected of damaging fertility”) or as STOT SE 3 (H335 “May cause respiratory irritation”) as PBS is. Otherwise, their classification is similar.

Sodium percarbonate has been registered under REACH in a tonnage band of 100,000 to 1,000,000 tonnes per annum.

Sodium percarbonate has been chosen as substitute for PBS, because it is less toxic. Sodium percarbonate decomposes into hydrogen peroxide and natural soda (Na_2CO_3) – or sodium ions and carbonate ions – when in contact with water. In the OECD (2006) report on sodium percarbonate, it is concluded that the toxicity of sodium percarbonate can be predicted from the toxicity of hydrogen peroxide. Sodium carbonate and hydrogen peroxide are very water soluble and will therefore remain in the water phase. Hydrogen peroxide is a naturally occurring substance in the environment and is rapidly degraded in a biological waste water treatment plant. Sodium carbonate will be

[4] http://www.wlchem.com/template/js02_en.htm

neutralised in biological waste water treatment plants. Hydrogen peroxide adsorbs poorly to sediment particles and is rapidly degraded, thus no accumulation in the sediment is expected. Both hydrogen peroxide and sodium carbonate are inorganic chemicals which do not bioaccumulate (OECD, 2006).

Similarly in the human body, most of the acute and local effects of sodium percarbonate can be explained by the release of hydrogen peroxide. The degradation products of sodium percarbonate are all naturally present in the human body. Hydrogen peroxide is expected to be degraded in the body, making it unlikely that hydrogen peroxide is systemically available. Sodium percarbonate has irritating effects, but is not sensitising. According to the OECD (2006) report, no genotoxic effects are expected, but hydrogen peroxide has shown local carcinogenic effects. It is, however, concluded that the carcinogenic properties of hydrogen peroxide should not be regarded as significant, as hydrogen peroxide itself also is degraded in the body. Finally, the OECD (2006) report concludes that it is expected that neither sodium percarbonate nor hydrogen peroxide and sodium carbonate will be systemically available under human exposure conditions and are therefore unlikely to have any relevant potential for toxicity to reproduction or developmental toxicity.

All in all the OECD (2006) report therefore concludes that sodium percarbonate does possess properties indicating a hazard for human health and the environment, but the effects are related to reversible effects (irritation) and acute toxicity which may become evident at high exposure levels. Therefore no further work on the substance is necessary.

9 RISK-RELATED INFORMATION

Conclusions:

Based on the reported information below, the following conclusions can be drawn:

- The main health concern of sodium perborates is the fact that sodium perborates are converted to boric acid (classified as Repr. 1B; H360Df), which suggests that sodium perborate may affect fertility (classified as Repr. 1B; H360Df). Sodium perborate shows both maternal and developmental toxicity.
- The following concerns are therefore valid for sodium perborates:
    - There is a need for limiting the risks to workers. This conclusion applies to highly exposed workers in the production of sodium perborate via inhalation of the dust. There is a concern for effects on the upper airways and for developmental effects.
    - There is a need for limiting the risks to the aquatic compartment (incl. sediment). This conclusion applies to production sites and formulation sites.

9.1 Risk-related information

PBS is listed in Annex VI of the CLP Regulation 1272/2008 with a harmonised classification and labelling (see Table 2).

Identification	EC No	CAS No	Hazard class	Hazard statement	Pictogram	Spec. Conc. limits
perboric acid (H3BO2(O2)), monosodium salt trihydrate; [1] perboric acid, sodium salt, tetrahydrate; [2] perboric acid (HBO(O2)), sodium salt, tetrahydrate; [3] sodium peroxoborate hexahydrate; [containing < 0,1 % (w/w) of particles with an aerodynamic diameter of below 50 µm]	239-172-9 [1] 234-390-0 [2] 231-556-4 [3]	13517-20-9 [1] 37244-98-7 [2] 10486-00-7 [3]	Repr. 1B STOT SE 3 Eye Dam. 1	H360Df H335 H318	GHS05 GHS08 GHS07 Dgr	Repr. 1B; H360 Df: C ≥ 14 % Repr. 1B; H360D: 10 % ≤ C < 14 % Eye Dam. 1; H318: C ≥ 36 % Eye Irrit. 2; H319: 22 % ≤ C < 36 %
perboric acid (H3BO2(O2)), monosodium salt, trihydrate; [1] perboric acid, sodium salt, tetrahydrate; [2] perboric acid (HBO(O2)), sodium salt, tetrahydrate; [3] sodium peroxoborate hexahydrate; [containing ≥ 0,1 % (w/w) of particles with an aerodynamic diameter of below 50 µm]	239-172-9 [1] 234-390-0 [2] 231-556-4 [3]	13517-20-9 [1] 37244-98-7 [2] 10486-00-7 [3]	Repr. 1B Acute Tox. 4 * STOT SE 3 Eye Dam. 1	H360Df H332 H335 H318	GHS05 GHS08 GHS07 Dgr	Repr. 1B; H360 Df: C ≥ 14 % Repr. 1B; H360D: 10 % ≤ C < 14 % Eye Dam. 1; H318: C ≥ 36 % Eye Irrit. 2; H319: 22 % ≤ C < 36 %

From **Error! Reference source not found.** it can be seen that the most severe classification is found for PBS compounds containing ≥ 0.1% (w/w) of particles with an aerodynamic diameter of below 50 µm compared to PBS compounds containing < 0.1%. Furthermore, the classification of sodium perborate monohydrate is more severe than the classification of the tetrahydrates.

The following concerns have been identified based on available data and assessments (EU RAR (2007a)):

- There is a need for limiting the risks to workers. This conclusion applies to highly exposed workers in the production of PBS via inhalation of the dust. There is a concern for effects on the upper airways and for developmental effects.
- There is a need for limiting the risks to the aquatic compartment (incl. sediment). This conclusion applies to production sites and formulation sites.

A summary of the findings from different studies and observations on hazards and risk identification for human health and the environment is presented in the next sections.

9.1.1 Human health

PBS is decomposed to hydrogen peroxide (H_2O_2) and to sodium metaborate ($NaBO_2$), which is mainly available as boric acid (H_3BO_3) in aquatic solutions. Hydrogen peroxide is further hydrolysed in water and therefore no exposure to hydrogen peroxide is expected. However, exposure to boric acid must be expected (EU RAR, 2007a).

It is therefore expected that the workers and consumers are exposed to the PBS through direct contact to the powder or tablets, but no exposure to hydrogen peroxide or boric acid is expected. However, humans may be indirectly exposed to boric acid via the environment.

According to the EU RAR (2007a) on PBS, the information on health effects is very weak for sodium perborate hydrates. Sodium perborate tetrahydrate is less toxic than sodium perborate monohydrate. This is in agreement with its higher water content. However, the differences are considered as minor, compared to other uncertainties in the evaluation of the database.

The local toxicity of PBS is mediated by hydrogen peroxide and boric acid, as these are the degradation products of PBS (HERA, 2004).

The following hazards and risks are observed for PBS (EU RAR, 2007a):

- Dermal absorption is considered to be very low, whereas oral absorption and absorption via inhalation are considered to be high.
- Sodium perborate monohydrate is considered to be acutely harmful if swallowed and if inhaled (Acute Tox. 4; H302 and H332) whereas the tetrahydrate has no acute toxicity due to its lower toxicity.
- PBS causes serious eye damage (Eye Dam. 1; H318).
- PBS is not considered to be a skin sensitising substance. Furthermore, there is no concern for respiratory sensitisation.
- Effects on the stomach, spleen and the haematopoietic system after repeated oral application of PBS can be attributed to the degradation products.
- Studies on PBS show a genotoxic potential which may be due to the generation of hydrogen peroxide.
- No carcinogenic effects of PBS are expected (HERA, 2004).
- Testicular toxicity of PBS cannot be dismissed. The fact that PBS is converted to boric acid suggests that PBS may affect fertility (classified as Repr. 1B; H360Df). PBS shows both maternal and developmental toxicity.

The EU RAR (2007a) concludes that there is no concern for acute toxicity, irritation, sensitisation, mutagenicity and carcinogenicity **for workers** exposed in production and formulation of PBS and from exposure to the end product – either by inhalation or by dermal exposure. However, the situation is different for effects on the upper airways. As a worst case, the assumption can be made that all PBS is deposited in the upper airways and decomposed to hydrogen peroxide. This will result in a concern for irritative effects at worst case concentrations of 12 mg/m^3. This fits very well to the actual experience with PBS (i.e. that accidentally effects have been reported) which probably can be related to high exposure concentrations. Therefore the conclusion is drawn that there is a need for limiting the risks for workers exposed in production and formulation of PBS. However, sufficient measures to mitigate the risks may already be in place. Furthermore, there is a need for limiting the risks regarding developmental effects for highly exposed workers in the production.

Concerning **consumers,** the EU RAR (2007a) considers that there is no risk for exposure from any endpoints by handling of detergents either as a powder or as tablets as the exposure – inhalation, dermal exposure and oral exposure – is negligible. Hydrolysis of PBS to hydrogen peroxide is neither of any concern. The risk of exposure to boric acid is, however, of concern as boric acid has a harmonised classification of Repr. 1B; H360FD ("May damage fertility. May damage the unborn child").

Furthermore, consumers may be indirectly exposed to boric acid via the environment through drinking water containing boric acid.

9.1.2 Environment

PBS is not classified as hazardous to the environment. PBS is instable in water and therefore it is the degradation products hydrogen peroxide and boric acid that are of importance for the environmental risks. In the EU RAR (2007a) report, it is concluded that the short-term effects are dominated by the presence of hydrogen peroxide whereas boric acid is assumed to be the relevant long-term degradation product.

Hydrogen peroxide is almost exclusively found in the water compartment, when released to the environment. Hydrogen peroxide is normally a short-lived substance in the environment and is readily degraded in the environment by an enzyme-mediated process. No bioaccumulation is expected in the environment. Hydrogen peroxide is not considered to be acutely toxic according to mammalian toxicity data. This means that the environmental effects of hydrogen peroxide are expected to be low (EU RAR, 2003).

The harmonised classification (Repr. 1B; H360FD "May damage fertility. May damage the unborn child") of boric acid does not indicate environmental hazards of boric acid. However, boric acid may be of concern for humans when exposed to boric acid indirectly via the environment.

10 CONCLUSION

The relevance for including PBS on the Candidate List for eventual inclusion in Annex XIV is in accordance with the criteria suggested in the Commission SVHC 2020 roadmap:

1. The substance is manufactured, imported and/or used in the EU in a relevant quantity; it has been registered under REACH.
2. The substance has not only been registered for intermediate use, as it is used as bleaching agent mainly in household and professional detergents.
3. The available information does not demonstrate a risk that is not adequately controlled and needs to be addressed at EU level. However, the risks to consumers from combined exposure to the degradation product, boric acid/borates, which have not been addressed in previous risk assessments, must be considered and may lead to significant risk characterisation ratios.
4. The known uses of the substance are not exempted from the scope of authorisation and are not already regulated by other specific EU legislation providing a pressure for substitution.

Thus, the substance fulfils the relevancy criteria for inclusion in the Candidate List.

The perborates are already increasingly being phased out of products in the EU and replaced by available alternatives. As alternatives exist, authorisation is considered a proportionate measure for pushing the substitution of the remaining use of PBS. Furthermore, the SVHC identification of PBS would ensure coherence with the SVHC identification of boric acid/borates.

It should be noted, that e.g. detergents containing PBS below the specific classification limits for the Repr 1B classification (i.e. 6.5%, 9% or 10% depending of degree of hydration of the PBS) will be out of the scope of a possible authorisation requirement.

In summary, based on the available information perboric acid sodium salts (PBS) qualify for inclusion in the candidate list.

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