SUBSPORT Specific Substances Alternatives Assessment – Lead and its inorganic compounds

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1 Profiling lead and its inorganic compounds

Lead is one of the most prevalent environmental pollutants in the world, and exposure to lead or its related compounds can affect the human body, causing significant damage to the body or death. Lead, a bluish grey metal widely distributed throughout the earth's crust, is used in many industrial applications. The most important uses of lead are in storage batteries, sheets, paints, ceramic glazes, solder and ammunition. Exposure occurs by inhalation and ingestion, the predominant route varying with the industry and process. The non-occupational exposure to lead can occur by eating foods or drinking drinks containing lead. In children, the ingestion of flaking paint, paint chips or soil is the major source of exposure.

1.1 Chemical identity

General information on lead and its inorganic compounds is provided in Table 1.

Table 1. General information on lead and its inorganic compounds

Chemical name (IUPAC)	Chemical formula	Identification number	Common names	Function/ uses
Lead	Pb	CAS 7439-92-1, EC 231-100-4	C.I. 77575; C.I. Pigment Metal 4; Lead element; Lead Flake; Lead S 2; Pb-S 100; SSO 1, Plumbum	friction material, electrode material, sealing material, plastic additive
Lead dichloride	$PbCl_2$	CAS 7758-95-4, EC 231-845-5	Lead chloride, lead(2+) chloride; lead(II) chloride; plumbous chloride; natural cotunite	reagents, synthesis of lead compounds, infrared transmitting glass stabiliser
Lead dinitrate	$Pb(NO_3)_2$	CAS 10099-74-8, EC 233-245-9	Nitric acid, lead(2+) salt; lead nitrate, lead(2+) bis(nitrate); lead(2+) nitrate; lead(II) nitrate; plumbous nitrate	oxidant; nylon and polyester stabiliser, photothermographic paper coating stabiliser, stabiliser for gold cyanidation
Lead monoxide	PbO	CAS 1317-36-8, EC 215-267-0	Lead oxide C.I. 77577; C.I. Pigment Yellow 46; lead oxide yellow; lead protoxide; lead(2+) oxide; lead(II) oxide; litharge; Litharge S; Litharge Yellow L-28; plumbous oxide; yellow lead ochre	glass stabiliser, ceramic pigment, coating pigment, cosmetic pigment

Chemical name (IUPAC)	Chemical formula	Identification number	Common names	Function/ uses
Lead tetroxide	Pb_3O_4	CAS 1314-41-6, EC 215-235-6	Orange Lead; Lead oxide, Azarcon; C.I. 77578; C.I. Pigment Red 105; Entan; Gold Satinobre; Heuconin 5; lead orthoplumbate; lead oxide (3:4); lead oxide red; Mennige; Mineral Orange; Mineral red; Minium; Minium Non-Setting RL 95; Minium red; Paris Red; red lead; red lead oxide; Sandix; Saturn Red; trilead tetraoxide; trilead tetroxide; plumboplumbic oxide	rust inhibitor for iron, pigment
Trilead dioxide phosphonate	$PbHPO_3 \cdot 2(PbO)$	CAS 12141-20-7, EC 235-252-2	Dibasic lead phosphite; Lead oxide phosphite; Lead oxide phosphonate, Trilead dioxide phosphonate	thermal stabiliser for PVC, stabiliser for wax chloride, stabiliser for other plastics, activator for foaming agent
Lead chromate	$PbCrO_4$	CAS 7758-97-6, EC 231-846-0	Chromic acid (H2CrO4), lead(2+) salt (1:1); lead chromate(VI); lead chromium oxide (PbCrO4); plumbous chromate; Royal Yellow 6000; chrome yellow	Reagents, oxidizer, pigments
Lead sulfochromate yellow	Pb(Cr,S)O4	CAS 1344-37-2, EC 215-693-7	C.I. Pigment Yellow 34, C 103 (pigment); 77600; 77603; C.P. Chrome Yellow Light 1066; Chrome Yellow Light 1074; Chrome Yellow Medium 1074;	pigment in paints, printing inks, vinyl, cellulose acetate plastics, textile printing, leather finishes, linoleum, paper
Lead chromate molybdate sulfate red	Pb(Cr,S,Mo)O4	CAS 12656-85-8, EC 235-759-9	C.I. pigment red 104; C.I. 77605; Chrome Vermilion; Horna Molybdate Orange MLH 84SQ; Krolor Orange KO 906D; Mineral Fire Red 5DDS;	coating pigment, cosmetic pigment
Tetrabasic lead sulphate	$Pb_5O_4(SO_4)$	CAS 12065-90-6, EC 235-067-7	Lead oxide sulphate, Pentalead tetraoxide sulphate	material of lead-acid batteries
Tetralead trioxide sulphate	$Pb_4O_3(SO_3)$	CAS 12202-17-4, EC 235-380-9	Lead oxide sulphate, Tribasic lead sulphate	pvc stabiliser, electric insulator
Sulfurous acid, lead salt, dibasic		CAS 62229-08-7, EC 263-467-1	Basic lead sulphite	pvc stabiliser, formulation in materials, formulation of preparations

IUPAC: International Union of Pure and Applied Chemistry
CAS: Chemical Abstracts Service Registry Number
EC: European Commission number

1.2 Hazard characteristics

Characterising lead and its inorganic compounds based on their inherent hazards is an essential component of conducting an alternatives assessment. This approach allows the reviewer to assess whether or not an alternative is indeed preferable from an environmental, health and safety perspective. The hazard properties are intrinsic to the chemical, which means that regardless of the way that a chemical is used, these characteristics do not change. The goal of the substitution processes is to advance inherently safer chemicals and products, consistent with the principles of green chemistry.

Sources that have been checked for hazard characterisation:

1. SUBSPORT Hazardous Substance Database according to SUBSPORT Screening Criteria (SDSC) including:

- CLP Regulation (CMR 1A or 1B)
- IARC (group 1, 2A or 2B carcinogens)
- CLP Regulation (Sensitiser: H317, H334)
- EC PBT Working Group
- OSPAR List of Substances of Possible Concern (PBT)
- EC Endocrine Disruptors Database
- SIN List (endocrine disruptors)
- Vela et al. (neurotoxins, cat 2-4)

2. The ESIS (European chemical Substances Information System), http://esis.jrc.ec.europa.eu/
3. TOXNET/ HSDB (Hazardous Substances Data Bank), http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

For green house gases and ozone depleting substances:
4. Greenhouse gases- Kyoto protocol- Annex A, as presented in IPCC (intergovernmental panel on climate change)
5. Ozone Depleting Substances List (Montreal Protocol)

6. Additional sources have been checked for information, especially for endpoints where no information is available in the previous mentioned sources, and also for getting the most up-to-date information. These sources include:

- REACH registration dossiers, http://apps.echa.europa.eu/registered/registered-sub.aspx
- Ordinary Google search
- Producer/ Distributor information, MSDS

Table 2. Hazard characteristics of lead

	Properties	Source of information
Physical Hazards		
Explosivity	Not applicable	REACH registration dossier
Flammability	No	REACH registration dossier
Oxidizing	Conclusive but not sufficient for classification	REACH registration dossier
Other properties of reactivity	Reacts with hot concentrated nitric acid, boiling concentrated hydrochloric or sulphuric acid. Attacked by pure water, but not tap water and weak organic acids	Lead_Health protection agency
Human Health Hazards		
Acute toxicity		
Highly toxic	Conclusive but not sufficient for classification high prevalence of lead-associated central nervous system and gastrointestinal symptoms	REACH registration dossier HSDB
Skin or eye corrosion / irritation	Conclusive but not sufficient for classification	REACH registration dossier
Chronic toxicity		
Carcinogenicity	2B carcinogen carcinogen	IARC[1] HSDB
Mutagenicity	Not applicable	REACH registration dossier
Reproductive toxicity (including developmental toxicity)	Conclusive but not sufficient for classification	REACH registration dossier
Endocrine disruption	Not applicable	
Respiratory or skin sensitization	Conclusive but not sufficient for classification	REACH registration dossier
Neurotoxicity	Neurotoxic cat. 4	Vela et al., 2003
Immune system toxicity	Not applicable	REACH registration dossier
Systemic Toxicity	Not applicable Toxic by ingestion and inhalation of dust or fume; cause toxic complications that are bullets lodged in soft tissues	REACH registration dossier HSDB
Toxic metabolites	Not applicable	REACH registration dossier
Environmental Hazards		
Acute/chronic aquatic toxicity	H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects	SIN List Database
Bioaccumulation	Bioackumulation factor (BCF) of 8,500 (dry wt) and 2,500 (w wt) were determined for the snail Lymnaea palustris (eggs from field-collected organisms).	REACH registration dossier
Persistence	For typical conditions in Europe, lead-ions are rapidly removed from the water-column (>70% within 28 days). Moreover, remobilization of Pb from the sediments to the water column is insignificant.	REACH registration dossier

[1] International Cancer Research, Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man from 2006

	Properties	Source of information
Greenhouse gas formation potential	Not listed	Kyoto protocol - Annex A
Ozone-depletion potential	Not listed	Montreal Protocol
Monitoring – has the substance been found in human or environmental samples?	Yes	REACH registration dossier

Table 3. Hazard characteristics of lead and its compounds

Chemical name (IUPAC)	Physical Hazards	Health Hazards[2]	Environmental Hazards[2]
Lead	flammable explosivity – n/a oxidizability – n/a	H332: Harmful if inhaled	H410: Very toxic to aquatic life with long lasting effects Animal carcinogen[3]
Lead dichloride	flammability – n/a explosivity – n/a oxidizability – n/a	H302: Harmful if swallowed H332: Harmful if inhaled H360: May damage fertility or the unborn child H360Df: May damage the unborn child. Suspected of damaging fertility H351: Suspected of causing cancer H372: Causes damage to organs	H410: Very toxic to aquatic life with long lasting effects
Lead dinitrate	flammability – n/a explosivity – n/a oxidizing	H272: May intensify fire; oxidiser H360: May damage fertility or the unborn child H332: Harmful if inhaled H302: Harmful if swallowed H318: Causes serious eye damage H373: May cause damage to organs	H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects
Lead monoxide	flammability – n/a explosivity – n/a oxidizability – n/a	H351: Suspected of causing cancer H360: May damage fertility or the unborn child H360Df: May damage the unborn child. Suspected of damaging fertility. H332: Harmful if inhaled. H302: Harmful if swallowed H372: Causes damage to organs H372: Causes damage to organs through prolonged or repeated exposure.	H410: Very toxic to aquatic life with long lasting effects
Orange lead	flammability – n/a explosivity – n/a oxidizable	H351: Suspected of causing cancer H360: May damage fertility or the unborn child H360Df: May damage the unborn child. Suspected of damaging fertility H332: Harmful if inhaled	H410: Very toxic to aquatic life with long lasting effects

[2] Globally Harmonized System of Classification and Labelling of Chemicals
[3] Hazardous Substances Data Bank, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

Chemical name (IUPAC)	Physical Hazards	Health Hazards[2]	Environmental Hazards[2]
		H302: Harmful if swallowed H372: Causes damage to organs	
Trilead dioxide phosphonate	flammable explosive oxidizability – n/a	H228: Flammable solid. H351: Suspected of causing cancer H360: May damage fertility or the unborn child H360DF: May damage the unborn child. Suspected of damaging fertility. H302: Harmful if swallowed H372: Causes damage to organs	H410: Very toxic to aquatic life with long lasting effects
Lead chromate[4]	flammability – n/a explosivility – n/a oxidizing	H350 May cause cancer H360Df: May damage the unborn child. Suspected of damaging fertility H373: May cause damage to organs	H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects Animal carcinogen[3]
Lead sulfochromate yellow	flammability – n/a explosivility – n/a oxidizability – n/a	H350: May cause cancer H360: May damage fertility or the unborn child H373: May cause damage to organs	H410: Very toxic to aquatic life with long lasting effects
Lead chromate molybdate sulfate red	non flammable no oxidising no explosive	H350: May cause cancer H360: May damage fertility or the unborn child H373: May cause damage to organs	H410: Very toxic to aquatic life with long lasting effects
Tetrabasic lead sulphate	flammability – n/a explosivility – n/a oxidizability – n/a	H351: Suspected of causing cancer H360: May damage fertility or the unborn child H360Df: May damage the unborn child. Suspected of damaging fertility. H332: Harmful if inhaled. H302: Harmful if swallowed. H372: Causes damage to organs H372: Causes damage to organs through prolonged or repeated exposure	H410: Very toxic to aquatic life with long lasting effects.
Tetralead trioxide sulphate	flammability – n/a explosivility – n/a oxidizability – n/a	H351: Suspected of causing cancer H360: May damage fertility or the unborn child H360Df: May damage the unborn child. Suspected of damaging fertility. H332: Harmful if inhaled. H302: Harmful if swallowed. H372: Causes damage to organs H372: Causes damage to organs through prolonged or repeated exposure.	H410: Very toxic to aquatic life with long lasting effects

[4] European chemical Substances Information System, http://esis.jrc.ec.europa.eu/

Chemical name (IUPAC)	Physical Hazards	Health Hazards[2]	Environmental Hazards[2]
Sulfurous acid, lead salt, dibasic	flammable explosive oxidizability – n/a	H351: Suspected of causing cancer H360: May damage fertility or the unborn child H360Df: May damage the unborn child H332: Harmful if inhaled H302: Harmful if swallowed. H372: Causes damage to organs	H410: Very toxic to aquatic life with long lasting effects

2 Identify functions and uses

2.1 Lead uses

A key first step in identifying appropriate alternatives is to determine the functions, uses and processes associated with lead and its inorganic compounds.

Following ECHA (European Chemicals Agency) lead has been registered according to REACH, in the tonnage band 1.000.000 – 10.000.000 tonnes per annum. Registered uses are:

- Lead battery production
- Lead sheet production
- Use of lead metal in the production of a range of lead articles (e.g. cast, rolled and extruded products, ammunition, lead shot)
- Use of lead metal in the production of leaded steels
- Lead powder production
- Use of lead metal in lead oxide production and use of lead oxide in stabiliser production

According to IARC, uses of lead in descending order of predominance are the following: batteries; pigments and other compounds; rolled and extruded products; alloys; shot/ ammunition; cable sheathing; gasoline additives (IARC, 2006).

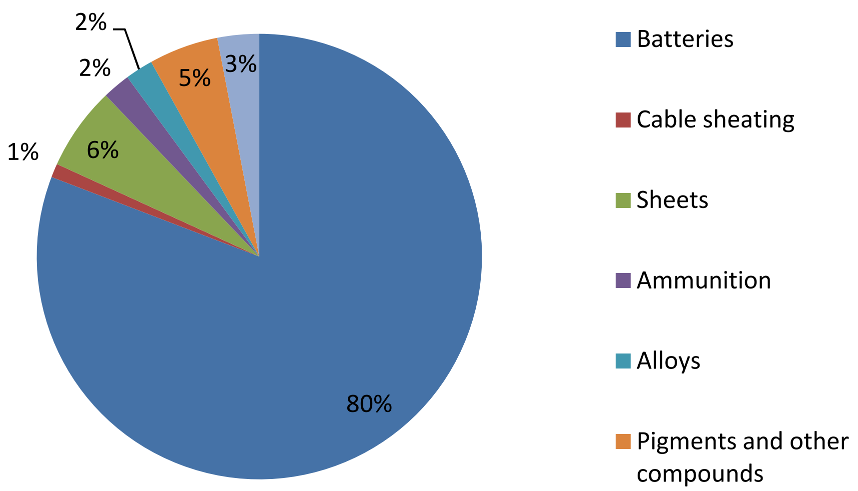
Lead metal is mainly used in lead-acid batteries, which are used in vehicles, and in emergency systems (e.g. hospitals) as well as in industrial batteries found in computers and fork lift trucks. Lead metal is further used in sheet form in the building trade, as shot for alloying and ammunition, in soldering alloys, cable sheathing, and for the production of oxides, pigments, stabilisers and other lead compounds. In 2011 world production was 10 million tonnes (London Metal Exchange, 2013).

In some countries such as Afghanistan, Yemen and Myanmar leaded fuel is still the only fuel sold (Süddeutsche, 2013).

2.2 Prioritizing uses

The estimated use of lead over the last five years is presented in Picture 1 (ILZSG, 2013). The lead battery industry is the dominant use sector, accounting for around 80% of lead use over the last five years. Rolled and extruded products, which mainly comprise lead sheet, account for 6% of use.

Pigments and other compounds comprise mostly oxides for glass manufacture and stabilisers for the PVC industry, accounting for 5% of the lead consumption. To pigments and other compounds belong also cable sheathing with the additional 1%. Lead consumption of ammunition constitutes 3%. The category of alloys is nearly all solder used in the electrical and electronic industries (2%).



Picture 1. Estimated use of lead by sector (ILZSG, 2013).

For this report, alternatives for the following uses will be identified:

- Batteries
- Sheets
- Pigments
- Jewelry
- PVC stabilisers

and screened:

- Batteries
- Sheets
- PVC stabilisers

The main focus will be the use of lead and its inorganic compounds in PVC heat stabilisers. There are three main reasons for this:

- PVC is expected to remain important among thermoplastics with a large number of products,
- The lead stabiliser systems should be substituted completely by 2015, according to the European Council of Vinyl Manufactures (ECVM, 2001),
- In cross-sectional clinical field surveys of PVC manufacturing workers, a high prevalence of lead-associated health symptoms were found (HSDB).

2.3 Exposure to lead and its inorganic compounds

The production rate in the EU exceeds 10 million tonnes per annum. Occupational exposure of workers to lead occurs in industries that are primarily involved either in producing and recycling lead, or consuming major amounts of lead and/ or lead compounds (battery and oxide/ stabiliser production). There are also the ceramics and lead crystal glass sectors and PVC processing. Exposure occurs by inhalation and ingestion, the predominant route varying with the industry and process. Lead can be present in the atmosphere as fumes, which are generated at temperatures greater than 500 °C, and as dust. The non-occupational exposure to lead can occur by eating foods or drinking drinks containing lead. In addition, lead may be inhaled in lead-contaminated air, such as exhaust fumes. For children, ingestion of flaking paint, paint chips or soil is the major source of exposure (Boreiko and Battersby, 2008). In monitoring occupational exposure to lead, two indicators are generally used: Pb in air (PbA) and Pb in blood (PbB).

Lead particles in the environment can attach to dust and can be carried long distances in the air. Such lead-containing dust can be removed from the air by rain and deposited on surface soil, where it may remain for many years. In addition, heavy rains may cause lead in surface soil to migrate into ground water and eventually into water systems (UNEP, 2013).

Illustrative levels of national standards for lead in blood are depicted in table 4.

Table 4. Standards – blood lead limit values in µg/dl (UNEP, 2013)

WHO (since 1980)	General population	20
Germany	General population	15
	Children, women of childbearing age	10
Switzerland	Fetus	10 - 15
	Children	10
Australia, Canada	General population	10
United States	Children	10

WHO has estimated that long-term ambient air concentration of 0.5 – 1.0 mg/m^3 would mean that 98% of the population would have blood levels below 20 µg/dl. For each 1 mg/m^3 increase in the air concentration of lead, the blood lead value in children is predicted to increase by appromiximately 1.9 µg/dl and that for adults by 1.6 µg/dl. Illustrative levels of national standards for lead in air can be found in table 5.

Table 5. Standards – air lead limit values in µg/m^3 (UNEP, 2013)

Canada	5.0
South Africa	4.0
European Union Directive	2.0
Australia, Namibia, United States	1.5
New Zealand, Switzerland	1.0
Czech Republic, Israel	0.5
Denmark	0.4
Russian Federation	0.3

Tabele 6 illustrates data on standards for lead in drinking water.

Table 6. Standards – water lead limit values in µg/l (UNEP, 2013)

Japan, Namibia, South Africa	100
European Union Directive	50
Pre-1993 WHO Guideline	50
Australia, Austria, Czech Republic, Denmark, France, Ireland, Israel, Italy, Mexico, Switzerland, United Kingdom, United States	50
Germany	40
Norway	20
1993 WHO Guideline	10
Canada, Finland, Sweden	10

3 Regulation of lead and its inorganic compounds

There are a lot of EU-level directives concerning lead and lead compounds; for example 2000/76/EC - Waste Incineration, 98/70/EC Leaded gasoline, 2006/66/EC – Batteries, 2000/53/EC on End-of Life Vehicles, 94/62/EC – Packaging, 2002/95/EC - Electrical and electronic equipment.
In addition each country has its own national regulation concerning lead and lead compounds. For example national German regulations are followed: WHG - Wastewater Charges Act, Clean Air Act, 17 BlmSchV, Sludge Ordinance, Biowaste Ordinance, Plant protection use regulation.

3.1 Batteries

Directive 2006/66/EC on batteries and accumulators and waste batteries and accumulators, commonly known as the Battery Directive, regulates the manufacture and disposal of batteries in the European Union with the aim of "improving the environmental performance of batteries and accumulators". Following the directive lead is no longer prohibited from batteries. The directive states to reduce heavy metals in batteries, to promote using less toxic substances in batteries, less batteries thrown in regular household waste, research initiatives in the above and in recycling, separation of battery types in disposal. Consumers should be informed of the dangers in non-compliant disposal of old batteries.
According to Article 21 on the batteries must indicate separate collections or recycling and the heavy metal content. Labels should state collection information and chemical content of batteries.

3.2 Electrical and electronic products

The Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment 2002/95/EC (commonly referred to as the Restriction of Hazardous Substances Directive or RoHS) was required to be enforced and become law in European Union after 1 July 2006. This directive restricts the use of lead in the manufacture of various types of electronic and electrical equipment. The maximum permitted concentrations are 0.1% or 1.000 ppm by weight of homogeneous material. RoHS restricted substances have been used in a broad array of consumer electronic products. Examples of leaded components include: paints and pigments, PVC (polyvinylchloride) cables as a stabiliser (e.g., power cords, USB cables), solders, printed circuit board finishes, leads, internal and external interconnects, glass in television and photographic products (e.g. television screens and camera lenses), metal parts, lamps and bulbs, batteries. There are twenty-one exceptions.

Final Measures for the Administration of the Control and Electronic Information Products (often referred to as China RoHS) has the stated intent to establish similar restrictions, but in fact takes a very different approach.

Japan does not have any direct legislation dealing with the RoHS substances, but its recycling laws have spurred Japanese manufacturers to move to a lead-free process in accordance with RoHS guidelines. A ministerial ordinance Japanese industrial standard for Marking Of Specific Chemical Substances (J-MOSS), effective from July 1, 2006, directs that some electronic products exceeding a specified amount of the nominated toxic substances must carry a warning label.

South Korea promulgated the Act for Resource Recycling of Electrical and Electronic Equipment and Vehicles on April 2, 2007. This regulation has aspects of RoHS, WEEE, and ELV.

Turkey announced the implementation of their Restriction of Hazardous Substances (RoHS) legislation effective June 2009.

Manufacturers will find that it is cheaper to have only a single bill of materials for a product that is distributed worldwide, instead of customizing the product to fit each country's specific environmental laws. Therefore, they develop their own standards, which allow only substances according the strictest legislation.

3.3 Other products

The European Parliament permitted deregulation in the Marketing and Use Directive (89/677/EEC) allowing the use of leaded paints for works of art and historic buildings. The Directive stated that lead carbonates and sulphates “may not be used as substances or constituents of preparations intended for use as paints, except for the restoration and maintenance of works of art and historic buildings and their interiors. The 1999/45/EC concerning the labeling of dangerous preparations states that “Labels of paints and varnishes containing lead in quantities exceeding 0.15% (expressed as weight of metal) of the total weight of the preparation must show the following particulars ‘Contains lead. Should not be used on surfaces liable to be chewed or sucked by children’.”

BASF, largest manufacturer of pigments in Europe is going to stop producing lead chromate pigments by the end of 2014 at the latest, and focus worldwide on the production and marketing of alternative products.

For more information please see point 3.2.

4 Preliminary identification of alternatives

4.1 Use in batteries

Substitution of lead in lead batteries from a practical and technical point of view is very difficult. Most alternative battery technologies are still emerging. There are available alternatives for some areas of application. Possible alternatives are shown in table 7. In general, there is a good infrastructure in place for recycling lead in batteries at product end of life.

Table 7. Alternatives for lead batteries

Alternative	Description	Source
Nickel/iron	For traction application,	NCM, 1992; Sigma Aldrich, 2013
Nickel/cadmium	Stationary batteries	NCM, 1992; Sigma Aldrich, 2013
Zinc-air	Electric cars	NCM, 1992; Sigma Aldrich, 2013
Lithium cell	Electric cars	NCM, 1992; Sigma Aldrich, 2013
Sodium-sulphur	For electricity storage for grid support, electric vehicles	NCM, 1992; Sigma Aldrich, 2013
Lithium-polymer	Solar planes, electric cars, mobile phones	NCM, 1992; Sigma Aldrich, 2013

4.2 Use in sheets

Lead sheets have multiple uses, including radiation shields, packing and sealing material, gasketing, ballasts, and corrosion resistant lining. There are many commercially available alternatives for lead roof flashing.

Table 8. Alternatives for lead sheets

Alternative	Description	Source
Copper	Kick panels for the front door at home or office; backsplashes behind an oven or stove; a unique surface for table top or bar; mounting[6]	http://www.onlinemetals.com/merchant.cfm?id=93&step=2, NCM, 1992
Zinc	Great for countertops, back-forms, range-hoods, roofing, flashing, artistic projects, mounting[6]	http://www.rotometals.com/ZINC-SHEETS-s/29.htm
Iron	Applications in industrial and residential sectors; roofing sheets	http://www.eisedicht.de/eisedicht-dacheindeckungen
Titanium- zinc	Roofing, façades, rain gutters, pipes, fittings, wind and other linings, window sills, roof decoration	http://www.cinkarna.si/en/files/default/teh_inf/titancink_ploevina/tehnina_navodila_ang_low.pdf
Shale schiefer	Stairs, window sills, tiles cover plates, floor plates, wall plates	http://www.doersam-bedachungen.de/leistungen/steildach/schiefer/
Thatch	Building material made from renewable resources; roof covering	http://www.dbu.de/ab/DBU-Abschlussbericht-AZ-25018.pdf
Concrete	roof covering, construction industry	http://www.build.com.au/floors/types-floors/types-sub-floor/concrete-sheeting-0
PVC, plastics, syntetic rubber	Chemical processing tanks, valves, fittings and piping systems, PVC sheets, rods and tubes, mounting, sanitary equipment	http://www.professionalplastics.com/PVCSHEETSRODS; NCM, 1992
Aluminium	Mounting	NCM, 1992
Bitumen	Mounting	NCM, 1992
GammaBlok® (plastic material)	Radiation shielding	http://www.saferad.com/Gammablok.htm

Alternative	Description	Source
Tin	Shielding protective clothing	http://www.ncbi.nlm.nih.gov/pubmed/18072491
Tin + bismuth	Shielding protective clothing	http://www.ncbi.nlm.nih.gov/pubmed/18072491
Tungsten impregnated silicone pieces (Silflex)	Sheets, tapes, blankets, piece of shielding, shielding a pipe, platform shielding, custom applications	http://www.marshield.com/nuclear-shielding/non-lead-alternative

4.3 Use in other products

Pigments

Most uses of lead pigments have been phased out. Lead pigments are used for paints in restauration of historical buildings and used for traffic paint.

Table 9. Alternatives for lead pigments

Alternative	Description	Source
Iron oxide	Pigment	NCM, 1992
Titanum dioxide	Food coloring and in toothpaste, sunscreen	Johnson at al., 2009
Zinc	to lighten mixtures subtly while maintaining transparency, in watercolors	Johnson at al., 2009
Zinc phosphate	Pigment	NCM, 1992
Zirconium	Pigment	NCM, 1992
Strontium	Pigment	NCM, 1992
Calcium	Pigment	NCM, 1992
Aluminium	Pigment	NCM, 1992

Jewelry, ornamental

Lead is still used for castings/ extrusion (jewelry, ornamental, etc.). There is a relatively high consumer exposure during use, especially in children's jewelry. Alternatives are commercially available.

Table 10. Alternatives for lead jewelry

Alternative	Description	Source
Copper	Stand-alone bracelets, necklaces and other	http://www.asia-gems.com/jewelry/alternative-metals.php
Bronze	Bracelets, ankles, and earrings, and beaded necklaces, fashion smaller items like brooches and pins	http://www.asia-gems.com/jewelry/alternative-metals.php
Brass (copper/zinc)	Bed frames, doorknobs, elegant finishes for picture frames, brass charms and stampings for bracelets, necklaces, rings, and body jewelry	http://www.asia-gems.com/jewelry/alternative-metals.php
Alpaca	Made of copper alloyed with nickel, zinc, and tin; fashion jewelry	http://www.asia-gems.com/jewelry/alternative-metals.php
Titanium	Jewelry, ornamental	http://www.asia-gems.com/jewelry/alternative-metals.php
Pewter	Jewelry, ornamental	http://www.asia-gems.com/jewelry/alternative-

Alternative	Description	Source
		metals.php
Surgical stainless steel	An alloy of steel, chromium, molybdenum, and sometimes nickel; body jewelry	http://www.asia-gems.com/jewelry/alternative-metals.php
PMC (Precious Metal Clay)	Made by adding finely ground silver or gold to clay, shaping it and firing it in a kiln;	http://www.asia-gems.com/jewelry/alternative-metals.php

Heat Stabilisers in PVC and Elastomers

PVC stabilisers are mixtures including metal oxides or metal salts. Following an Austrian research study, stabilisers account for 1 to 5% of PVC products (Windsperger et al., 2007). Many lead-free heat stabilisers are commercially available, and companies are partially adopting alternative heat stabilisers. There is little or no recycling at the end of life for PVC products containing lead. The following were identified as potential alternatives to lead-based heat stabilisers for PVC.

Table 11. Alternatives for lead heat stabilisers for PVC

Alternative	Description	Source
Calcium-zinc	Stabiliser used for PVC wire and cable, slush toys, films, hoses and other PVC products with different profiles.	NCM, 1992; UBA, 2003
Barium-zinc	Stabiliser used in flexible foils (e.g.: for membranes, stationery and automotive applications), flooring, wall covering, flexible tubing and footwear.	NCM, 1992; TURI, 2006
Magnesium-zinc	Stabiliser	TURI, 2006
Magnesium aluminum hydroxide carbonate hydrate	Stabiliser	www.subsport.eu/case-stories/294-en
Magnesium zinc aluminum hydroxide carbonate	Stabiliser	TURI, 2006
Tin/ organic tin compounds	Stabiliser	NCM, 1992

Alternatives for lead products such as pigments, jewelry, ammunition, solders, wheel weights and fishing snikers are listed without priority and will not be assessed by SUBSPORT and described in detail. A prescreening of the alternatives against the SUBSPORT SDSC can be found in chapter 5.

5 Screening out regrettable substitutes

The purpose of this chapter is to eliminate any alternatives that would pose a high risk to the environment or human health. SUBSPORT developed a database containing substances that are not acceptable as alternatives due to their hazards. The alternatives are all screened against this database. It can be found on the SUBSPORT database by following this link: http://www.subsport.eu/listoflists?listid=3. If a substance does not meet any of the SUBSPORT screening criteria, it is removed from further consideration as an appropriate alternative, unless SUBSPORT regards the alternative safer under certain conditions than the original substance.

5.1 Screening of alternative batteries

Alternatives that were screened out are nickel-cadmium, iron-nickel and lithium cell batteries because of the carcinogenicity of nickel, cadmium and carbon. Most alternative battery technologies are still emerging.

Table 16. Screening of alternative batteries

Alternative	SDSC	Comments	Source
Nickel-Cadmium (Ingredients:Nickel: CAS 7440-02-0, Cadmium: CAS 7440-43-9)	Nickel and cadmium are listed on the SDSC as carcinogenes.	IARC classified cadmium as carcinogen category 1 and nickel as carcinogen category 2B. Cadmium: H250, H350, H341, H361fd, H330, H372 **, H400, H410; Nickel: H351, H372**, H317, H412	IARC[1], SDSC
Iron-Nickel (Ingredients:Nickel: CAS 7440-02-0, Iron: 7439-89-6)	Nickel is listed on the SDSC as carcinogen.	IARC classified nickel as carcinogen category 2B. H351, H372**, H317, H412. Low rate-performance, slow recharge rate.	IARC[1], SDSC, Sigma Aldrich' 2013
Zinc-air (Ingredients: Zinc: CAS 7440-66-6, potassium hydroxide: CAS 1310-58-3; carbon: CAS 7782-42-5; manganese dioxide: CAS 1313-13-9)	The ingredients are not listed on the SDSC.	Chemical ingredient is hermetically sealed in a vessel, so the product is neither dangerous nor toxic as a cell. Potassium hydroxide which is the contents of cell is an acute toxic substance and corrosive. If adhering to skin, it ulcerates skin. If getting into eyes, cornea and conjunctiva are acutely attacked, causing poor eyesight and blindness. If inhaled, bronchi, lung and throat are attacked, resulting possibility in pulmonary edema. If a person is exposed to powder for a long time or repeatedly, the lung and the nervous system may be affected, possibly causing bronchitis pneumonia, nervous disease or mental disease. Cells have a short operational life, low power density	http://www.microbattery.com/assets-tech/h-aid/nexcell-msds.pdf, SDSC, Sigma Aldrich, 2013, http://link.springer.com/article/10.2478%2Fs11536-012-0058-0
Lithium cell (Ingredients: lithium: CAS 7439-93-2, lithium cobaltite: CAS 12190-79-3, ethyl acetate: CAS 141-78-6, ethyl carbonate: CAS 96-49-1, dimethyl carbonate: CAS 616-38-6, lithium hexafluoro phosphate: CAS 21324-40-3, carbon: 1333-86-4)	Carbon is listed on the SDSC as corcinogen.	Lithium intoxication leads to severe renal insufficiency. Batteries based on lithium cell for cars are still in the research phase. Lithium cobaltite is classified by Chemicals (Hazard Information and Packaging for Supply) Regulations 2009 (CHIP) as R42 and R43 May cause sensitization by inhalation and skin contact. Lithium hexafluoro phosphate and organic solvents mix are classified by CHIP as R43 May cause sensitization by skin contact.	http://www.uscg.mil/hq/cg4/cg432/docs/msds/MSDS_LiIon.pdf, http://pubs.acs.org/doi/abs/10.1021/jz1005384, SDSC

5.2 Screening of alternative sheets

Zinc and copper as roofing material, gutters and downspouts are not recommended in Germany if they have no permanent surface coating that prevents flushing of metallic pollutants according to German Federal Environment Agency (UBA, 2005).
PVC is harmful to human health and to the environment during its full life cycle. The monomer vinyl chloride (Cas no. 75-01-4) is listen on the SDSC as carcinogen a category 1.
A hazard assessment of Silflex and GammaBlok® systems is an example for radiation shielding. According to the producer, these products do not include any lead but information regarding risk assessment could be not found.

Table 17. Screening of alternative sheets

Alternative	SDSC	Hazardous properties	Source
Copper CAS 7440-50-8	Copper is not listed on the SDSC.	Inhalation of fumes or dust may result in irritation of the nasal mucous membranes. Inhalation of copper oxide may cause irritation of the upper respiratory tract and may result in a form of metal fume fever, characterized by flu-like symptoms such as chills, fever, nausea, and vomiting. Ingestion of copper metal may cause nausea, vomiting, headaches, dizziness, and gastrointestinal irritation. Direct eye contact may cause redness or pain. Direct skin contact may result in irritation. Discoloration of the skin often occurs from handling copper, but does not indicate any actual injury. Long-term exposure to copper in aquatic and terrestrial environments or processing of the product can lead to the release of the constituent copper compounds in more bioavailable forms. These bioavailable forms have the potential to yield toxic effects on aquatic organisms.	http://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=3&ved=0CEMQFjAC&url=http%3A%2F%2Fwww.teck.com%2FDocumentViewer.aspx%3FelementId%3D128033%26portalName%3Dtc&ei=8sY5UbGIN4iCtAa18ICQAg&usg=AFQjCNFOY98Ec0IVg6SERXzi3boZFvXL-Q&bvm=bv.43287494,d.Yms, SDSC
Zinc CAS 7440-66-6	Zinc is not listed on the SDSC.	Zinc is classified as spontaneously flammable in air, contact with water liberates extremely flammable gases and very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. (R15, R17 and R50/53).	ESIS, SDSC
Iron CAS 7439-89-6	Iron is not listed on the SDSC.	Slightly hazardous in case of skin and eyes contact (irritant), of ingestion, of inhalation. The substance may be toxic to liver, cardiovascular system, upper respiratory tract, pancreas. Repeated or prolonged exposure to the substance can produce target organs damage.	http://www.sciencelab.com/msds.php?msdsId=9924400, SDSC
Titanium-zinc (Ingredients: zinc oxide: CAS 1314-13-2, titanium dioxide: CAS 13463-67-7)	Titanium dioxide is listed on the SDSC as carcinogen.	Zinc oxide is classified as R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.	SDSC, http://turfscreen.com/Turfscreen_MSDS.pdf, ESIS
Tin CAS 7440-31-5	Tin is listed on the SDSC as neurotoxicant.	Slightly hazardous in case of skin and eyes contact (irritant), of ingestion, of inhalation.	SDSC, https://www.rotometals.com/v/vspfiles/downloadables/MSDS_Tin.pdf

Alternative	SDSC	Hazardous properties	Source
PVC CAS 9002-86-2	PVC is not listed on the SDSC.	Dust associated with the handling of PVC powder as well as fumes or vapors liberated from both PVC powder and pellets at high temperatures may be irritating to the eyes, skin and respiratory tract if not adequately ventilated. Chronic exposure to fumes and vapors from heated or thermally decomposed plastics may cause an asthma-like syndrome due to the inhalation of process vapors or fumes. The onset of irritation maybe delayed for several hours. Fumes or vapors may accumulate within the facility during normal operating procedures that involve elevated temperatures. Exposure to these elevated concentrations, if not adequately ventilated, may have significant health effects. IARC has determined that there is inadequate evidence of carcinogenicity of a polyvinyl chloride resin in both animals and humans. The overall evaluation of polyvinyl chloride is Group 3, meaning that it is not classifiable as a carcinogen (IARC Vol. 19, 1979).	SDSC, http://www.gravitationalsystems.org/pvs-msds.pdf, IARC
Bitumen CAS 8052-42-4	Bitumen is listed on the SDSC as carcinogen.	Hot bitumen and bitumen fumes may cause severe irritation and burns in eyes and skin contact. Cold bitumen may cause eyes and skin irritation. Bitumen dust may cause irritation characterized by burning, redness, swelling and watering in eyes contact and irritation characterized by in skin contact. Bitumen fumes may cause moderate to severe irritation of the nose, throat and respiratory tract. May cause headache, nausea, sore throat, nasal congestion, dizziness and nervousness. Confined spaces may accumulate hydrogen sulfide gas. Hydrogen sulfide may cause respiratory tract irritation, nausea, headache, dizziness, pulmonary edema, loss of consciousness, brain damage and death.	SDSC, http://demo.rkmsuk.com/MSDS/5%20bitumen.pdf
Shale schiefer	Non-chemical alternative.	Non-chemical alternative	
Thatch	Non-chemical alternative.	Non-chemical alternative	
Concrete (Ingredients: quartz: CAS 14808-60-7 and portland cement: CAS 65997-15-1)	Quartz is listed on the SDSC as carcinogen.	Product becomes alkaline when exposed to moisture. Exposure can dry the skin, cause alkali burns and affect the mucous membranes. Dust can irritate the eyes and upper respiratory system. Toxic effects noted in animals include, for acute exposures, alveolar damage with pulmonary edema.	SDSC, http://www.quikrete.com/PDFs/MSDS-J1-Concretes.pdf
Tungsten impregnated silicone pieces (Silflex)	Identification number of ingredients are not available.	According to the producer lead-free alternative. MSDS is not available.	http://www.marshield.com/nuclear-shielding/non-lead-alternative

Alternative	SDSC	Hazardous properties	Source
GammaBlok® (plastic material)	Identification number number of ingredients are not available.	According to the producer lead-free alternative. MSDS is not available.	http://www.saferad.com/Gammablok.htm

Other alternative which is not listed on the SDSC is iron. There are also non-chemical alternatives such as shale schiefer and thatch.

5.3 Screening of alternative PVC stabilisers

Table 18. Screening of alternative PVC stabilisers

Alternative	SDSC	Comments	Source
Calcium-zinc (Ingredients: zinc stearate[5]: CAS 557-05-0, calcium stearate[6]: CAS 1592-23-0)	The ingredients are not listed on the SDSC.	Calcium/zinc salts of any of the acids are approved for food contact use, although specific approval would depend on the co-stabiliser incorporated into the stabilising system. Solid calcium/zinc stabilisers have to meet the general requirements for dust emissions in the workplace although dust-free forms are readily available.	http://www.seepvcforum.com/en/content/20-calcium-slash-zinc-stabilisers
Barium-zinc (Ingredients: barium oxide, zinc oxide, phosphorus oxide, carbon monoxide: CAS 630-08-0, carbon dioxide when burned)	Carbon monoxide is listed on the SDSC as neurotoxicant.	No specific hazards are likely with barium/zinc stabilisers when normal handling procedures are observed. Barium compounds are classified as 'harmful' and this type of product is not approved for food contact applications, toys or medical applications.	SDSC, http://www.seepvcforum.com/en/content/21-barium-slash-zinc-and-related-stabilisers, http://www.mercotape.com/html/msd_m219-229.html
Magnesium-zinc (Ingredients: inorganic compounds, zinc stearate, calcium cilicate, magnesium compounds, organic compounds)	Identification numbers are not available.	MSDS ist not available (trade secret).	http://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0CDgQFjAA&url=http%3A%2F%2Fwww.turi.org%2Fcontent%2Fdownload%2F4705%2F53074%2Ffile%2FTable%25203.4.4%2520R_List%2520of%2520Mixed%2520Metal%2520Heat%2520Stabilizers.pdf&ei=chI_UZL2OonusgbowID4BQ&usg=AFQjCNFHI1KVG0J2VKWkw3OkPSifnPEHSg&bvm=bv.43287494,d.Yms

[5] http://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0CDMQFjAA&url=http%3A%2F%2Fnoracadditives.com%2Findex.php%3Foption%3Dcom_docman%26task%3Ddoc_download%26gid%3D75%26Itemid%3D108&ei=oRE_UZTWA4rKtAaw5YHYBQ&usg=AFQjCNFBlt1Lt2EBQUfy64SY-61nsUVi8A&bvm=bv.43287494,d.Yms

[6] http://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0CDgQFjAA&url=http%3A%2F%2Fwww.turi.org%2Fcontent%2Fdownload%2F4705%2F53074%2Ffile%2FTable%25203.4.4%2520R_List%2520of%2520Mixed%2520Metal%2520Heat%2520Stabilizers.pdf&ei=chI_UZL2OonusgbowID4BQ&usg=AFQjCNFHI1KVG0J2VKWkw3OkPSifnPEHSg&bvm=bv.43287494,d.Yms

Alternative	SDSC	Comments	Source
Magnesium aluminum hydroxide carbonate hydrate (Ingredients: CAS 11097-59-9, water: CAS 7732-18-5)	The ingredients are not listed on the SDSC.	The alternative stabiliser has no harmonised classification (CLP).	http://www.swchem.co.kr/design/default/images/down/Synthetic%20Hydrotalcite/HI-TAL%20P4%20MSDS_En_%28SWI-MSDS-TA4-02%29.pdf, SDSC
Magnesium zinc aluminum hydroxide carbonate (Ingredients: CAS 169314-88-9, fatty acid C16~18: CAS 67701-03-5)	The ingredients are not listed on the SDSC.	Classification according to the producer: H302, H332, H411.	http://www.swchem.co.kr/design/default/images/down/Synthetic%20Hydrotalcite/HI-TAL%20P4%20MSDS_En_%28SWI-MSDS-TA4-02%29.pdf, SDSC
Organotin (Ingredients: dimethyltin: CAS 57583-35-4, dioctyltin oxide: CAS 870-08-6, dibutyltin: CAS 818-08-6)	The ingredients are not listed on the SDSC.	Stabilisers contain about 19% tin and are soluble in organic solvents. Octyltin is toxic to the immune system. Methyltin and butyltin present a potential risk to locally represent the aquatic environment. Butyltin oxide is CMR cat.2 (R25,R36/37/38, R8/20/21/22, R63, R51/53)	http://eur-lex.europa.eu/LexUriServ/site/de/com/2000/com2000_0469de01.pdf, http://fscimage.fishersci.com/msds/36217.htm SDSC

The alternative that was screened out is the magnesium-zinc alternative because the identification numbers (CAS, EC, INDEX) of ingredients are unknown and a hazard assessment could not be done. Barium-zinc stabilisers cannot be recommended because of their properties which is listed on the SDSC.

6 Characterizing alternatives for PVC stabilizer

Polyvinyl chloride (PVC) is one of the most important commercial plastic materials. Thermal and processing **stabilizers are required for PVC processing.** Lead is still used as a thermal stabiliser for PVC and has been severely criticised based on human health and environmental concerns.

Stabilisers for polymers are used directly or in combinations to prevent the various effects such as oxidation, chain scission and uncontrolled recombinations and cross-linking reactions that are caused by photo-oxidation of polymers. Polymers are considered to be weathered by the direct or indirect impact of heat and ultraviolet light. The effectiveness of the stabilisers against weathering depends on solubility, ability to stabilize in different polymer matrixes, the distribution in a matrix and the evaporation loss during processing and use. The effect on the viscosity is also an important issue for processing.

The lead stabiliser systems were reduced from 145,000 tonnes in the year 2000 in the European Union (EU17) to 100,000 tonnes in the year 2007 (EU 25) and should be substituted completely by 2015 by lead-free stabiliser systems (Wernicke and Großman, 2009).

Generally substitution of lead stabilisers is still prevented by technical factors such as product quality, standards, testing requirements and economic reasons (higher costs). It is expected that the price difference between lead stabilisers and zinc stabilisers is going to reduce in the next future. Tin stabilisers have less hazards to the environment and human health. Calcium/zinc stabiliser systems may be the preferred alternative now for all major applications of lead stabilisers (hard and soft PVC) that meet the demanding technical requirements. A promising alternative seems to be magnesium aluminum hydroxide carbonate hydrate systems (UBA, 2003).

6.1 Hazard characteristics of alternatives

The hazard characterisation of the alternatives is performed according to the same methodology as described for the hazard characterisation of lead and its inorganic compounds.

Some of the alternatives have disadvantages in terms of toxicity and environmental pollution. The metal salts and organo-tin stabilisers are alternatives to lead salts.

Tables 19-21 present the hazard characteristics of alternative stabilisers.

Table 19. Hazard characteristic of calcium-zinc stabiliser

Calcium-zinc stabiliser		
Physical Hazards		
Explosivity	Potential explosive hazard when concentrated dust is present.	http://www.seepvcforum.com/en/content/20-calcium-slash-zinc-stabilisers
Flammability	No	MSDS
Oxidizing	No	MSDS
Other properties of reactivity	Not applicable	MSDS
Human Health Hazards		
Acute toxicity	No	http://www.seepvcforum.com/en/content/20-calcium-slash-zinc-stabilisers
Skin or eye corrosion / irritation	May cause irritation with symptoms of redness, swelling, itching and pain. Eye contact may cause irritation with symptoms of redness and pain.	MSDS
Carcinogenicity	No	MSDS
Mutagenicity	Not applicable	UBA, 2003
Reproductive toxicity (including developmental toxicity)	Not applicable	UBA, 2003
Endocrine disruption	Not applicable	UBA, 2003
Respiratory or skin sensitization	Not applicable	UBA, 2003
Neurotoxicity	Not applicable	UBA, 2003
Immune system toxicity	Not listed	UBA, 2003
Systemic Toxicity		UBA, 2003
Toxic metabolites	Not applicable	UBA, 2003
Environmental hazards		

Calcium-zinc stabiliser		
Acute/chronic aquatic toxicity	No	UBA, 2003
Bioaccumulation	Not applicable	UBA, 2003
Persistence	Not applicable	UBA, 2003
Greenhouse gas formation potential	Not listed	Kyoto protocol- Annex A
Ozone-depletion potential	Not listed	Ozone Depleting Substances List (Montreal Protocol)
Monitoring – has the substance been found in human or environmental samples?	Not applicable	UBA, 2003

Calcium-zinc salts and their acids are approved for food contact use. Solid calcium-zinc stabilisers have to meet the general requirements for dust emissions in the workplace although dust-free forms are readily available. Zinc is an essential element to human activity and health and has been subject to various risk assessments. The conclusion of these has been that there are no risks to human health or the environment arising from the use of zinc stearate in PVC heat stabilisers (PVC, 2013).

Table 20. Hazard characteristic of magnesium aluminum hydroxide carbonate hydrate stabiliser

Magnesium aluminum hydroxide carbonate hydrate stabiliser		
Physical Hazards		
Explosivity	No	REACH registration dossier
Flammability	No	REACH registration dossier
Oxidizing	Not applicable	REACH registration dossier
Other properties of reactivity	Not applicable	MSDS
Human Health Hazards		
Acute toxicity	No-threshold effect and/or no dose-response information available	REACH registration dossier
Skin or eye corrosion / irritation	May cause irritation with symptoms of redness, swelling, itching and pain. Eye contact may cause irritation with symptoms of redness and pain.	MSDS
Carcinogenicity	No	REACH registration dossier
Mutagenicity	Not applicable	REACH registration dossier
Reproductive toxicity (including developmental toxicity)	Not applicable	REACH registration dossier
Endocrine disruption	Not applicable	REACH registration dossier
Respiratory or skin sensitization	Not applicable	REACH registration dossier
Neurotoxicity	Not applicable	REACH registration dossier
Immune system toxicity	Not applicable	MSDS
Systemic Toxicity	Not applicable	REACH registration

Magnesium aluminum hydroxide carbonate hydrate stabiliser		
		dossier
Toxic metabolites	Not applicable	REACH registration dossier
Environmental hazards		
Acute/chronic aquatic toxicity	No significant inhibition in respiration rate of the slugde was recorded at 100 mg substance.	REACH registration dossier
Bioaccumulation	Not available information	REACH registration dossier
Persistence	Not available information	REACH registration dossier
Greenhouse gas formation potential	Not listed	Kyoto protocol- Annex A
Ozone-depletion potential	Not listed	Ozone Depleting Substances List (Montreal Protocol)
Monitoring – has the substance been found in human or environmental samples?	Not applicable	REACH registration dossier

Hydrotalcite is confirmed to be an environmentally and effective co-stabiliser for rigid PVC to obtain properties like static thermal stability (through oven testing) and dynamic thermal stability (via torque rheometry). Hydrotalcite is a natural mineral and the large-scale synthesis of magnesium-aluminum hydroxides carbonates is carried out as a precipitation reaction in a strongly alkaline medium (Wernicke and Großman, 2009).

Table 21. Hazard characteristic of organotin stabiliser

Organotin stabiliser		
Physical Hazards		
Explosivity	No	MSDS
Flammability	Yes	MSDS
Oxidizing	Not applicable	MSDS
Other properties of reactivity	Not applicable	MSDS
Human Health Hazards		
Acute toxicity	Not applicable	MSDS
Skin or eye corrosion / irritation	Skin and eye irritation in humans exposed for a short period of time to high amounts. May be harmful if absorbed through skin. May cause skin irritation. May cause eye irritation.	ATSDR, 2005 MSDS
Carcinogenicity	There are no studies of cancer in humans exposed to organotin compounds.	ATSDR, 2005
Mutagenicity	Not applicable	MSDS
Reproductive toxicity (including developmental toxicity)	Toxic to reproduction, category 2	Decision 2009/425/EC[7]
Endocrine disruption	Not applicable	MSDS

[7] Commision Decision of 28 May 2009 amending Council Directive 76/769/EEC as regards restrictions on the marketing and use of organostannic compounds for the purpose of adapting its Annex I to technical progress

Organotin stabiliser		
Respiratory or skin sensitization	Respiratory irritation in humans exposed for a short period of time to high amounts. Some neurological problems have persisted for years after the poisoning occurred.	ATSDR, 2005
Neurotoxicity	Neurological problems in humans exposed for a short period of time to high amounts.	ATSDR, 2005
Immune system toxicity	Immunotoxicity via the thymus gland	Decision 2009/425/EC[7]
Systemic Toxicity	Not applicable	MSDS
Toxic metabolites	Not applicable	MSDS
Environmental hazards		
Acute/chronic aquatic toxicity	In animal studies with repeated oral application of dimethyl tin compounds toxic effects were observed on the immune system.	MSDS
Bioaccumulation	Tin stabilisers do not bio--accumulate in the environment and in the human body	Forschungszentrum für Umwelt und Gesundheit' in Germany (GSF)
Persistence	Methyltin compounds proved to be not readily biodegradable in degradation tests.	MSDS
Greenhouse gas formation potential	Not listed	Kyoto protocol- Annex A
Ozone-depletion potential	Not listed	Ozone Depleting Substances List (Montreal Protocol)
Monitoring – has the substance been found in human or environmental samples?	Organotin compounds may be taken up into the tissues of water animals.	ATSDR, 2005

According to Decision 2009/425/EC[7] all tin stabilisers are classified as toxic and a few are also classified as toxic for reproduction. Therefore, sufficient precautions have to be taken to avoid ingestion, skin absorption and inhalation. The allowable exposure to tin stabiliser vapours in the atmosphere is controlled by national regulations. However, in practice, the typical exposure levels are so low that any risks to health are considered to be negligible (PVC, 2013a). Organotin stabilisers are not persistent in the environment due to microbial activity. All organotin stabilisers degrade into inorganic tin (Scheirs, 2003).

6.2 Technical and economic aspects of substitution

Calcium-zinc stabilisers are in general more complex and expensive than the lead products mainly because of the specialised co-stabilisers required to meet the specific requirements of these applications (PVC, 2013). Tin-based stabilisers are the most expensive on the market (Alibaba, 2013). Hydrotalcite stabilisers have similar material costs compared to lead stabilisers. All alternatives mentioned are good substitutes from a technical point of view and are commercially available. Some are disadvantageous regarding higher costs and their lower stabilization than lead salts.

Table 22. Technical and economical comparison of feasible alternatives to lead stabilisers

Product	Use	Cost	Performance	Use pattern	Avaliability
Calcium-zinc stabiliser	Stabilisers for PVC wire and cable coatings including energy and telecom-munications. Used for both primary insu-lation and sheathing.	Higher material costs	Technically viable alternative	Similar to lead stabiliser	Commercially available
Hydrotalcite stabiliser	Stabilisers for PVC wire and cable coatings, can be used as a flame retardant.	Comparable material costs	Technically viable alternative	Similar to lead stabiliser	Commercially available
Tin stabiliser	Stabilisers for sheet, bottles, profiles,injection moulded fittings, credit cards, blister packs, food containers and display trays	Higher cost of substance	Technically viable alternative	Similar to lead stabiliser	Commercially available

7 Comparing alternatives

There are many alternatives to lead available for use as a heat stabiliser for PVC applications. Therefore, SUBSPORT conducted an assessment to determine those alternatives that are most feasible and/or that are representing a class of alternatives, based upon the SUBSPORT methodology criteria.

Lead stabiliser replacement has gradually taken place in the PVC industry. The presented alternatives of lead stabilisers have achieved growing market acceptance as non-lead heat stabilisers for PVC wire and cable applications. Each of the alternatives are used by at least one major heat stabiliser manufacturer. Calcium-zinc and hydrotalcite stabilisers which do not contain lead are the preferred alternatives. Table 22 presents the comparison of the alternatives.

Table 22. Comparing alternatives

	Calcium-zinc stabiliser	Hydrotalcite stabiliser	Organotin stabiliser
Health aspects	PROS: no suspected risks to human health CONS:	PROS: natural product, not suspected to contain dangerous substances CONS: chemical synthesis occurs in a strongly alkaline medium	PROS: CONS: tin stabilisers are classified as toxic and a few are also classified as toxic for reproduction

	Calcium-zinc stabiliser	Hydrotalcite stabiliser	Organotin stabiliser
Environmental aspect	PROS: no suspected risks to the environment CONS:	PROS: no suspected risks to the environment, natural product CONS:	PROS: CONS: in animal studies, toxic effects on the immune system were observed
Performance aspects	PROS: performance aspects similar to lead stabiliser CONS:	PROS: performance aspects similar to lead stabiliser CONS:	PROS: performance aspects similar to lead stabiliser CONS :
Cost aspects	PROS: CONS: Higher material costs	PROS: Comparable cost of substance CONS:	PROS: CONS: High cost of substance

Examples of related case stories:

Environmentally friendly PVC-Stabilization using synthetic hydrotalcites, http://www.subsport.eu/case-stories/294-en

An alternative to PVC in wires and cables. A kind of plastic completely free from halogens, BFR´s (brominated flame retardants), PVC and plasticizers, http://www.subsport.eu/case-stories/084-en

Cables without lead, PVC and phthalates, http://www.subsport.eu/case-stories/039-en

8 Conclusion

Lead is recognised as a well-known human toxin a.o. by the EU Commission, WHO as well as OSHA. Despite the extensively studied toxic properties of lead, there is currently no harmonized classification for lead in its metallic form, though lead compounds listed in annex VI, table 3.1 of the CLP Regulation have previously all been classified as category 1A reproductive toxicants.

One can suspect that most humans are being exposed to lead, given its widespread distribution. Lead is present in the environment due to man-made and non-site sources. Possible routes of lead exposure include:

- ingestion of lead-contaminated water, soil, paint chips, or dust;
- inhalation of lead-containing particles of soil or dust in air; and
- ingestion of foods that contain lead from soil or water.

This study considered aspects of the substitution of lead and its inorganic compounds and identifies available alternatives. The focus is however on lead-free PVC stabilisers. It has to be noted that the PVC polymer is harmful to human health and to the environment during its full life cycle.

Many alternative products that are allowed in the EU for stabilisation of PVC, investigated by the hazardous Substance Database according to SUBSPORT Screening Criteria (SDSC), pass these criteria.

In this reports the following substances that are not included in SDSC were further assessed:

- calcium-zinc stabiliser

- hydrotalcite stabiliser
- organotin stabiliser

Organic tin compounds are suspected to be toxic and a few are classified as toxic for reproduction. The two other calcium-zinc and hydrotalcite stabilisers are confirmed to be environmentally-friendly and effective additives for PVC. They are a better alternatives with regard to human health than lead and tin stabilisers.

9 References

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Boreiko C., Battersby R. (2008) Voluntary risk assessment report on lead and some inorganic lead compounds. Human health section. Under contract to the LDAI Lead Risk Assessment Working Group. Final draft

EC (European Commision) (1991) Directive 91/157/EEC of the European Parliament and Council of 18 March 1991 on batteries and accumulators containing certain dangerous substances, available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0157:EN:HTML

EC (European Commision) (1994) Directive 94/62/EC of the European Parliament and Council of 20 December 1994 on packaging and packaging waste, available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31994L0062:en:NOT

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