Annex XV dossier

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

Substance Name:	**Lead 2,4,6-trinitro-m-phenylene dioxide (lead styphnate)**
EC Number:	**239-290-0**
CAS Number:	**15245-44-0**

Submitted by:	European Chemical Agency at the request of the European Commission
Version:	August 2011

PUBLIC VERSION: *This report does not include the Confidential Annexes referred to in Part II*

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

Substance Name:	**Lead 2,4,6-trinitro-m-phenylene dioxide (lead styphnate)**
EC Number:	**239-290-0**
CAS Number:	**15245-44-0**

- The substance is proposed to be identified as substance meeting the criteria of Article 57 (c) of Regulation (EC) 1907/2006 (REACH) owing to its classification as toxic to reproduction category 1A[1] which corresponds to classification as toxic to reproduction category 1[2].

Summary of how the substance(s) meet(s) the CMR (1A or 1B) criteria

Lead styphnate is covered by index numbers 609-019-00-4 and 609-019-01-1 of Regulation (EC) No 1272/2008 and classified in Annex VI, Part 3, Table 3.1 (list of harmonised classification and labelling of hazardous substances) as toxic to reproduction, Repro. 1A ((H360-Df: 'May damage the unborn child. Suspected of damaging fertility'). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is toxic to reproduction category 1 (R61: "May damage the unborn child. Suspected of damaging fertility').

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

Registration dossiers submitted for the substance? Yes

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[1] Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances.

[2] Classification in accordance with Regulation (EC) No 1272/2008, Annex VI, part 3, Table 3.2 List of harmonised classification and labelling of hazardous substances (from Annex I to Council Directive 67/548/EEC).

PART I

JUSTIFICATION

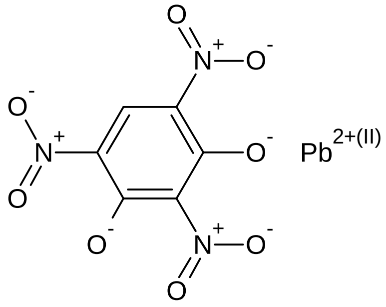
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1.1: Substance identity

EC number:	239-290-0
EC name:	lead 2,4,6-trinitro-m-phenylene dioxide
CAS number (in the EC inventory):	15245-44-0
CAS number:	15245-44-0 66778-13-0 (mono hydrate)
Deleted CAS numbers:	4219-19-6; 6594-85-0; 59286-40-7; 63918-97-8
CAS name:	1,3-Benzenediol, 2,4,6-trinitro-, lead(2+) salt (1:1)
IUPAC name:	Lead(2+) 2,4,6-trinitrobenzene-1,3-diolate
Index number in Annex VI of the CLP Regulation	609-019-00-4
Molecular formula:	$C_6 H N_3 O_8 Pb$
Molecular weight:	450.3 g/mol
Synonyms:	2,4-Dioxa-3-plumbabicyclo[3.3.1]nona-1(9),5,7-triene, 3,3didehydro-6,8,9-trinitro- Lead, [styphnato(2-)]- Resorcinol, 2,4,6-trinitro-, lead(2+) salt (1:1) Lead styphnate Lead tricinate Lead trinitroresorcinate Tricinat

Structural formula:



1.2 Composition of the substance

Name: lead 2,4,6-trinitro-m-phenylene dioxide

Description: not relevant

Degree of purity: > 75 – 100%

Table 1.2: Constituents

Constituents	Typical concentration	Concentration range	Remarks
lead 2,4,6-trinitro-m-phenylene dioxide EC number: 239-290-0	> 90 %	> 75 – 100 %	Based on the registration dossiers received

Table 1.3: Impurities

Impurities	Typical concentration	Concentration range	Remarks
See confidential Annex 2		> 0 – 21 %	Based on the registration dossiers received

Table 1.4: Additives

Additives	Typical concentration	Concentration range	Remarks
See confidential Annex 2			

1.3 Physico-chemical properties

Table 1.5: Overview of physicochemical properties[3]

Property	Value	Remarks	
Physical state at 20°C and 101.3 kPa	Solid Orange or reddish brown rhombical explosive crystals	*Discussion and the value used for Chemical Safety Assessment (CSA) reported in the endpoint summary*	Bornscheuer, U.; Roempp; Georg Thieme Verlag KG, 2008
Melting/freezing point	Decomposing at 190 °C	*idem*	Bornscheuer, U.; Roempp; Georg Thieme Verlag KG, 2008
Water solubility	0.5 – 0.7 g/l at 20 °C	*idem*	Lawrentz U.; Water solubility based on an „OECD Guideline for the Testing of Chemicals"; RUAG Laboratories, 2010
Partition coefficient n-octanol/water (log value)	-2.19 at 20 °C	*idem*	Determination of the partition coefficient of n-octanol/water of "Lead styphnate" according to OECD 107; RUAG laboratories, 2010

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[3] *The references of the values reported in Table 5 will be available in the technical dossier. In case references need to be included an additional column could be added manually to Table 5.*

2 HARMONISED CLASSIFICATION AND LABELLING

Lead styphnate is covered by Index number numbers 609-019-00-4 and 609-019-01-1 in Annex VI, part 3 of Regulation (EC) No 1272/2008 as follows:

Table 2.1: Classification according to part 3 of Annex VI, Table 3.1 ((list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Index No	**International Chemical Identification**	**EC No**	**CAS No**	**Classification**		**Labelling**			**Spec. Conc. Limits, M-factors**	**Notes**
				Hazard Class and Category Code(s)	**Hazard statement code(s)**	**Pictogram Signal Word Code(s)**	**Hazard statement code(s)**	**Suppl. Hazard statement code(s)**		
609-019-00-4	Lead 2,4,6-trinitro-*m*-phenylene dioxide; lead 2,4,6-trinitroresorcinoxide; lead styphnate	239-290-0	15245-44-0	Unst. Expl. Repr. 1A Acute Tox. 4* Acute Tox. 4* STOT RE 2* Aquatic Acute 1 Aquatic Chronic 1	H200 H360-Df H332 H302 H373** H400 H410	GHS01 GHS08 GHS07 GHS09 Dgr	H200 H360Df H332 H302 H373** H410			1
609-019-01-1	Lead 2,4,6-trinitro-*m*-phenylene dioxide; lead 2,4,6-trinitroresorcinoxide; lead styphnate (≥20% phlegmatiser)	239-290-0	15245-44-0	Expl. 1.1 Repr. 1A Acute Tox. 4* Acute Tox. 4* STOT RE 2* Aquatic Acute 1 Aquatic Chronic 1	H201 H360-Df H332 H302 H373** H400 H410	GHS01 GHS08 GHS07 GHS09 Dgr	H200 H360Df H332 H302 H373** H410			1

Note 1:

The concentration stated or, in the absence of such concentrations, the generic concentrations of this Regulation (Table 3.1) or the generic concentrations of Directive 1999/45/EC (Table 3.2), are the percentages by weight of the metallic element calculated with reference to the total weight of the mixture.

Table 2.2: Classification according to part 3 of Annex VI, Table 3.2 (list of harmonized classification and labelling of hazardous substances from Annex I of Council Directive 67/548/EEC) of Regulation (EC) No 1272/2008

Index No	**International Chemical Identification**	**EC No**	**CAS No**	**Classification**	**Labelling**	**Concentration limits**	**Notes**
609-019-00-4	Lead 2,4,6-trinitro-*m*-phenylene dioxide; lead 2,4,6-trinitroresorcinoxide; lead styphnate	239-290-0	15245-44-0	E; R3 Repr. Cat. 1;R61 Repr. Cat.3; R62 Xn; R20/22 R33 N; R50-53	E; T; N R: 61-3-20/22-33-50/53-62 S: 53-45-60-61		E 1

Note E (Table 3.2) :

Substances with specific effects on human health (see Chapter 4 of Annex VI to Directive 67/548/EEC) that are *classified as carcinogenic, mutagenic and/or toxic for reproduction in categories 1 or 2 are ascribed Note E if they are also classified as very toxic (T+), toxic (T) or harmful (Xn). For these substances, the risk phrases R20, R21, R22, R23, R24, R25, R26, R27, R28, R39, R68 (harmful), R48 and R65 and all combinations of these risk phrases shall be preceded by the word 'Also'.*

3 ENVIRONMENTAL FATE PROPERTIES

Not relevant.

4 HUMAN HEALTH HAZARD ASSESSMENT

See section 2 on harmonised classification and labelling.

5 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant.

6.2 CMR assessment

Lead styphnate is covered by index numbers 609-019-00-4 and 609-019-01-1 of Regulation (EC) No 1272/2008 and classified in Annex VI, Part 3, Table 3.1 (list of harmonised classification and labelling of hazardous substances) as toxic to reproduction, Repro. 1A ((H360-Df: 'May damage the unborn child. Suspected of damaging fertility'). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is toxic to reproduction category 1 (R61: "May damage the unborn child. Suspected of damaging fertility').

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

6.3 Substances of equivalent level of concern assessment

Not relevant.

PART II

The underlying work for development of Part II of this Annex XV report was carried out under contract ECHA/2010/174 SR27 by DHI[4] in collaboration with Risk & Policy Analysts Limited (RPA)[5] and TNO[6]. The technical work on the current project has been led by RPA.

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

1 EXECUTIVE SUMMARY

1.1 Manufacture, Imports and Exports

Lead styphnate is typically prepared by precipitation from a magnesium trinitroresorcinate solution with a lead nitrate solution. The manufacture of lead styphnate takes place in at least fourteen locations in the EU, in the Czech Republic, France, Germany, Italy, Poland, Spain and the UK. The overall EU production tonnage lies in the 10-100 t/y range.

The substance is not imported into or exported from the EU as a substance. However, articles containing the substance (e.g. ammunition, detonators) may well be imported into or exported from the EU. There have been suggestions that significant quantities of ammunition may be imported from the USA, Russia and South Africa but also of significant exports as well. In addition, the Federation of European Explosive Manufacturers estimates that 0.8 tonnes of lead styphnate are exported from the EU in the form of civilian detonators.

1.2 Uses

Confirmed uses of lead styphnate identified in literature include:

- as an initiator in primers for percussion caps for small calibre and rifle ammunition;
- as an initiator in detonators for civilian and military use;
- in pyrotechnic igniters used in military munitions (fuzes);
- as a primer in cartridge actuated devices both for aerospace/defence/safety applications but also for cartridges used in fastening power tools; and
- as an initiator in pyrotechnics including automotive airbag inflators and seat belt pre-tensioners
- as a primer in cattle killer cartridges.

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[4] DHI, Agern Alle 5, 2970 Hørsholm, Denmark

[5] Risk & Policy Analysts Limited, Farthing Green House, 1 Beccles Road, Loddon, Norfolk, NR14 6LT, UK

[6] TNO, Schoemakerstraat 97, 2826 VK Delft, The Netherlands

Based on the available information and a series of assumptions, it is estimated that firearm ammunition accounts for ca. 90% of total EU consumption (with sport/hunting ammunition representing the significant majority). Among the rest of the uses, munition pyrotechnics, powder actuated devices and detonators for civilian use are the most prominent. Automotive pyrotechnics for airbags and seat pre-tensioners and (especially) Cartridge Actuated Devices account for a very small tonnage.

With regard to the concentration of lead styphnate in articles:

- primer mixtures may contain significant percentages of lead styphnate; for example in small calibre ammunition, concentrations may reach 55% by weight;
- primer caps and igniters contain a much lower concentration of lead styphnate. In primer caps for small calibre ammunition, this can be as high as 10%. For other devices, for instance automotive airbag igniters, concentrations below 0.1% by weight are common;
- final articles, e.g. assembled ammunition shells, detonators, military munitions, powder actuated cartridges for power tools, concentration can be even lower. In some cases, such as large munition articles (e.g. artillery shells), the concentration of lead styphnate typically is well below 0.1%. For powder actuated cartridges, it is generally above 0.1% by weight.

1.3 Releases from Manufacture and Use

1.3.1Manufacture and First Use

Information from the IPPC BREF Document for Speciality Inorganic Chemicals indicates that lead styphnate is not released to the environment during manufacture. Only releases to water are of relevance and these are treated to break down the explosive molecules by using sulphuric acid. Lead contained in wastewater is precipitated by the addition of sulphate to obtain solid lead sulphate. High removal efficiencies are possible to achieve. Some very low releases to air and waste may occur during the testing of articles. It should be noted that manufacture of the substance and the production of its articles (i.e. formulation and use of primer mixtures) takes place on the same site.

With regard to worker exposure, some key parameters of the manufacture and subsequent use of lead styphnate are important:

- the substance is typically manufactured in a ‘wetted’ form (roughly, up to 20% water) which is the typical approach when intended for use in small calibre ammunition, powder actuated cartridges and automotive airbag initiators. On the other hand, when used in detonators and munitions, it may be prepared using ‘wet’ chemistry but then dried and used in dry form (typically in mixtures with dry lead diazide);
- skin exposure and (to a lesser extent) inhalation exposure may occur during certain activities such as sieving, washing, transferring and dispensing, and cleaning which might be undertaken manually. However, the majority of companies which have provided detailed accounts of their processes indicate that some – if not all – of the processes that might result in worker exposure (sieving, mixing, washing, etc.) are undertaken using automated systems behind reinforced walls with workers being located in isolated, remote ‘cells’;
- protective gloves and glasses are typically used by workers, although at least one company involved in the production of military detonators avoids the use of gloves when handling dry material to avoid the development of static (which could lead to accidental explosions). A

very commonly used piece of equipment for handling 'wetted' material is a rubber container; and

- the manufacture (and subsequent use of the substance) typically involves a small number of workers, takes place in a strictly controlled environment in closed and controlled areas only and with rigorous cleaning procedures, for obvious reasons

Exposure levels are estimated by companies to be nil or very low. Yet, for the purposes of this study, estimates of inhalation and dermal exposure were undertaken using the Stoffenmanager and RISKOFDERM models. The results are shown below expressed as lead (lead is accounts for ca. 46% of the molecular weight of lead styphnate). These only demonstrate exposure levels during use of personal protection equipment (PPE) (calculations without PPE are given in the main part of the report).

Table 1: Modelled Occupational Inhalation and Dermal Exposure to Lead Styphnate during Manufacture

Exposure parameters	**Transfer of wetted material**		**Transfer of dry material-manual**	**Sampling**	**Cleaning**
	Manual	**Automated**			
Worst case (90%) estimation of **inhalation** exposure level (mg Pb/m³)-8 hours' time average - With PPE	0.01	0.01	0.02	4.60E-03	0.01
Worst case (90%) estimation of dermal **exposure** level hand loading (mg/kg bw Pb/day)-full shift - With PPE	0.01	0.02	8.56E-05	4.60E-06	-

Table 2: Modelled Occupational Inhalation and Dermal Exposure to Lead Styphnate during First Use in the Production of Articles

Exposure parameters	**Transfer of wetted material**		**Transfer of dry material-manual**		**Sampling**	**Cleaning**
	Manual	**Automated**	**Several hundred grams**	**Filling devices**		
Worst case (90%) estimation of **inhalation** exposure level (mg Pb/m³)-8 hours' time average - With PPE	5E-03	5E-03	9E-03	9E-03	5E-03	5E-03
Worst case (90%) estimation of dermal **exposure** level hand loading (mg Pb/kg bw/day)-full shift - With PPE	5.98E-03	1.06E-02	8.88E-05	5.84E-05	2.30E-06	-

To assess inhalation exposure, we have used as a benchmark value the lowest known Occupational Exposure Limit (OEL) for organic lead compounds (tetramethyl and tetraethyl lead) applicable in EU Member States, i.e. 0.05 mg/m3. Overall, when the effect of PPE is taken into account, exposure levels for all scenarios considered are below 0.05 mg/m3. Therefore, the worker health risks via inhalation are probably low.

To assess dermal exposure, we have assumed a conservative 100% absorption rate and have compared the daily dermal intakes to the intake implied by the inhalation OEL shown above (i.e. 0.5 mg per day, based on a 10 m3inhaled air volume in a workday under light activity).

The intake estimates for “Transfer of wetted material-manual” and “Transfer of wetted material-automated” for both manufacture and first use would appear to exceed this ‘baseline’ figure of 0.5 mg/day, even when PPE is used. Nevertheless, these estimates are based on a series of conservative assumptions on the processes used and on the behaviour of the substance. In this context, we certainly note the engineering and worker protection measures taken by companies, especially given that contact with the substance has to be eliminated, where possible.

1.3.2Fabrication and End Use of Articles

With regard to the use of articles containing primer mixtures in the fabrication of larger, more complex articles (e.g. a primer cap becomes a component of an ammunition shell), the primer mixture is loaded under pressure into metal cups or sleeves and sealed after filling. The subsequent user will not come into contact with the ingredients. Thus, lead styphnate is captive within the component, it is not intended for release during these fabrication processes and it is conceivable that any releases may occur only as a result of an accident or misuse.

Finally, no exposure during the handling and use of the final articles is expected. Lead styphnate is consumed during firing/detonation and forms reaction products (lead, lead oxides and nitrogen oxides), thus only insignificant (if any) lead styphnate releases are expected, although exposure to lead forms is possible. On a per article basis, the quantities of lead released are generally very small. Still, the entire EU lead styphnate consumption contains an estimated <37 tonnes of lead part of which may be released through the use of ammunition, detonators, munitions and powder actuated cartridges.

1.4 Current Knowledge of Alternatives

Several potential substitutes for lead styphnate have been identified in the literature such as:

- picrates and styphnates;
- diazodinitrophenol (DDNP);
- triazine triazide (TTA) or cyanuric triazide (CTA);
- potassium 4,6-dinitro-7-hydroxy-7-hydrobenzofuroxan (KDNBF) and potassium or sodium 7-hydroxy 4,6-dinitrobenzofuroxan (KDNP);
- mixtures of aluminium nanoparticles and heavy metal oxides such as molybdenum trioxide and bismuth trioxide;
- complex metal dianions and environmentally benign cations; and
- zirconium/potassium perchlorate.

Some of the above options have been identified by companies as potentially able to replace lead styphnate. However, consultation suggests that:

- not all companies are currently working on alternatives and several of them could not name any substance/system as a possible alternative;
- there is significant concern among companies with regard to the qualification and certification of alternative primer mixtures. In particular, articles intended to be used by

military personnel (ammunition, detonators, munitions, cartridge actuated devices) need to meet specific requirements typically set by relevant authorities/defence agencies;

- R&D work and changes to products and processes would be needed; and
- suggestions on the timeframe of R&D required for the development and qualification of alternative compositions range from 5 years to more than 25 years without a clear indication (at present) that efforts may be fruitful for all applications of lead styphnate.

Whilst picrates and lead azide are not believed to be technically suitable alternatives for lead styphnate, it appears that research is currently on-going on the suitability of potassium-calcium styphnate, basic potassium-calcium styphnate and basic calcium styphnate as replacements for lead styphnate. The absence of heavy metals would suggest that the hazard profile of these styphnate might be more favourable than lead styphnate. Yet, the small number of companies that expressed a view on their suitability did not believe that they could act as suitable replacements.

2 DIFFERENT FORMS AND PURITY OF THE SUBSTANCE

Lead styphnate has several forms: (a) the amorphous lead styphnate forms a yellowish powder, needle-like crystals or granules; (b) the red basic lead styphnate forms reddish or reddish-brown square prisms or reddish hexagonal plates; and (c) the normal lead styphnate forms yellowish-orange crystals (Taylor et al, 1975).

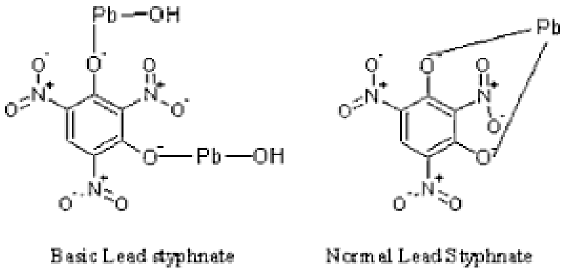

Figure 2.1: Basic and Normal Lead Styphnate

Source: Ledgard (2007)

All these forms of lead styphnate detonate when heated to about 260°C. All forms are initiating explosives for use in blasting caps/detonators and they are also used in the preparation of priming mixtures for a variety of applications (e.g. small calibre ammunition). Similarly, all forms of lead styphnate are sensitive to shock, heat, friction and percussion, but the red basic lead styphnate tends to be the most unstable form (Ledgard, 2007).

Basic lead styphnate is a different substance to normal lead styphnate. It is associated with EC Number 235-642-2 and CAS Number 12403-82-6.[7] Basic lead styphnate appears as "dihydroxy[styphnato(2-)]dilead" in the ECHA list of pre-registered substances, apparently not

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[7] See a relevant Safety Data Sheet at: http://www.winchester.com/SiteCollectionDocuments/pdf/msds/msds_w79.pdf.

related to any other substance8. On the other hand, normal lead styphnate is present on the list under EC Number 239-290-0, CAS Number 15245-44-0 and name “lead 2,4,6-trinitro-m-phenylene dioxide”. This substance is related to another eight (including styphnic acid and the magnesium salt that is involved in the production process of normal lead styphnate).

Ledgard (2007b) summarises the production processes for the different types of lead styphnate as follows (more detail on the manufacturing process for normal lead styphnate is provided in Section 3.1):

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[8] The searchable list is available at: http://apps.echa.europa.eu/preregistered/pre-registered-sub.aspx.

Styphnic acid +

$NaOH/Pb(NO_3)_2$ [100°C] → Yellow basic lead styphnate

$NaOH/Pb(NO_3)_2$ [70°C] → Red basic lead styphnate

$Pb(NO_3)_2/NH_3$ [45°C] → “Normal” basic lead styphnate

MgCO3 [55°C] →→$Pb(NO_3)_2$ [80°C] → Normal lead styphnate

A 1975 patent by Taylor *et al* suggests that basic lead styphnate is superior to the commonly used normal salt in that the former beings to decompose only above 200°C as compared with a decomposition temperature of 130°C for the latter. Furthermore, the reaction of the basic salt in the presence of moisture is almost neutral as compared with the definite acidity of the normal salt. Despite these advantages, basic lead styphnate has been little used commercially. This is due mainly to the complex crystallising properties associated with its existence in at least three polymorphic modifications. Thus, the compound usually assumes crystal habits which give it poor flowing and poor mixing characteristics and consequently make it unsatisfactory for technical use. In addition, such a product presents handling hazards because of its excessive sensitiveness to ignition by electrostatic sparks of low energy. Although well-formed crystals of the beta polymorph, or so-called red variety have been prepared experimentally, no process for preparing basic lead styphnate in a satisfactory form on a commercial scale has been described at the time that the patent documents had been submitted (Taylor *et al*, 1975).

It is understood that lead styphnate manufactured in the EU is most likely to be of the normal type. Those companies that have identified the type of lead styphnate they manufacture have confirmed that they manufacture the normal type, apart from one company , which confirmed the manufacture of both normal and basic lead styphnate. It is not known for which purposes the basic salt is manufactured.

Lead styphnate comes in dry and wet forms. When dry, it can be readily detonated by static discharges from the human body. When wetted with at least 20% water, it is given a hazard Class of 1.1A and a transport identification number of UN0130. Transport of lead styphnate (dry) is forbidden. Transport of lead styphnate, wetted with <20% water is forbidden by cargo aircraft or passenger aircraft/rail (KGHM, 2011). Generally, for use in initiation (ignition) compositions, all forms of lead styphnate should be desensitised with small amounts of arabic gum, sulphur, carbon black, dextrose, magnesium sulphate or starch and mixed with an oxidiser such as boron chromate, lead chromate, copper permanganate, copper perchlorate or magnesium (Ledgard, 2007). A manufacturer notes that the transport of such an explosive (1.1A) is allowed only in special trucks (ADR 2011: Chapters 9.1 to 9.4), under special conditions (ADR 2011: Chapters 2.2.1 and 8.5) and the highest transportable mass is 6.25 kg per truck (EX/II) or 18.75 kg per truck (EX/III) (see ADR 2011: Chapter 7.5.5.2). Thus, the transportation of explosives class 1.1 A is expensive and limited to very small amounts.

According to the UK Health and Safety Executive, lead styphnate is accompanied by the R3 risk phrase for explosives (“Substances or preparations, which create extreme risks of explosion by shock, friction, fire or other sources of ignition (these types of explosives are more commonly known as primary explosives”). The threshold limits for such substances stored by facilities under the Seveso II Directive are 10 tonnes (lower tier of the corresponding UK COMAH Regulations) and 50 tonnes (top tier of the corresponding UK COMAH Regulations) (UK HSE, undated).

3 INFORMATION ON MANUFACTURE, IMPORT, EXPORT AND RELEASES FROM MANUFACTURE

3.1 Manufacturing Process

3.1.1Typical Manufacture of Lead Styphnate

According to literature, lead styphnate is made in batches or continuously by precipitation from a magnesium trinitroresorcinate solution at a pH of ca. 5.4 with a lead nitrate solution ($Pb(NO_3)_2$) (Eagleson, 1994).

The following reactions apply (EC, 2007)[9]:

$$MgO + C_6H(NO_2)_3(OH)_2 \rightarrow Mg\text{-}C_6H(NO_2)_3(O)_2 + H_2O$$

$$Pb(NO_3)_2 + Mg\text{-}C_6H(NO_2)_3(O)_2 \rightarrow Pb\text{-}C_6H(NO_2)_3(O)_2 + Mg(NO_3)_2$$

Normal lead styphnate presents considerable static risk during handling and is therefore made under conditions of high relative humidity with adequate earthing of buildings and equipment (Agrawal, 2010).

The manufacture of lead styphnate necessitates raw and auxiliary materials as shown in Table 3.1. This information is provided in the IPPC Best Available Techniques Reference (BREF) Document for Speciality Inorganic Chemicals (SIC), hereafter referred to as the SIC BREF Document.

Table 3.1: Raw Materials Needed for the Industrial Manufacture of Lead Styphnate

Substance	**Use**	**Manufacturing step**	**Quantity (in kg/kg of lead styphnate produced)**
Lead nitrate	Raw material	Reaction	0.74
Magnesium oxide (or magnesium hydroxide)	Raw material	Reaction	0.09
Trinitroresorcine	Raw material	Reaction	0.54
Sodium hydroxide	pH adjustment	Reaction	Confidential
Acetic acid		Reaction	Confidential
Ethyl alcohol	Washing of lead styphnate	Purification	Confidential

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[9] Information on the production of basic lead styphnate is also provided by Ledgard (2007). This generally agrees with the information presented elsewhere, i.e. the precipitation of the salt from a styphnic acid/sodium hydroxide solution with lead nitrate.

Table 3.1: Raw Materials Needed for the Industrial Manufacture of Lead Styphnate

Substance	**Use**	**Manufacturing step**	**Quantity (in kg/kg of lead styphnate produced)**
Sodium polysulphides	Chemical destruction of explosive impurities	Waste water treatment	0.27
Hydrochloric acid		Waste water treatment	0.41
Sodium hydroxide	pH adjustment	Waste water treatment	0.14
Sulphuric acid	Chemical destruction of explosive impurities in waste water and precipitation of lead sulphate as part of the lead removal treatment	Waste water treatment	Confidential
Activated carbon	Adsorption of coloured organic impurities in waste water	Waste water treatment	Approximately 0.27

Source: EC (2007)

The process description below is based on the information from the SIC BREF Document (EC, 2007).

Reaction

The material solutions are brought to the reactor (stirred tank of <100 litres capacity) by means of pipes and valves where they are agitated and heated up to approximately 50°C. The reaction (i.e. precipitation) is carried out by adding two or more water solutions to the vessel. The temperature and the pH both have a significant influence on the quality properties of the explosive produced (e.g. particle size and shape). The reaction takes place at atmospheric pressure and leads to the formation of the precipitated lead salt (EC, 2007).

Residence time in the reactor is about one hour. The temperature is controlled by external heating and/or cooling through jackets. Agitation of the solution is stopped to allow explosive crystals (of about 70 µ in size) to settle at the bottom of the reactor. The mother liquor (containing explosive impurities and unreacted lead nitrate) is removed from the reactor and sent to wastewater treatment (EC, 2007).

Purification

At reaction temperatures, lead styphnate is always insoluble in the reacting media. Therefore, purification is usually carried out by solid-liquid separation and washing with water and a small quantity of organic solvents (mainly ethyl alcohol) is used to minimise organic impurities. The explosive powder is loaded up on antistatic trays (containing less than 5 kg of products) and manually transported to the drying area. Wastewater (containing explosive impurities and unreacted lead nitrate) which comes from the purification step is sent to wastewater treatment (EC, 2007).

Drying

The SIC BREF Document suggests that lead styphnate is not dried; instead, it is directly mixed with other products in a 'wet' phase (EC, 2007).Consultation suggests otherwise; the drying phase depends on the nature of its applications:

- when lead styphnate is used in the preparation of primer charges for small calibre ammunition (the main use of the substance), the substance is indeed used in its 'wet' form. Lead styphnate is manufactured under water. Initially, it is partially dried by discarding part of the water (the quantity of water to be removed depends on the kind of primer mixture it will subsequently be used in). In any case, lead styphnate will have a water content above 20%. This is then used to produce primer mixtures (the mixture has a variable water content which depends on the kind of primer mixture; in any case it has a water content between 10% and 20%). The mixture is then used to load primer caps. Finally, the primer caps are placed in an oven to dry and only then lead styphnate is completely dry but by then out of reach of the user. A similar process is followed when manufacturing automotive igniters and powder actuated cartridges for power tools (these are explained further later in this report); and

- when lead styphnate is used in detonators and pyrotechnic devices for military munitions (e.g. mortar shells), the substance is left to dry completely and then it is used in its dry from, typically combined with substances such as lead azide. However, it was also brought to our attention that some applications of 'wet' lead styphnate concern the production of fuze heads (but only small quantities of lead styphnate are apparently involved).

Handling and Storage

Finished products are stored in storage buildings equipped with extensive electrical protection (e.g. ground lines) and safety systems. Storage buildings are located at safe distances from any other building to prevent a 'domino effect' in the event of an accidental detonation. Security systems are also in operation in every handling and storage area, particularly to prevent intrusion (EC, 2007).

Some additional confidential detail on this manufacturing process is given in the Confidential Annex (Section A2.1).

3.1.2Alternative Manufacture of Lead Styphnate

Smyth Wallace (2008) suggests a different way of manufacturing lead styphnate within an article (ammunition cartridge): lead styphnate is made from mixtures of lead monoxide and styphnic acid.

In 1979, Eley, a UK ammunition producer working on a dry powder mixture for filling .22 cases, discovered that it was non-explosive until exposed to water, whereupon a chemical reaction converted it to conventional lead styphnate (Metcalf, undated).This new type of primer manufacturing process (closely guarded and patented) is known as Eleyprime process and it eliminated the risk of explosion from the preparation and dispensing of priming compounds, and also allowed the amount of priming material applied to each individual rimfire case to be very closely controlled in a normal workshop environment using automatic equipment (Metcalf, undated).

The Eleyprime system allows exactly identical amounts of the inert powder to be put in each case. Then a round-tip rod is inserted down into the case to press the powder evenly into, and around, the rim, and a single, metered drop of water is added, which activates the compound over a several-hour period.

After drying, the cases can then be conventionally charged with precisely metered propellant. Before Eleyprime, there was an average 31 to 39 milligram spread in the amount of priming material round-to-round in ammunition. With the Eleyprime system, the spread was reduced to only plus/minus 1.0 milligram (Metcalf, undated). Smyth Wallace (2008) suggests that the final product when dry is no different from a conventional primer.

3.2 Production Sites and Volumes

3.2.1Information from Literature

The SIC BREF Document suggests that European consumption of lead styphnate in the mid-2000s exceeded 100 t/y (EC, 2007).The reported manufacturing capacity of lead styphnate in Europe in 2004 was somewhat lower than 100 t/y and is given in Table 3.2.

Table 3.2: EU Manufacturing Capacity for Lead Styphnate – Mid-2000s

Production location	**Manufacturing capacity in 2004 (tonnes)**
Vsetin, Czech Republic	<5
Clérieux, France	~25
Héry, France	<5
Survilliers, France	<5
Tarbes, France	~1
La Ferté-Saint-Aubain, France	<1
Troisdorf, Germany	Unknown
Rivalta, Italy	~20
Galdácano, Spain	<10
Total	***<75***

Source: EC (2007)

Other European producers of lead-based primary explosives (lead styphnate, lead azide and lead picrate) reportedly existed in Italy, Germany, Portugal and probably in Sweden, Austria and Poland (EC, 2007); however, it is not clear which of these locations may have specifically related to lead styphnate.

3.2.2Information from Consultation

Based on information from consultation, literature and available REACH Registration dossiers, it would appear that the number of manufacturers is at least 14. These are located in the Czech Republic, France, Germany, Italy, Poland, Spain and the United Kingdom.

Among the nine plants implied in Table 3.2, on-going manufacture has been confirmed for seven; for one, data are not available from the company itself but Internet searches and general consultation would suggest on-going manufacture. Finally, the ninth company has disputed its presence in the Table and suggested that it did not manufacture any lead styphnate in 2004 or later. More detail is given in the Confidential Annex (Section A2.2).

Confidential information on the production volumes collected through consultation is given in the Confidential Annex to this document (Section A2.2).The level of production of lead styphnate in the EU is in the 10-100 t/y range. Notably, six EU companies manufacture both lead styphnate and lead azide.

3.3 Imports and Exports of the Substance into and from the EU

Information from literature and consultation would suggest that mixtures and articles (ammunition, detonators, igniters and pyrotechnic devices) containing lead styphnate are formulated and produced at the very same sites where the substance is manufactured. No consultee has indicated that the substance is imported into the EU as a substance. Similarly, no manufacturer has indicated that the substance is exported as such to third countries. This is in line with the transport requirements for lead styphnate discussed in Section 2.

On the other hand, primers based on lead styphnate may well be imported into the EU as part of imported ammunition and detonators. This discussed further in Section 4.10.

3.4 Recent and Future Trends

The SIC BREF Document suggests that, for SIC explosives that are used as initiating charges for organic explosives and blasting agents, manufacture figures follow those of these secondary explosives. Therefore, as the manufacture figures of secondary explosives remained nearly constant (or were slightly declining) in the 2000s, the manufacture figures for the SIC substances used as initiating systems also remained constant (EC, 2007).

Confidential information summarised in the Annex (Section A2.3) shows that a large proportion of manufacturers has not experienced any significant change in production tonnages in the period 2005-2010 while a somewhat smaller proportion appear to suggest increases in the tonnage manufactured (and used on-site) in the 10-25% range in the same period. Only a few respondents have suggested a decrease.

3.5 Information on Releases from Manufacture

3.5.1Environmental Emissions

Information from Literature

Air Emissions

The SIC BREF Document notes that there are no significant atmospheric emissions from the manufacture of SIC explosives. Some low volume emissions arise from the chemical destruction of the dissolved explosive residues contained in the wastewater. Fugitive air emissions are neither collected nor treated due to their very low volume and negligible impact on the environment (EC, 2007).

Water Emissions

Wastewater from the manufacture of SIC explosives (originating from the reaction and purification steps) mainly contain lead soluble salts (i.e. lead nitrate raw material) and organic coloured materials (i.e. traces of trinitroresorcine raw material, partially soluble in water) (EC, 2007).

Wastewater is generally treated in several steps; pre-treatment steps are carried out within the SIC installation, followed by treatment in a central wastewater treatment plant (EC, 2007). A relevant figure available from the SIC BREF Document is reproduced overleaf.

The first operation in the pre-treatment steps consists of destroying the traces of explosives material (i.e. lead styphnate) contained in the wastewater by using sulphuric acid. Activated carbon is used for the adsorption of organic impurities (e.g. trinitroresorcine) responsible for the yellow/green colour of the wastewater. After such a treatment, COD is reduced to <600 mg O2 per litre (EC, 2007).

Lead contained in wastewater is precipitated by the addition of sulphate to obtain solid lead sulphate – this treatment is carried out together with the destruction of traces of lead styphnate. The efficiency of the lead removal pre-treatment used at a Spanish manufacturing installation is shown in Table 3.3. It appears to exceed 99.9%. Although the effluent would still appear to have a considerable concentration of lead (particularly if seen in the context of the 7.2 µg/L Environmental Quality Standard for lead and its compounds under the Water Framework Directive 2000/60/EC), the figures shown in the table reflects the concentration before discharge to the central on-site wastewater treatment plant.

Table 3.3:Total Lead Concentration at a Spanish Lead Styphnate Production Plant

Wastewater before pre-treatment	**Wastewater after pre-treatment and before discharge to a central on-site wastewater treatment plant**
30,000 mg/L	15 mg/L

Source: EC (2007)

The example Spanish installation discussed in the SIC BREF Document sends its sludge to an off-site contractor authorised to deal with such waste (EC, 2007).

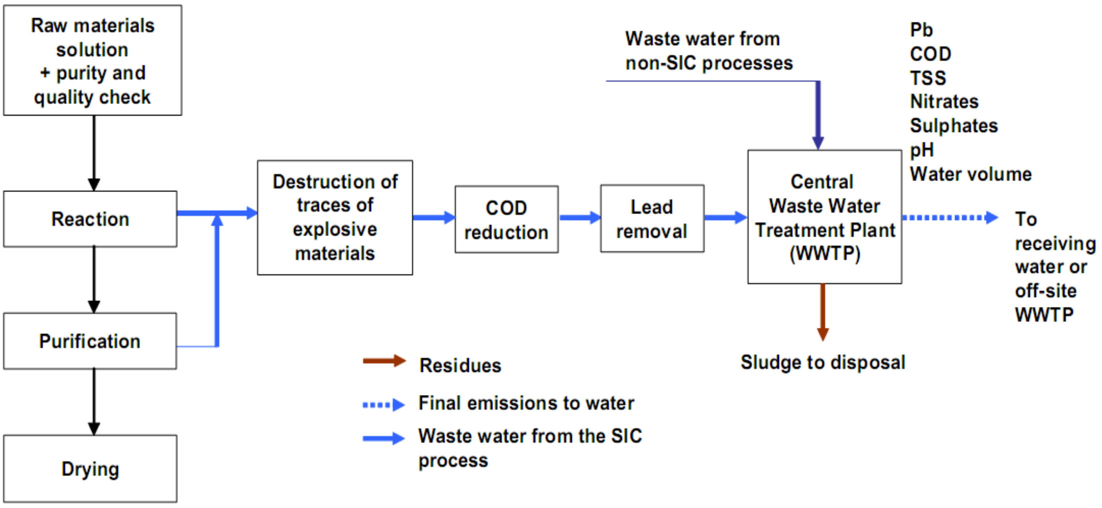

Figure 3.1: Treatment of Wastewater arising from the Manufacture of Lead Styphnate

Source: EC (2007)

Solid Waste

In the lead styphnate manufacturing process, waste arises from wastewater treatment sludge (containing $PbSO_4$) which is collected and disposed of by an external contractor. Another type of waste is made of solid materials contaminated with traces of explosives (EC, 2007).**Table 3.4** shows the quantity of solid wastes generated at a Spanish installation in 2003, which was considered typical.

Table 3.4:Typical Quantity of Solid Wastes Generated at a Spanish Production Plant

Solid waste type	**Quantity generated in 2003**
Solid waste containing traces of explosives (e.g. coming from the hand washing of production equipment)	63 kg/tonne of explosives
Sludge containing $PbSO_4$	210 kg/tonne of lead styphnate
Spent activated carbon	270 kg/tonne of lead styphnate

Source: EC (2007)

Information from Consultation

Information on releases presented in non-confidential form in questionnaire responses of individual companies is shown below. A significant proportion of responses has been requested to be treated as confidential thus are only available in the Confidential Annex (Section A4.1). The Annex also provides details of emissions presented in REACH Registration dossiers that have been submitted by certain companies.

Table 3.5: Releases during Manufacture from Individual EU-based Companies

Manufacturer	**Details of releases**

Company 2	Releases from combined manufacture of lead sulphate waste from both the manufacture and the on-site use of lead styphnate in the fabrication of detonators. Waste arisings: 0.05 kg of lead sulphate per kg of lead styphnate manufactured and used each year
Company 3	No releases to any compartment (estimate)
Source: Consultation	

The key conclusion is that emissions of lead styphnate itself should largely not be expected. Lead styphnate emitted to wastewater in particular is treated to transform into another lead salt (typically lead sulphate) which is removed from wastewater for disposal.

3.5.2Worker Exposure

The majority of information submitted by companies is claimed to be confidential, hence it is available in the Confidential Annex (Section A5.1). It is important to note that handling lead styphnate is very hazardous and there is always a risk from explosion due to impact, friction or static electricity.

Only one company, **Company 2** has provided information that is not claimed to be confidential; this is shown in **Table 3.6**. The table also includes relevant information from the collective questionnaire response of the Federation of European Explosives Manufacturers (2011b). The response of the Federation combines the exposure from the manufacture of lead styphnate and that from the use of the substance in the fabrication of detonators. The Federation indicates that the manufacturing process is very strictly controlled and only a very small number of EU workers interact with the substance.

Table 3.6: Worker Exposure to Lead during Manufacture of Lead Styphnate – Consultation

Worker exposure parameter	**Federation of European Explosives Manufacturers**	**Company 2**
Type of product handled	Precipitation with a solution of lead nitrate from a solution of magnesium trinitroresorcinate in a reaction vessel	Substance of purity ca. 93%
Relevant process step where exposure occurs Mode of use	No exposure during manufacture – closed reactors Automated filling of primer caps Service, repair and cleaning	Synthesis Product transfer
Route of occupational exposure	Not applicable	Skin, inhalation
Exposure level (mg/m^3)	0.001 mg/m^3	<0.05 mg lead/m^3
Ventilation conditions	Not applicable – automated process	Ventilation present
Other exposure control measures	Not applicable – automated process. For service, repair & cleaning purposes PPE is part of the job risk analysis and process description. Gloves, respirators, glasses with close to 100% effectiveness are being used	Disposable latex gloves and visors (type: 3M-680). No respirator used

Table 3.6: Worker Exposure to Lead during Manufacture of Lead Styphnate – Consultation

Worker exposure parameter	**Federation of European Explosives Manufacturers**	**Company 2**
Frequency of exposure (days per year)	Approx. 300 days per year per manufacturer	10
Duration of exposure per day (minutes per day)	Few minutes to several hours for service & maintenance	300
Number of employees exposed	Approx. 50 workers in the whole of Europe	4

Source: Consultation; Federation of European Explosives Manufacturers (2011b)

Accidents during the handling of lead styphnate do happen. In 2005, a woman handling lead styphnate in a UK explosives manufacturing plant lost her life through an explosion. The woman was working alone and the exact causes of the explosion could not be established (UK HSE, 2010). Press reports suggested that the explosion may have been the result of static electricity developing during a sieving process (Chorley Guardian, 2010). It is understood that the plant no longer produces lead-based primary explosives.

3.5.3Model-based Estimates of Occupational Exposure

Overview

TNO has undertaken estimates of exposure of workers to lead styphnate during its manufacture based on information in the report and expert judgment. The approach followed takes into account relevant research on occupational exposure including work under taken by Bouwer et al, 2001; Marquart et al, 2008; Schinkel et al, 2010; Tielemans et al, 2008; Tielemans et al, 2008; Warren et al, 2006.

Due to its explosive and sensitive nature, lead styphnate has essentially three life cycle steps: (a) manufacturing of the substance, (b) manufacturing of articles containing the substance and (c) use of the articles.

Lead styphnate is manufactured and used during manufacturing of articles under very strict conditions. Even though the exact situation may vary from site to site and less proper examples may be found, the following description of the manufacturing process is considered as reasonable and common in Europe:

- the material solutions are brought to the reactor by means of pipes and valves;
- the reaction takes place in a closed reactor;
- the separation of lead styphnate from the mother lye by sieving is commonly in an insulated room without operator or in a closed reactor system;
- lead styphnate is then (frequently automated or semi-automated) transferred on to antistatic trays each containing less than 5 kg of finished products and the closed trays are manually transported to well ventilated closets where the crystals dry in the trays;
- after drying, the product is sieved and/or weighed and transferred for further processing;
- based on the information provided by manufacturers, these steps (filtering, washing, drying, weighing, mixing, sieving, compression) are commonly all realised automatically in closed rooms by remote control;

- closed vessels containing dry material are handled (one by one) only during short transfer (few meters);
- even though the manufacturers indicated that the worker commonly does not have contact with the product, we cannot exclude that "*transfer of the dry material into or from the closed vessels/drying trays*" is not operated by remote control but manually; and
- alternatively, lead styphnate is not fully dried; the wetted (~ 20% water) material is then transferred for further processing (frequently automated or semi-automated).

Scope of Exposure Estimates

For the process steps in closed systems or for remotely controlled activities in closed rooms no calculations are made, as exposure is expected to be negligible.

Exposure estimates with exposure models are made for the activities with potential for exposure:

- transfer of wetted material for further processing either during or after the manufacturing process, incl. transfer to the drying trays. Both an "automated transfer" (not remote controlled) and "manual transfer" have been assessed up to kilogram amounts;
- manual transfer of dry material into or from the closed vessels/drying trays;
- sampling; and
- cleaning (final cleaning of equipment and cleaning of the workplace).

Inhalation Exposure Estimates

Inhalation exposure was estimated using the Stoffenmanager 4.0 model10. The input parameters and resulting exposure estimates are presented in Table 3.7.

Considerations regarding some parameters include:

- manual transfers of kilograms of wet materials are considered to be performed in an enclosure with exhaust ventilation. A manual transfer of dry material only happens at smaller scale (maximum 200-300g) but with (dust collection) exhaust ventilation;
- automated or semi-automated transfer of the wetted material results in an activity where release is highly unlikely;
- sampling is due the scale of the process assumed to be at gram scale with at least local exhaust ventilation or in an enclosure;
- due to the in general closed systems and remotely controlled activities, cleaning involves removing at the most milligrams of lead styphnate from the equipment or workplace;
- the use of wet chemistry prevents inadvertent detonation and reduces risk of exposure. The use of wet chemistry also ensures dust emission is not possible, for Stoffenmanager the product characteristic thus are best described as: "*firm polymer granules, granules covered with a layer of wax, bound fibres, such as in cotton. No dust emission possible*". The exception is during cleaning. During cleaning very small amounts of coarse dust are being removed, emission is reduced by wetting the deposits (e.g. wet wiping);
- the dry products are best described as: granules/grains/flakes;
- the work area is cleaned daily (due to the danger caused by dried product residues) and the equipment is regularly inspected and well maintained;

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[10] Available here: https://www.stoffenmanager.nl/default.aspx.

- the distance of the source from the worker is conservatively chosen as within 1 metre for the manual transfer of the wetted material, during sampling and during cleaning, except when the transfer is at least semi-automated. When the transfer is at least semi-automated, the distance of the source from the worker is chosen as more than 1 metre;
- conservatively it has also been assumed that more than one person is handling the substance in the same room;
- room temperature is chosen as the default temperature range for transfer;
- manufacture and storage buildings are commonly scattered as a safety measure. Even though transfer therefore often occurs outside, the worst-case situation would be indoors in a large hall. Therefore, only indoors has been used for the estimations;
- indoor use in rooms with a size of 100-1000 m^3 is chosen as typical for these kinds of industrial situations;
- due to danger of dust deposits general ventilation (mechanical or natural by open door(s) or window(s)) is assumed to be common for the activities assessed;
- manufactures indicated manufacturing lead styphnate can be a full-time (8h/day) task. However, most of the processes steps are in closed systems or remotely controlled. The activities assessed therefore are not expected to take more than 2 hours. Manual transfer of the dry material has been specifically indicated by a company not to exceed 1 hour of exposure. Other companies indicate transfer of the dry material is only once a day and 200-300g, which is also unlikely to take longer than 1 hour. Furthermore, 1 hour for the cleaning activities and 1 hour for the sampling activities is considered reasonable worst case, because it is considered highly unlikely that these activities would take more than this duration. Sampling in general should be a short-term activity. Cleaning in some places might take more than 2 hours, but not if it is done on a daily basis;
- exposure levels are estimated with and without the use of respiratory protective equipment (RPE) with a reduction effect of 60%, which is the effect conservatively assumed in the Stoffenmanager model. The assumed effect of RPE is used as an indication of typical reduction with a Filter mask P2 (FFP2). With more advanced RPE, such as equipment with an independent air supply, higher reduction effects can be achieved; and
- the 90 percentile of the output distribution estimated with Stoffenmanager 4.0 is used as the reasonable worst case estimate.

The results of the calculations made with the Stoffenmanager model are shown in **Table 3.7**. The bottom of the table shows the results expressed in mg of lead per cubic metre (lead accounts for 46% of the molecular weight of lead styphnate).

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Table 3.7: Input and Results – Inhalation Exposure Estimates during the Manufacture of Lead Styphnate

Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-maximum several hundred grams**	**Sampling**	**Cleaning**
Product and substance data					
Physical state of the substance	Solid-wetted	Solid-wetted	Solid-dry	Solid-wetted	Solid-wetted
Concentration	Up to 100%	Up to 100%	Up to 100%	Up to 100%	Up to 100%
Dustiness (category)	Solid granules/grains/flakes	Solid granules/grains/flakes	Granules/grains/flakes	Solid granules/grains/flakes	Coarse dust
Handling data					
Handling category	Handling of product with low speed or with little force or in medium quantities	Handling of product in very small amounts or in situations where release is highly unlikely	Handling of product in small amounts or in situations where only low quantities of product can be released	Handling of product in very small amounts or in situations where release is highly unlikely	Handling of products in negligible amounts
Duration of task or process (hour)	2	2	1	1	1
Exposure control data					
Local controls used to limit emission from the source	Containment of the source with local exhaust ventilation	No control measures at the source	Local exhaust ventilation or containment of the source.	Local exhaust ventilation or containment of the source.	Use of a product that reduces the emission: wetting of product
Source in the near field:	Yes	No	Yes	Yes	Yes
Other sources of Lead Styphnate in the same room:	Yes	Yes	Yes	Yes	Yes
Room volume:	Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3
General ventilation:	General ventilation (mechanical or natural)	General ventilation (mechanical or natural)	General ventilation (mechanical or natural)	General ventilation (mechanical or natural)	General ventilation (mechanical or natural)

Table 3.7: Input and Results – Inhalation Exposure Estimates during the Manufacture of Lead Styphnate

Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-maximum several hundred grams**	**Sampling**	**Cleaning**
Immission controls:	The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin
Work area regularly cleaned:	Yes	Yes	Yes	Yes	Yes
Equipment regularly inspected and well maintained:	Yes	Yes	Yes	Yes	Yes

Table 3.7: Input and Results – Inhalation Exposure Estimates during the Manufacture of Lead Styphnate

Task or process assessed		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-maximum several hundred grams**	**Sampling**	**Cleaning**
Resulting exposure level estimates						
Worst case (90%) estimation of exposure level (mg/m^3) per task	Without PPE	0.21	0.17	0.94	0.21	0.44
	With PPE	0.08	0.07	0.38	0.08	0.18
Worst case (90%) estimation of exposure level (mg/m^3)-8 hours’ time average	Without PPE	0.05	0.04	0.12	0.03	0.06
	With PPE	0.02	0.02	0.05	0.01	0.02
Worst case (90%) estimation of exposure level (**mg Pb/m³**) per task	Without PPE	**0.10**	**0.08**	**0.43**	**0.10**	**0.20**
	With PPE	**0.04**	**0.03**	**0.17**	**0.04**	**0.08**
Worst case (90%) estimation of exposure level (**mg Pb/m³**)-8 hours’ time average	Without PPE	**0.02**	**0.02**	**0.06**	**0.01**	**0.03**
	With PPE	**0.01**	**0.01**	**0.02**	**4.60E-03**	**0.01**

Source: TNO calculations

We have examined the occupational exposure limits (OELs) for inorganic and organic lead compounds that apply in the EU and individual Member States (as well as selected non-EU countries such as the USA, Australia and New Zealand). For lead and inorganic lead compounds, the OELs range between 0.05 and 0.15 mg/m^3 (the EU binding OEL under Annex I of Directive 98/24/EC is 0.15 mg/m^3). For organic lead compounds such as tetraethyl lead and tetramethyl lead, OELs identified generally range between 0.05-0.10 mg/m^3 for the former and 0.05-0.15 mg/m^3 for the latter. Only in Romania[11], a lower OEL appears to apply for tetraethyl lead at 0.01 mg/m^3 and in Lithuania[12] an OEL of 0.005 mg/m^3 applies for lead salicylate.

Given that lead styphnate is an organic compound of lead, we compare the above inhalation exposure estimates to the OELs that apply to organic lead compounds and more specifically to tetraethyl and tetramethyl lead for which the presence of OELs in national legislation is very common. In the absence of a specific OEL for lead styphnate, we will compare the exposure estimates to the lowest OELs for tetraethyl and tetramethyl lead, i.e. 0.05 mg/m^3.

We also understand that in the case of lead there is an onus/expectation on employers to ensure exposure is below the relevant OEL before any consideration of the effect of PPE (which is expected to be enforced in addition to this limit). Therefore, our comparison looks into the exposure estimates both with and without the use of PPE.

Overall, only the estimated exposure for the Scenario "*Transfer of dry material-manual – maximum several hundred grams*" would appear to result in the selected OEL value of 0.05 mg/m^3 marginally being exceeded when no PPE is used; the estimated 8-hour time weighted average exposure level is ca. 0.055 mg/m^3 (rounded to 0.06 in the table). When the effect of PPE is considered, exposure levels for all scenarios considered are below the OEL of 0.05 mg/m^3. Therefore, based on the assumptions and calculations made, the worker health risks via inhalation are low. The measures taken by manufacturers of lead styphnate (including PPE) are also noted.

Dermal Exposure Estimates

Dermal exposure has been estimated with RISKOFDERM version 2.1[13].

For dermal exposure during cleaning no proper exposure model exists. Exposure depends a lot on the amount of lead styphnate on the surfaces cleaned. Due to the general closed systems and remotely controlled activities, and the high frequency of cleaning (on daily basis), exposure during cleaning is expected to be low. Exposure is further reduced by applying suitable risk management measures for example:

- wet cleaning methods to prevent dispersion; and
- chemical-resistant (and antistatic) gloves, apron and conductive shoes

The input parameters and resulting exposure estimates for the other activities with exposure potential are presented in **Table 3.8**.

Considerations regarding some parameters include:

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[11] OELs available at: http://substantepericuloase.protectiamuncii.ro/pdfs/anexa_31.pdf.

[12] OELS available at: http://www3.lrs.lt/pls/inter3/dokpaieska.showdoc_l?p_id=306641.

[13] Available here: http://www.tno.nl/downloads/RISKOFDERM potential dermal exposure model vs 2.1t.xls.

- when the substance is generally pure but wetted with water to prevent preliminary decomposition, this results in a not highly dusty type of product (input in RISKOFDERM: Light or moderately dusty solid);
- when the substance is dry, the material is described as more granular then powdery; input in RISKOFDERM: Light or moderately dusty solid;
- due to the danger of dust deposits ventilation is assumed to be normal to good;
- because of the nature of the product contact with the product is expected to be rare (less than once per scenario) and only light;
- manufacturers have indicated that manufacture of lead styphnate can be a full-time (8h/day) task. However most of the processes steps are in closed systems or remotely controlled. The activities assessed therefore are not expected to take more than 2 hours. Manual transfer of the dry material has been specifically indicated by a company not to exceed 1 hour of exposure. Other companies indicate transfer of the dry material is only once a day and 200-300g, which is also unlikely to take longer than 1 hour. Furthermore1 hour for the cleaning activities and 1 hour for the sampling activities is considered reasonable worst case, because it is considered highly unlikely that these activities would take more than this duration. Sampling in general should be a short-term activity. Cleaning in some places might take more than 2 hours, but not if it is done on a daily basis;
- a default body weight of 70 kg has been used to calculate exposure in a unit, which makes it suitable for comparison with a DNEL. We assume dermal absorption of 100%;
- manual transfer of the wetted material is assumed to be applicable for the smaller batches which were indicated to be 15 kg. During the manual transfer activities approximately 4 times 15 kg (60kg) is being transferred during 2 hours. This results in an application rate of product 0.5 kg/min;
- during the automated or semi-automated transfer of the wetted material, approximately 4 times 40 kg is being transferred during 2 hours. This results in an application rate of product 1.3 kg/min;
- manual transfer of the dry material is only performed when transferring no more than several hundreds of grams. These small batches were indicated to be approximately 300g (during 1 hour). This results in an application rate of product 0.005 kg/min;
- sampling has been estimated as maximum 12 grams (or 6 times 2 gram) during an hour. This results in an application rate of product 0.0002 kg/min; and
- exposure levels are estimated with and without the use of gloves with a reduction effect of 90%. The assumed effect of gloves is used as an indication of typical reduction effects of chemical protective gloves. Very good gloves with proper training of workers in how to use the PPE and intensive management supervision may have a higher effectiveness.

The results of the calculations made with the RISKOFDERM model are shown in **Table 3.8**.

Table 3.8: Input and Results – Dermal Exposure Estimates during the Manufacture of Lead Styphnate

Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material – manual - several hundred grams**	**Sampling**
Product and substance data				

Table 3.8: Input and Results – Dermal Exposure Estimates during the Manufacture of Lead Styphnate

Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material – manual - several hundred grams**	**Sampling**
Type of product	Light or moderately dusty solid	Light or moderately dusty solid	Light or moderately dusty solid	Light or moderately dusty solid
Concentration	Up to 100%	Up to 100%	Up to 100%	Up to 100%
Handling data				
Handling category	Filling, mixing or loading	Filling, mixing or loading	Filling, mixing or loading	Filling, mixing or loading
Duration of task or process (hour)	2	2	1	1
Exposure control data				
Quality of the ventilation:	Normal or good	Normal or good	Normal or good	Normal or good
Frequency of skin contact:	Rare contact	Rare contact	Rare contact	Rare contact
Kind of skin contact:	Light contact	Light contact	Light contact	Light contact
Significant amount of aerosols:	No	No	No	No
Level of automation	Manual	Automated or semi-automated	Manual	Manual task
Application rate of product (kg/min)	0.5	1.3	5.00E-03	2.00E-04

Table 3.8: Input and Results – Dermal Exposure Estimates during the Manufacture of Lead Styphnate

Task or process assessed		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material – manual - several hundred grams**	**Sampling**
Resulting exposure level estimate					
Worst case (90%) estimation of exposure level hand loading (mg/shift)	Without PPE	18.80	31.50	0.13	7.00E-03
	With PPE	1.88	3.15	0.01	7.00E-04
Worst case (90%) estimation of exposure level hand loading (mg/kg bw/day)-full shift	Without PPE	0.27	0.45	1.86E-03	1.00E-04
	With PPE	0.03	0.05	1.86E-04	1.00E-05
Worst case (90%) estimation of exposure level hand loading (**mg Pb/shift**)	Without PPE	**8.7**	**14.5**	**5.98E-02**	**3.22E-03**
	With PPE	**0.87**	**1.45**	**5.98E-03**	**3.22E-04**
Worst case (90%) estimation of exposure level hand loading (**mg Pb/kg bw/day**)-full shift	Without PPE	**0.12**	**0.21**	**8.56E-04**	**4.60E-05**
	With PPE	**0.01**	**0.02**	**8.56E-05**	**4.60E-06**

Source: TNO calculations

In assessing the intake of lead through the skin based on the above estimates, we have looked into past research on the topic. This appears to have focused on the intake of metallic lead and inorganic lead compounds. For instance, the SCOEL recommendation for lead and its inorganic compounds references work by Florence *et al* (1988) suggesting that dermal absorption is minimal. The US Occupational Health and Safety Administration also suggest that lead is not absorbed through the skin (US OSHA, 1991).

According to the Voluntary Risk Assessment Report for Lead, dermal intake of lead would appear to be extremely limited, i.e. less than 0.01%. Rates of 0.1% have been identified in the literature but the analysis presented in the Voluntary Risk Assessment Report would suggest that the assumption of any dermal absorption rate above 0.01% is absolutely unfeasible (ILZRO & EBRC, 2008).

Therefore, if it were to be assumed that lead styphnate would behave as an inorganic form, the maximum daily systemic intake via the skin for any of the scenarios considered would be those shown in **Table 3.9**. Alternatively, if it were assumed that the lead compound behaves like an organic form of lead, then the absorption via the skin would be much higher. INCHEM (1994) suggests that dermal absorption is an efficient process: organic compounds of lead are capable of penetrating the intact skin rapidly. Thus, a precautionary approach might be to assume a 100% intake, which would suggest the maximum daily absorptions shown in **Table 3.9**.

Table 3.9: Estimates of Lead Dermal Intake during the Manufacture of Lead Styphnate

Dermal intake estimates		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual- several hundred grams**	**Sampling**
Dermal absorption rate: 0.01%					
Worst case (90%) estimation of exposure level hand loading (**mg Pb/shift**)	Without PPE	8.65E-04	1.45E-03	5.98E-06	3.22E-07
	With PPE	8.65E-05	1.45E-04	4.60E-07	3.22E-08
Dermal absorption rate: 100%					
Worst case (90%) estimation of exposure level hand loading (**mg Pb/shift**)	Without PPE	8.7	14.5	5.98E-02	3.22E-03
	With PPE	0.87	1.45	4.60E-03	3.22E-04

Source: TNO & RPA calculations

To obtain a view as to whether the intake estimates in the table are excessive or not, we could compare them to the burden of lead inhaled at a concentration of exposure equivalent to the assumed inhalation OEL, i.e. 0.05 mg/m^3. Assuming a full absorption of lead through inhalation (as per the Voluntary Risk Assessment Report) and an inhaled volume in a work day with light activity of 10 m^3, the OEL of 0.05 mg/m^3 results in a lead intake of 0.05 x 10 x 100% = 0.5 mg per day.

A review of the estimates in **Table 3.9** suggests that should lead styphnate be assumed to behave as an inorganic lead compound and a skin absorption rate of 0.01% (max.) is assumed, there would be no obvious reason for concern for workers, even in the absence of PPE.

On the other hand, when the more conservative approach is taken assuming that the substance behaves as a typical organic lead compound and its rate of absorption through the skin is 100%, then intake estimates for two scenarios "*Transfer of wetted material-manual*" and "*Transfer of wetted material-automated*" would appear to exceed the 'baseline' figure of 0.5 mg/day even when PPE is used. For "*Transfer of dry material-manual- several hundred grams*" marginal exceedance of the 'benchmark' value is noted in the absence of PPE. It is acknowledged that this comparison to inhalation intake is for illustrative purposes only and the estimates are based on a series of conservative assumptions on the processes used and on the behaviour of the substance. It is indeed assumed that the engineering and PPE measures taken by companies drastically reduce dermal exposure of workers (which in any case needs to be avoided for fear of electrostatic discharge accidentally igniting the substance).

A general note on the above estimates may also be of use at this point. The tables above suggest that automated transfers lead to higher estimates of dermal exposure, compared to manual transfers. The effect of the difference in use rate outweighs the influence of automation in this case.

TNO has suggested that this may partly be due to the model and the data underneath the model. The RISKOFDERM model is built by direct statistical analyses between determinants in measured situations and the measured exposure levels in these situations. Therefore, the model only works correctly if the meaning of e.g. ‘automated or semi-automated’ in the model and of ‘automated’ in the situation under assessment is sufficiently similar. Unfortunately, that can hardly ever be properly evaluated.

It is relevant to understand what kind of situations are under ‘manual’ and ‘automated or semi-automated’ in the definition of the RISKOFDERM model. Manual is e.g. dumping powders from a bag while holding the bag, scooping with a hand-held tool, pouring liquids from a tap in a bucket. Automated or semi-automated is e.g. a filling line for powders where the filling is automated, but the worker has to manually tug in the top of the bag, or filling of cans of paint on a filling line where a worker has to ensure that the containers are placed correctly on the filling line and may have to put lids on the containers or move the filled containers from a holding station onto a tray. The situations with automated or semi-automated transfer in this case therefore still involve some manual handling of potentially contaminated packages. The exposure is lower for (semi-)automated than for manual, if all other parameters the same. However, the effect of a large difference in use rate is bigger. In this case, the use rate for automated is much bigger than for manual. Therefore, this outweighs the difference between manual and automated.

It is well possible that the situation for automated transfer of the lead substances are very different from the data underlying the model and that the model is therefore not applicable. However, since both the boundaries of validity of the model are not clear-cut and the exact situation described by ‘automated’ for the lead substances is currently unknown, it is conservatively assumed that the ‘automated’ situations fall within the scope of the model.

4 INFORMATION ON USES

4.1 Overview of Uses

4.1.1Lead Styphnate as a Primary Explosive

Lead styphnate is a primary explosive (a subcategory of high explosives). A high explosive is defined as an explosive substance or mixture which invariably detonates when initiated, irrespective of the ambient condition of confinement (i.e. in the open) (Trace, 2011). High explosives can be divided into two sub-categories: primary high explosives and secondary high explosives (the latter include boosters, such as pentaerythritol tetranitrate (PETN) and research department explosive (RDX), and main charges such as dynamite, binary explosives, water gels, emulsions, trinitrotoluene (TNT) and ammonium nitrate/fuel oil (ANFO) (Trace, 2011), as shown in **Figure 4.1**.

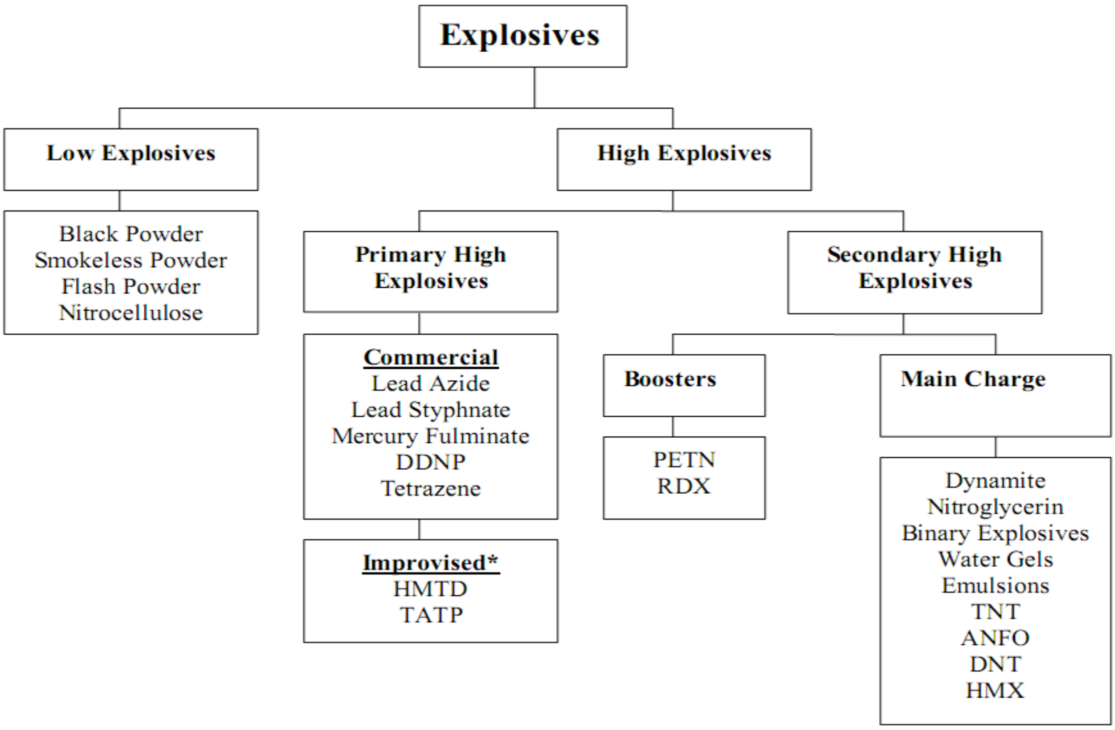

Figure 4.1: Classification of Explosives

Source: US DHS (2008)

Primary explosive is a sensitive explosive which nearly always detonates by single ignition from such means as spark, flame, impact and other primary heat sources of appropriate magnitude.An initiating explosive must be highly brisant and must have a high triggering velocity. Primary explosives have a low deflagration-to-detonation transition (also known as DDT), thus go from burning to detonation very quickly (Trace, 2011).

4.1.2Range of Uses for Lead Styphnate

Lead styphnate is used in a variety of applications and apparently finds considerably wider use compared to lead azide. In summary, uses identified in literature include:

- as an initiator in primers for percussion caps for small calibre and rifle ammunition, typically in the form of the Sinoxyd (also known as Sinoxid) mixture;
- as an initiator in blasting caps/detonators, for example in the ASA (lead azide, lead styphnate and aluminium) mixtures;
- in pyrotechnic devices used in military munitions (e.g. fuzes used in medium calibre munitions and grenades);
- as an initiator in air-bag inflators and seat belt pre-tensioners, pyrotechnic igniters and bullet hit squib igniters for theatrical/film productions;
- as a primer in cartridge actuated devices both for aerospace/defence/safety applications but also for cartridges used in fastening power tools;
- in primers for cattle killer cartridges; and

- as igniting power to detonate propellants used at the micro/nano scale in microelectromechanical systems (MEMS) used for defence and aerospace applications (including satellites).

The above applications are discussed further below.

4.2 Use in Firearm Ammunition Primers

4.2.1Description of Use

A cartridge is made up of four basic parts: the bullet, the case, the propellant powder and the primer that ignites the powder. Pulling the trigger releases the firing pin from the bolt and this flies forward and strikes the primer. The compound in the primer explodes violently and projects a very hot flame through the flash hole into the case igniting the propellant (powder). The ignition of the powder generates pressure which propels the bullet forward and out of the barrel (Rifles in the UK, undated).

Lead styphnate is found in the primer mixture (often called 'primers'). Small arms primers consist of an explosive, an oxidiser, a fuel, and a frictionator. Other compounds act as sensitisers and binders (Smyth Wallace, 2008):

- explosives used include azides, fulminates, diazo compounds, nitro or nitroso compounds, for example, lead styphnate, lead or silver azide, TNT, and PETN (which also act as sensitisers);
- oxidisers used include barium nitrate, potassium chlorate, lead dioxide and lead nitrate;
- fuels used include antimony sulphide (which also acts as a frictionator), arabic gum (which also acts as a binding agent), calcium silicide (which also acts as a frictionator), nitrocellulose, carbon black, lead thiocyanate and powdered metals such as aluminium, magnesium, zirconium, or their alloys;
- frictionators used include ground glass and aluminium powder (which also acts as a fuel);
- sensitisers used include tetrazene, TNT, and PETN; and
- binders used include arabic gum, gum tragacanth, glue, dextrin, sodium alginate, rubber cement, and karaya gum.

The first practical non-mercuric, non-corrosive primer mixture with satisfactory ignition properties and good shelf life was produced in 1928. This type of primer was given the general name of "Sinoxyd" (Sinoxid) and has the following general composition (Smyth Wallace, 2008)[14]:

- lead styphnate: 25% to 55%;
- barium nitrate: 24% to 25%;
- antimony sulphide: 0% to 10%;
- lead dioxide: 5% to 10%;
- tetrazene: 0.5% to 5%;
- calcium silicide: 3% to 15%; and
- glass powder: 0% to 5%.

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[14] Lead styphnate has also been used in other forms. In 1944, a patented rimfire priming mix included a triple salt, basic lead styphnate–lead styphnate–lead hypophosphite at 50% content, while in the 1960s, primers with mixtures of lead nitroaminotetrazole-lead styphnate, which became known as stabanate, were also patented and had much better thermal stability than lead styphnate (Smyth Wallace, 2008).

This was the forerunner of all modern non-mercuric, non-corrosive priming compositions (Smyth Wallace, 2008). It is believed to have been developed with normal lead styphnate.

In centrefire ammunition, the primer caps are the only part containing lead styphnate. In rimfire ammunition, there is no primer cap and the primer charge is “spun into” the rim of the case[15].

Examples of some modern priming mixtures are shown in Table 4.1. Compositions A to D are found in the UK and are referred to by Smyth Wallace (2008) while compositions E to I were relevant in the mid-1990s and have been presented by Warlow (1996).

Table 4.1: Modern Compositions of Lead Styphnate Primers

Component	**Composition (%)**								
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
Lead styphnate	35	46	44.2	38	36	41	39	43	37
Tetrazene	3	4	3.3	2	3	3	4	3	3
Lead peroxide	15	25		5				6	6
Barium nitrate	47		20.4	39	29	39	40	36	38
Antimony sulphide		20		5	9	9	11		11
Aluminium		5							
Ground glass			25.0						
Lead hypophosphite			6.8						
Arabic gum			0.3						
Calcium silicide				11		8		12	
Lead dioxide					9				
Zirconium					9				
PETN					5				5
Nitrocellulose							6		

Source: Smyth Wallace (2008); Warlow (1996)

Also, note the discussion in Section 3.1.2 on the formation of lead styphnate within the cartridge under the Eleyprime method.

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[15] A centrefire cartridge is a cartridge with a primer located in the centre of the cartridge case head. Unlike rimfire cartridges (where instead of the firing pin striking the primer cap at the centre of the base of the cartridge to ignite it, the pin strikes the base’s rim), the primer is a separate and replaceable component. The centrefire cartridge has replaced the rimfire in all but the smallest cartridge sizes. Except for low-powered .22 and .17 calibre cartridges, and a handful of antiques, all modern pistol, rifle and shotgun ammunition are centrefire (UK Deer Management, 2011).

Some addition information of a confidential nature on the use of lead styphnate in firearm ammunition is provided in the Confidential Annex (Section A3.1). Submissions from producers would suggest that concentrations vary but figures up to over 50% in the primer mixture are possible.

4.2.2 Locations and Quantities Used

Locations

The majority of companies known to manufacture lead styphnate use the substance in-house in the preparation of primers for ammunition. Locations where fabrication takes place appear to include the Czech Republic, France, Germany, Italy, Spain and the United Kingdom. The number of identified companies is fewer than ten.

There are also EU-based companies which purchase primer caps that already contain the substance and use these in manufacturing of the final ammunition cartridges.

In this context, the term ammunition includes both ammunition for hunting/sport shooting but also small calibre ammunition to be used by military and security forces.

Quantity

The amount of lead styphnate used in firearm ammunition primers is in the 10-100 t/y range and account for ca. 90% of the amount of lead styphnate manufactured in the EU. Between hunting/sports ammunition and military/security forces ammunition, the former has a considerably higher share. More detail is provided in the Confidential Annex (Section A3.1).

It may be useful to consider at this point a comparison to what is widely referred to as lead ammunition, essentially lead shot ammunition. Lead shot ammunition appears to represent 3% of global lead consumption[16] and in 2010, the global usage of lead was 9,575,000 tonnes, as shown by the ILZSG[17]. This would make the global consumption of lead in lead shot ammunition 287,250 tonnes in 2010. The Voluntary Risk Assessment for lead compounds that was undertaken by industry in the late 2000s (and which did not encompass lead styphnate or lead azide uses) indicates that the consumption of lead for shot ammunition in the EU in 2002 was 56,600 tonnes. It is clear that lead styphnate can only represent a very small percentage of total lead in ammunition.

Concentration in Articles

As shown above, the concentration of lead styphnate in primer mixtures could be between 20% and ca. 55%. When this is added into a primer cap (such as those made of brass), the concentration of lead styphnate is evidently lower, in the region of 2-10%. On the other hand, in shotgun cartridges (where primer caps are not present), the concentration is below 1%.

In the final article, concentrations of lead styphnate vary. In hunting ammunition, concentration is typically below 0.1% but in sports rimfire ammunition it may exceed 0.5%. It is important to note that primer caps are often sold as ready-made articles by one company to another for the final

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[16] See graph available here: http://www.ilzsg.org/static/enduses.aspx?from=2.

[17] See statistics available here: http://www.ilzsg.org/static/statistics.aspx?from=1.

article (ammunition shell to be assembled). The confidential information presented in the Confidential Annex (Section A3.1) gives additional quantified detail.

4.2.3 Recent and Future Trends

The market for primer caps for hunting and sporting ammunition was in decline in the 2000s, and new products without lead (e.g. DDNP) have been investigated (EC, 2007). As the ammunition is generally produced on the same sites where manufacture of the substance takes place, the trends discussed in Section 3.4 (and in the Confidential Annex) will largely apply to this application.

4.2.4 Structure of Supply Chain

Generally, lead styphnate-based ammunition is produced by those companies that manufacture the substance itself. The final customers do not buy the substance directly, but articles containing it. These articles could be the final complete article (ammunition shell) or components used further down the supply chain (e.g. primer caps, partially filled hulls) in the production of the final article (small calibre ammunition, rimfire shotshells).

4.3 Use in Detonators and Pyrotechnics for Military Munitions

4.3.1 Description of Use

Civilian Detonators

A detonator(also known as a blasting cap in the USA) is a small thin-walled cylindrical case containing a sensitive explosive and serves as an initiator of explosive charges. A cylindrical capsule (typically copper or aluminium) contains a primary charge of an initiating explosive or a mixture of initiating explosives (e.g. lead azide with lead styphnate); in order to achieve a higher brisance, they also contain a secondary charge of a high brisance explosive (e.g. Tetryl; PETN; Cyclonite). A detonator can be ignited by the flame of a safety fuse, electrically, or not electrically (as in the case of shock tube). In the past, ten standard types of detonators were marketed; these differed from each other by the quantity of the explosive in the charge and by their size. Currently, No. 8 detonator (0.3 g primary charge. 0.8 g secondary charge, 4-50mm in length and 7.0 mm in external diameter) is, for all practical purposes, the main type of detonator on the market (Mayer et al, 2007).

With regard to the presence of lead styphnate in ignition charge (priming mixture), consultation suggests that lead azide is relatively insensitive to ignition by flame, say from a safety fuse. To overcome this, the effects of incorporating various ignition agents with lead azide were examined. Of the numerous materials examined, the only material which, when mixed with lead azide, satisfied all the requirements as to good running and loading, fast binding (when subjected to pressure) and certain firing was lead styphnate. It has become standard practice to use lead styphnate in conjunction with lead azide in detonators. Lead styphnate serves as a heat insulator and also helps to consolidate the priming charge in the detonator. Lead styphnate also has a low hygroscopicity, a very favourable characteristic for use in detonators.

Many detonators' priming mixture is a material called ASA compound. This compound is formed from lead azide, lead styphnate and aluminium and is pressed into place above the base charge, usually TNT or PETN (Explosives.org.au, 2009; Mayer et al, 2007). Aluminium is added to enhance the likelihood of lead azide burning to detonation (Zukas et al, 2002).

Detonators (blasting caps) containing lead styphnate are commercially employed in a range of applications for which secondary explosives are utilised (e.g. mining, construction, tunnelling and oilfield use). It is of note that this application is the most important one for lead azide but is not as important for lead styphnate.

A company has advised that lead styphnate detonators may be used in the aerospace sectors for blade-off tests. Blade-off tests are used to prove that an engine will contain a blade in the event of catastrophic failure. These are essential to product safety and integrity and required by the aerospace regulators US Federal Aviation Administration (FAA) and European Aviation Safety Agency (EASA). This use is considered essential and the company believes it should be exempt from Authorisation based on either Article 58(2) as a conflicting regulation mandating the use of this test or as a substance subject to product and process oriented research and development (PPORD) as it is an engine test method.

Military Detonators

Lead styphnate detonators such as those used in civilian applications may also be used in a military environment. An example of a military detonator containing lead styphnate is shown by Mondial Defence Systems (2011) on their website. This is an electric detonator comprising an aluminium tube with an output charge of PETN initiated with a primary charge of ASA compound. This product is supplied to the UK Armed Forces.

Military Fuzes or Initiators

A type of “detonator”, which is much less common in the civilian world, is known as “fuzes” or initiators. These are devices, usually mechanical in nature, but they can be electronic as well. They utilise the same explosive trains found in blasting caps, however, they are used in artillery shells, mortar bombs, aerial bombs, some types of rockets and tank shells. Fuzes initiate the munition at specific times and without the aid of setting an initial countdown such as the flip of a switch, or ignition of a black powder fuse by the operator. Another example is a grenade fuze which detonates the grenade only after the pin has been removed and the grenade thrown by the operator. Artillery fuzes detonate the shell upon impact using a series of mechanical adjustments which trigger a detonator housed within (Ledgard, 2007). Lead styphnate is mainly used to give a flame to initiate for example pyrotechnic composition or propellant or a propelling charge in a munition.

The US army use a range of lead styphnate-containing detonators, including the M7 non-electric blasting cap which can be used to detonate all military explosives (US Army, 2008). Hand grenades may also contain primers that contain lead styphnate. A 1994 guidance document suggests that the substance was contained in several types of grenades of the US Army, typically in combination with lead azide and PETN or RDX (US Army, 1994b; US Navy, 2000).

Information from Consultation

The Federation of European Explosives Manufacturers (2011) advises that lead styphnate is contained in 52 million civilian detonators of the electric type[18] produced in the EU. A small

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[18] The information on commercial products presented in **Table 4.4** appears to confirm the assertion that lead styphnate is generally used in electric detonators. However, Safety Data Sheets for non-electric and electronic detonators may also show the presence of lead styphnate (see References 8 and 14 in **Table 4.4**). However, these may not be relevant to the EU market, according to the Federation of European Explosives Manufacturers.

number of companies have also confirmed their use of the substance in the production of detonators for civilian and military applications.

It should be noted that in the above applications, lead styphnate is used in its dry form, occasionally coated with conducting media such as graphite[19].

4.3.2 Locations and Quantities Used

Locations

Information collected from literature (e.g. the SIC BREF Document) and through consultation confirms that lead styphnate is used on-site for the production of articles. Given the relatively small number of lead styphnate manufacturers in the EU, it is believed that fewer than 10 sites currently use the substance in the production of detonators and munition pyrotechnics. Locations identified as relevant include the Czech Republic, France, Germany, Poland, Spain and the UK.The majority of these sites uses the substance for articles intended for military applications.

Quantity

Civilian and military detonators and fuzes appear to represent a small percentage of the amount of lead styphnate manufactured in the EU, ca. 7% of overall EU production with the relevant tonnage in the 1-10 t/y range. Within this, military detonators and igniters have a higher tonnage share.

Specific information on tonnages is provided in the Confidential Annex (Section A3.2). As noted above, the Federation of European Explosives Manufacturers (2011) has advised that lead styphnate is contained in 52 million civilian detonators of the electric type produced in the EU. With an average content of 50 mg lead styphnate per detonator, the amount of the substance consumed in the EU is 52 million x 5×10^{-8} = 2.6 tonnes of lead styphnate.

Concentration in Articles

Information has been provided by consultees but the majority of this is considered confidential. The non-confidential response of Company 2 suggests a concentration of lead styphnate of 20% in the ignition charge (primer mixture) and a concentration of 0.2% when the whole (civilian) detonator is considered.

Company 20 indicates the use of lead styphnate-containing devices in military munitions. The proportion of the detonator as part of the complete article is so small that the proportional content of lead styphnate for a more complex and heavier nature of munition could be in the order of 0.001%.

According to the Estonian Health Board, Department of Chemical Safety (2011), five detonators containing lead styphnate were demonstrated to the Estonian Defence Forces. These contained 1 mg of lead styphnate.

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[19] Concentrations of graphite of a few % are known to be used – see a UK Ministry of Defence guide here: http://www.dtic.mil/cgi-bin/GetTRDoc?Location=U2&doc=GetTRDoc.pdf&AD=ADA492034.

4.3.3 Recent and Future Trends

No significant trends in the consumption of lead styphnate in detonators have been identified by consultees. Relevant (but limited) information is provided in the Confidential Annex (Section A3.2).

It is known that efforts are being made by the US military to replace lead-based primary explosives. It has also come to our attention that national defence agencies as well as the European Defence Agency may also be looking into 'greener' explosives but specific information on the extent to which EU organisations are following the US example is not available.

4.3.4 Structure of Supply Chain

The available information suggests that the manufacturers of the substance fabricate the detonators in-house and sell these on to the end-users directly. However, it is possible that weapon fuzes will be sold by one company to another for the production of the final article (e.g. an artillery shell or a hand grenade). The end users are mining and construction/demolition companies as well as the defence departments/agencies of EU national governments.

4.4 Use in Powder Actuated Cartridges for Power Tools

4.4.1 Description of Use

A powder-actuated tool (often called a 'Hilti gun' or a 'Ramset gun', after their producers) is a 'nail gun' used in construction and manufacturing to join materials to hard substrates such as steel, concrete and masonry (Hilti, 2007). Known as "direct fastening", this technology relies on a controlled explosion created by a small chemical propellant charge, similar to the process that discharges a firearm.

The technical documentation of a relevant commercially available product describes the elements of the cartridges as follows (Hilti, 2007):

- **case**: the cartridge case is formed from brass in one piece. The end of the case is crimped and sealed to prevent the loss of any propellant;
- **primer**: the primer is Sinoxyd, a mixture of lead styphnate and other components, (as discussed earlier). It is situated in the rim of the base of the cartridge. Ignition is effected by striking the rim, thereby compressing the primer and causing it to ignite. It burns rapidly and detonates the propellant charge; and
- **propellant**: the propellant is a mixture of nitrocellulose and nitro-glycerine. It is ignited by the primer after this has been activated by a blow from the firing pin of the tool to the cartridge rim. Combustion takes place within a few milliseconds at around 3,700°C.

4.4.2 Locations and Quantities Used

Locations

The information available would suggest that at least three EU companies use lead styphnate in the production of powder actuated cartridges – one of them has not confirmed this. The three companies are located in three different EU Member States. Additional detail is provided in the Confidential Annex (Annex 3.4).

It has been suggested that all EU-based power tools producers who manufacture 'nail guns' use powder actuated cartridges use cartridges based on lead styphnate. It is understood that at least four EU-based power tool manufacturers may use lead styphnate cartridges.

Quantity

The Finnish Safety and Chemicals Agency (2011) has confirmed that less than 1 tonne of lead styphnate can be found on the Finnish market in power tool cartridges. This tonnage appears to be rather high, judging from the information collected from consultation with individual companies. This application would appear to account for ca. 4% of the total tonnage of lead styphnate manufactured in the EU.

Concentration in Articles

Table 4.2 shows the weight of primer in individual cartridges. Lead styphnate represents only part of the indicated weight. The Finnish Safety and Chemicals Agency (2011) has advised that the concentration of lead styphnate in these articles ranges between 0.1 and 10%. On the other hand, the figures provided by industry are lower but still above the 0.1% by weight level (these are available in Section A3.3 of the Confidential Annex).

Table 4.2: Examples of Primer Content of Powder Actuated Cartridges for Power Tools

Cartridge size	Weight of primer (g)
5.6/16	0.01-0.02
6.3/10	0.02-0.03
6.8/11	0.02-0.03
6.8/18	0.02-0.03

Source: Hilti (2007)

Note: the cartridge size figures show calibre (i.e. width) and length of an individual cartridge

4.4.3 Recent and Future Trends

As the information available relates to one specific company only, it is presented in the Confidential Annex (Section A3.3).

4.4.4 Structure of Supply Chain

As information available relates to one specific company only, it is presented in the Confidential Annex (Section A3.3). It is understood that at least four EU-based power tool producers may use lead styphnate cartridges.

4.5 Use in Automotive Igniters

4.5.1 Description of Use

Information from Literature

In high-speed moving bodies such as automobiles, an airbag is quickly inflated by a gas generator called an inflator. The gas generator contains a gas-generating agent, and an initiator for causing the gas-generating agent to start a gas-generating reaction. Conventionally, the initiator includes a reactant, and a filament-shaped bridgewire serving as a heating resistor that causes the reactant to start a reaction. In the rear of the initiator a connector is present for the application of electricity (Amano & Nishina, 2004).

In an emergency, such as a car collision, a voltage is applied from a battery to the bridgewire through the electrodes. In response, the bridgewire generates heat, and the reactant is ignited to start a reaction. High-pressure gas and heat are generated by the reaction of the reactant, and a gas-generating agent causes a gas-generating reaction. With the reaction, hot gas is emitted (Amano & Nishina, 2004).

The reactant may include a first reactant composed of a mixture of lead styphnate and aluminium powder surrounding the bridgewire, and a second reactant composed of $BKNO_3$ or gunpowder surrounding the first reactant. The first reactant rapidly reacts to generate heat, and the second reactant starts to react in response to the heat from the first reactant, thereby producing high-pressure hot gas and fine particles (Amano & Nishina, 2004).

It is understood that lead styphnate is used in its ‘wet’ form and is transferred in individual igniters after mixing it with a film-forming binder. Igniters are placed in an oven so that lead styphnate dries and is ‘glued’ inside the igniter.

Gas generators may be incorporated in various air bag devices, such as a driver’s seat air bag, a passenger’s seat air bag, a rear-seat air bag, a side air bag, a head-protection air bag, and a pedestrian-protection air bag, and in seat belt pre-tensioners (Amano & Nishina, 2004).

Information from Consultation

The three leading producers of airbags and seat pre-tensioners in the EU have confirmed their past and/or current use of lead styphnate in automotive pyrotechnics. Additional detail by company is given in the Confidential Annex (Section A3.4).

The companies have eliminated the use of the substance in all new applications, but one may still find lead styphnate in a few spare parts under the exemption prescribed by the End-of-Life Vehicles Directive (Directive 2000/53/EC). It was explained that, as the re-qualification of a complete vehicle is a costly activity, it makes sense to still use the substance in spare parts. This is also beneficial to the environment from a lifecycle perspective.

4.5.2 Locations and Quantities Used

Locations

The airbag manufacturing process may or may not be vertically integrated:

- one of the companies directly owns a facility manufacturing the substance and another which incorporates the initiator component of the airbag;
- a second company purchased in the past lead styphnate initiators from two lead styphnate manufacturers; and
- the third company also purchases ready-made igniters from an (unidentified) supplier.

The number of sites using lead styphnate in this application is small, below 10. Some additional detail is given in the Confidential Annex to this report (Section A3.4).

Quantity

Although a 2001 report by Ökopol reported that in 75% of European cars lead styphnate was the chemical compound used to initiate ignition, it appears that the quantity of lead styphnate currently used is very small and now represents <<1% of the total EU manufacture of the substance (it is estimated at <1 t/y). As older car models are withdrawn from the market the amount consumed will further decline and eventually cease in the coming years. Additional information is available in the Confidential Annex (Section A3.4).

Concentration in Articles

An airbag producer suggests that the amount of lead styphnate per initiator is around 10 mg and there is in principle one initiator per airbag. In the late 1990s, vehicles were equipped with one airbag. In the early 2000s, a second airbag was added and by 2002, four airbags per vehicle were common. Today, vehicles may include four to eight airbags, but new models do not contain lead styphnate. The amount of lead used per car was quoted by Ökopol in 2001 as 50 to 310 mg lead (Ökopol, 2001).

4.5.3 Recent and Future Trends

In 2001, two different ignition systems were used in European cars, the low- and high-energy systems which were ignited by a small or high electrical current respectively. For high-energy systems, which were used in 25% of European cars, lead-free ignition chemicals were available and used. Alternative techniques and/or chemicals for low-energy systems were under investigation but uncertainties remained as to whether this would be successful. At the time, vehicle producers stated that it was uncertain whether the change to lead-free initiators would be made by change to high-energy systems or by developing new pyrotechnic chemicals. In either case, considerable time would be needed for the change because of the necessary development, validation and qualification procedures in these safety sensitive applications (Ökopol, 2001). The result is that Annex II of the End-of-Life Vehicles Directive (Directive 2000/53/EC) includes an exemption for lead in pyrotechnic devices. This applies for vehicles type-approved before 1 July 2006 and spare parts for these vehicles.

A later report by Öko-Institut, published in 2008, reported that the findings of the 2001 report were still valid and justified. Almost all vehicle producers did still have vehicles in current series production which had been type approved prior to July 2006. The production volume of these mentioned vehicle models however, was far lower than the production volume of vehicles using lead-free systems (Öko-Institut, 2008). Industry argued at the time in favour of maintaining the Annex II exemption as this was "*absolutely necessary to avoid the safety concerns associated with changing running series…the same argument is valid when it comes to providing replacement parts. These should be provided "as originally produced." Thus it would be possible to produce* *and repair or service "old" vehicle generations using the technology which has been developed, tested and validated for this generation*” (Öko-Institut, 2008).

While the exemption remains, members of the European Association of Automotive Suppliers (CLEPA) have introduced lead-free alternatives for all product developments for vehicles type approved after 1 July 2006, in line with the Annex II exemption. The number of lead-containing pyrotechnical applications has gradually decreased in recent years. According to CLEPA, the production volume of initiators with lead for vehicles type approved before 1 July 2006 was about 10% of an annual total volume of 80 million initiators and was constantly decreasing (Öko-Institut, 2008).

4.5.4 Structure of Supply Chain

Some information is provided in the Confidential Annex (Section A3.4). Generally, the lead styphnate igniters are produced on the same site where the substance is manufactured and then are supplied to another site where the gas generator is fabricated. The gas generator may then be supplied to another site where the final article (e.g. the airbag) is assembled.

4.6 Use in Cartridge Actuated Devices

4.6.1 Description of Use

Cartridge-actuated devices (CADs) are small, self-contained energy sources that are used to do mechanical work. The energy is generated by the burning of a propellant or pyrotechnic material and is often used to push a piston or initiate an explosive train. This differentiates CADs from similar devices, such as rocket igniters, where heat energy, not mechanical work, is the desired output. CADs are simply devices that utilise cartridges as mechanical power sources (Grote, undated).

Valenta (2009) discusses efforts being made in the USA to replace lead-based compounds (as well as perchlorate and chromate oxidisers) from CADs. Examples of CADs uses include:

- thrusters/removers
- cable cutters
- parachute mortars
- explosive bolts/nuts
- explosive fracturing/cutting systems
- safe/arm & arm/fire devices
- gas generators
- electro-explosive devices (hot wire, percussion primers)
- ignition elements
- linear explosive systems
- laser ordnance
- inflation and fire extinguishing devices
- thermal batteries
- escape system sequencers
- rocket systems
- escape applications
- rocket catapults
- thrusters (rocket powered)

Blachowski (undated) further provides a figure of the F-18 fighter jet which contains a significant number of CAD systems in:

- aircrew survival equipment: 2 CADs;
- aircrew escape sequencing system: 26 CADs;

- ejection seat: 18 CADs;
- engine/Auxiliary Power Unit fire extinguishing system: 1 CAD;
- dry bay fire extinguisher system: 18 CADs;
- deployable flight incident recorder: 13 CADs; and
- stores ejection equipment: various.

Non-aircraft CAD applications have included emergency systems for deep diving submersibles and submarines, propulsion units for mine field markers, release mechanisms for allowing separation of missile stages, timing systems for hand grenade fuses, and inflation systems for marking locations of buoys (Grote, undated). It is also understood that applications outside the aerospace/defence sector are possible, for example in mechanisms installed in buildings or technical facilities.

A typical primer used by the US armed forces is the NOL-130 stab primer containing basic lead styphnate (40%), lead azide (20%), barium nitrate (20%) and tetrazene (5%). Normal and basic lead styphnate may also be found in percussion primers at a concentration of 24-38% (Valenta, 2009). A typical percussion primer used in CADs in the USA is the PVU-1/A, which contains 24% lead styphnate and is found in most aircraft in the US Navy fleet (Ostrowski et al, undated).

4.6.2 Locations and Quantities Used

Only one company has indicated the use of lead styphnate in this application. The tonnage involved is well below 1 t/y[20]. Additional detail is given in the Confidential Annex (Section A3.5). In addition, two well-known companies with a worldwide presence in the aerospace sector have confirmed the relevance of lead styphnate in defence products. It is likely that military equipment produced in countries such as the USA and operated by EU national armed forces may well contain CADs that depend on lead styphnate.

4.6.3 Recent and Future Trends

No information is available.

4.6.4 Structure of Supply Chain

No information is available.

4.7 Use in Cattle Killer Cartridges

Only one company has confirmed the use of the substance as a primer in cattle killer cartridges used to stun animals before slaughtering. The amount of lead styphnate involved is low. Additional detail is provided in the Confidential Annex (Section A3.6).

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[20] A second company suggested its involvement but the nature of its articles appears to better suit the munitions category.

4.8 Use in Shuttles and Satellites

4.8.1 Description of Use

Information from Literature

Space Applications for MEMS

Microelectromechanical systems (MEMS) is the technology of very small mechanical devices driven by electricity; it merges at the nano-scale into nanoelectromechanical systems (NEMS) and nanotechnology. MEMS are also referred to as micromachines (in Japan), or Micro Systems Technology - MST (in Europe).

MEMS devices are suited to replace larger and heavier components, then replace entire subsystems, and finally enable the microfabrication of highly integrated pico-satellites. Very small satellites (1 to 100 kg) stand to benefit the most from MEMS technologies because reaching the desired performance levels is only possible using a highly integrated approach. The small satellites are typically used for science or technology demonstration missions, with much higher risk tolerance than multi-tonne telecommunication satellites (de Rooij et al, 2009).

Literature search has revealed on-going efforts to use lead styphnate. Examples include:

- a micro-thruster array for use on micro-, nano- and pico-satellites successfully demonstrated its functionality in 2001 in a live fire test aboard a Scorpius sub-orbital sounding rocket. Individual MEMS thrusters, each a poppy seed-sized cell fuelled with lead styphnate ignition powder, fired more than 20 times at 1-second intervals during the test staged at the White Sands Missile Range. The creators believed that micro-thrusters have the potential to provide on-orbit propulsion for station keeping, orbital correction and attitude control for future, very small satellites weighing from less than a pound (0.45 kg) to as much as 50 pounds (22.7 kg) (Business Wire, 2001);
- Youngner *et al* (2000) discuss how small satellites flying in clusters may work. The researchers created a MEMS thruster array containing a quarter of a million separate thrusters on a 1.3” x 1.3” silicon die. A two-stage approach to detonating the fuel and creating thrust was selected. In stage 1, a small (ca. 1 nanogram) charge of lead styphnate was heated to its auto-ignition temperature (270°C). In stage 2, the exploding styphnate ignites a nitrocellulose mixture in the overhead cavity;
- Okada *et al* (2005) further discuss research undertaken in the 2000s on the use of substances such as lead styphnate as an igniter for propellant in MEMS rocket arrays; and
- Ren *et al* (2008) presented a micro MEMS thruster array. Granular lead styphnate was used as the ignition powder to initiate the solid propellant.

Several other sources beyond the selected ones above can easily be identified in the open literature.

Defence Applications for MEMS

Several aerospace and military applications for MEMS are possible. Examples are micro jet arrays forflow control, IMUs (Inertial Measurement Units) for inertial measurement and navigation, fuse/safety andarming for munitions, and health monitoring of machinery (NATO, 2004). Although our review of literature has not positively confirmed the use of lead styphnate in MEMS specifically aimed at military applications, this cannot be precluded.

Information from Consultation

The US Aerospace Industries Association has suggested that good examples of the use of lead styphnate (and potentially lead azide) are in solid rocket motor boosters, detonation cords, and blasting caps used on shuttle and satellite launch vehicles.

4.8.2 Locations and Quantities Used

No information is available. The quantities involved must be small.

4.8.3 Recent and Future Trends

No information is available.

4.8.4 Structure of Supply Chain

No information is available.

4.9 Use of Lead Styphnate in Performance Arts Pyrotechnics

4.9.1 Description of Use

Lead styphnate may be used as a primer in igniters often referred to as ‘electric matches’. In them, the current is supplied via two wires; across the two contacts is a bridgewire. When a current is passed through this wire, it burns out creating a very small white spark. A sensitive pyrotechnic composition is then pressed over the bridgewire and this composition may contain lead styphnate. The lead styphnate is dipped in a protective lacquer which when dried protects the head from the elements, damage and insulates it from static discharge (Pyromark, 2008).

A particular type of ignite is bullet hit squibs. Bullet hits are used for staging projectile impacts in theatre productions, television recordings, and film recordings. When deflagrating explosives like black powder are used, application of flame is insufficient for firing. Squibs are used for this purpose (Mukhopadhyay & Datta, 2007). These are special, low-shrapnel arrangements of small, electrically triggerable detonators, which are loaded with different amounts of primary explosive, sometimes together with secondary explosives as well (Kohler, 2005).

Two main groups are differentiated, “soft bullet hits” and “high bullet hits”; “soft bullet hits” being charged with only uncompressed primary explosive or mixtures containing primary explosive and being intended for use on or in the immediate vicinity of people. In principle, “high bullet hits” refer to a plastic-sheathed, electrically triggerable detonator comprising a small primary charge and a secondary charge (the main charge), which is highly compressed in some types, made of nitropenta or hexogen, for example. This very strong line of products is mainly used in earth, snow and water, and in the field of stage building. The composition weight (soft bullet hits) is typically 2 to 384 mg. These pyrotechnic special detonators have the shape of either a 0.5-2 mm thick disk, the diameter of which differs depending on the loading weight, or a cylinder (Kohler, 2005).

Normal lead styphnate can be used as the primary explosive. It is also technically possible to use lead azide, however, this is much too brisant in unmixed form for such an intended use and has safety problems with regard to production and handling. The detonation reaction of unmixed lead azide also displays too large an explosion flame (Kohler, 2005).

4.9.2 Locations and Quantities Used

Information is not available from literature or consultation. However, if the application is relevant to the EU, the number of relevant companies and the associated tonnages are likely to be very small.

4.9.3 Recent and Future Trends

Kohler (2005) shows a patent for the development of lead-free bullet hit squibs. It is very likely that issues of exposure to lead released from these devices generally drive efforts for the replacement of lead styphnate with alternative explosives.

4.9.4 Structure of Supply Chain

No information is available.

4.10 Imports and Exports of Articles into and from the EU

4.10.1 Information from Consultation

Imports

As shown above, the most important use of lead styphnate is in small calibre firearm ammunition. Consultation with a leading EU producer of such ammunition suggests that there are very significant imports of lead styphnate-containing articles from countries such as the USA, Brazil and Russia. Another company has confirmed the import of a small tonnage of lead styphnate in the form of primer caps for small calibre ammunition from one of the three non-EU countries mentioned above.

With regard to imports of lead-based detonators into the EU, these are only a small fraction of the EU consumption of detonators and mostly relate to specialist products, for example for the oil & gas industry. The oil well industry (e.g. in the North Sea) may require ca. 10,000 units imported from abroad (for example, from the USA) (Federation of European Explosives Manufacturers, 2011). The Federation of European Explosives Manufacturers estimates that 0.01 t of the substance may be imported into the EU each year by its members in the form of articles (Federation of European Explosives Manufacturers, 2011b).

Exports

With regard to civilian detonators, the Federation of European Explosives Manufacturers has advised that exports of civilian lead-based detonators to non-EU customers account for ca. 30% of EU production, i.e. 36.4 million detonators containing lead styphnate remain in the EU and 15.6 million are exported with a lead styphnate content of 0.8 tonnes (Federation of European Explosives Manufacturers, 2011). No specific information was provided on military detonators.

4.10.2 Information on Trade Statistics

Information on the trade of key articles is available from the DG Trade Market Access Database and is reproduced in Table 4.3.

Table 4.3: 2009-2010 Statistics on Imports and Exports of Key Articles

Product nomenclature	**2009 Imports and Exports**		**2010 Imports and Exports**		**Import-export balance**	
	Import Qty to the EU/MS (1000 kg)	**Export Qty from the EU/MS (1000 kg)**	**Import Qty to the EU/MS (1000 kg)**	**Export Qty from the EU/MS (1000 kg)**	**2009**	**2010**
9306.21 - Shotgun cartridges	764.0	17,933.6	1,283.1	15,846.3	-17,169.6	-14,563.2
9306.30.10 – Cartridges for revolvers and pistols and for sub-machine-guns	1,106.5	734.9	1,305.7	370.2	371.6	935.5
9306.30.30.00 - Cartridges and parts thereof for military weapons	275.0	207.9	979.7	583.1	67.1	396.6
9306.30.91.00 - Centrefire cartridges	898.0	1,515.7	1,478.8	120.3	-617.7	1,358.5
9306.30.93.00 - Rimfire cartridges	806.0	748.1	1,066.7	923.4	57.9	143.3

Source: DG Trade Market Access Database, http://madb.europa.eu/mkaccdb2/statistical_form.htm#

Unfortunately, it is not possible to establish which elements of the statistical data may specifically relate to lead azide-containing articles. The Association of European Manufacturers of Sporting Ammunition which represents the major manufacturers of lead styphnate suggests that the table is accurate in describing a significant outflow of ammunition from the EU towards non-EU countries. The Association confirms that this balance of imports and exports is confirmed by the experience of the European ammunition manufacturers (AFEMS, 2011).

4.11 Descriptions of Use Categories and Examples of Relevant Products

Table 4.4 presents the composition of some relevant articles (primer caps, small calibre ammunition, igniters, detonators and powder actuated cartridges for power tools) that contain lead styphnate which have been identified in the open literature. The information is based on Safety Data Sheets.

The table is followed by **Table 4.5**, which shows the relevant process categories, environmental release categories, process categories and sectors of end use for lead styphnate in the EU. The table also gives the relevant NACE codes for the end uses identified[21].

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[21] NACE codes available here: http://ec.europa.eu/competition/mergers/cases/index/nace_all.html.

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	Description of product	Lead styphnate content	Other ingredients	Notes	Year	Source
CCI (US)	Small pistol competition primer	Not given	Barium nitrate (CAS No. 10022-31-8) Antimony sulphide (CAS No. 1345-04-6) Copper (primer cup component) (CAS No. 7440-50-8) Zinc compounds (primer cup component) (CAS No. 7440-66-6)		2007	1
Remington Arms (US)	Component primers and percussion caps (centerfire/ shotshell/muzzleload)	Less than 1-26%	Copper (CAS No. 7440-50-8) – 1-67% Zinc (CAS No. 7440-66-6) - Less than 1-29% Antimony (CAS No. 7440-36-0) – 0.3-7.8% Arsenic (CAS No. 7440-38-2) – Less than 0.1% Iron (CAS No. 1309-37-1) – 0-98% Barium (CAS No. 7440-39-3) – Less than 1-29% Tetrazene (CAS No. 109-27-3) – Less than 0.1-3.3%		2011	2
Winchester (US)	Rimfire primer	1.2-2.4%	Copper (CAS No. 7440-50-8) – 55-94% Zinc (CAS No. 7440-66-6) – 3-38% Iron (CAS No. 7439-89-6) – 0-97% Barium nitrate (CAS No. 10022-31-8) – 1.1-2.7% Fibrous glass dust (CAS No. 65997-17-3) – 0.9-22%		2011	3

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	**Description of product**	**Lead styphnate content**	**Other ingredients**	**Notes**	**Year**	**Source**
Winchester (US)	Centrefire primer	4-6%	Copper (CAS No. 7440-50-8) – 55-94% Zinc (CAS No. 7440-66-6) – 3-38% Iron (CAS No. 7439-89-6) – 0-97% Barium nitrate (CAS No. 10022-31-8) – 1.1-2.7% Antimony sulphide (CAS No. 1345-04-6) – 1.5-2.5% Lead thiocyanate (CAS No. 592-87-0) – 0.1-0.6%		2011	4
Winchester (US)	Shotshell 8 gauge industrial cartridges, steel slug	0.1-1%	Zinc powder - zinc dust (pyrophoric) (CAS No. 7440-66-6) – 1-6% Copper (CAS No. 7440-50-8) – 5-12% Nitrocellulose (CAS No. 9004-70-0) – 1-5%		2008	5
B&T (CH)	40 mm Ballistic Smoke The cartridge fires two projectiles each with a mass of just under 50g, which begin to eject white smoke approximately one second after being fired	Not given	Priming agents (32-77% by weight, incl. lead styphnate) Tetrazene (CAS No. 31330-63-9) Oxidation agents (18-52% by weight) Barium nitrate (CAS No. 10022-31-8) Lead dioxide (CAS No. 1309-60-0) Reducing agents + additives (5-16% by weight) Antimony sulphide (CAS No. 1345-04-6) Calcium silicide (CAS No. 12013-56-8) *All the above constitute the priming compound: Synoxyd max. 26 mg*	Also contains propellant powder, fuse cord, boron igniter, and active charge	2011	6

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	Description of product	Lead styphnate content	Other ingredients	Notes	Year	Source
Austin Star (US)	Electric detonators Explosive components are PETN or RDX (possibly TNT) and lead compounds sealed in a metal shell	Not given	PETN, Pentaerythritol tetranitrate (CAS No. 78-11-5) RDX, Cyclotrimethylene Trinitramine (CAS No. 121-82-4) Lead Azide (CAS No. 13424-46-9) TNT, Trinitrotoluene (CAS No. 118-96-7)		2010	7
Austin Star (US)	Non-electric detonators Explosive components are PETN or RDX and lead compounds sealed in a metal shell	Not given	PETN, Pentaerythritol tetranitrate (CAS No. 78-11-5) RDX, Cyclotrimethylene Trinitramine (CAS No. 121-82-4) Lead Azide (CAS No. 13424-46-9)		2010	8
Austin Star (US)	Electric detonators Explosive components are RDX and lead compounds sealed in a metal shell	Not given	Lead Azide (CAS No. 13424-46-9) RDX, Cyclotrimethylene Trinitramine (CAS No. 121-82-4) HNS, Hexanitrostilbene (CAS No. 20062-22-0)		2010	9

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	**Description of product**	**Lead styphnate content**	**Other ingredients**	**Notes**	**Year**	**Source**
Austin (CZ)	Electric Fusehead, Electric Igniter	Not given	4,6-dinitro-2-amino-lead phenolate (CAS No. 111802-21-2) – max. 3 mg/kg Lead orthoplumbate (CAS No. 1314-41-6) – max. 6 mg/kg Potassium perchlorate (CAS No. 7778-74-7) – max. 3 mg/kg Zirconium powder (non-stabilized) (CAS No. 7440-67-7) Antimony sulphide (CAS No. 1345-04-6) Lead dioxide (CAS No. 1309-60-0) – max. 11 mg/kg Aluminium powdered (non-stabilised) (CAS No. 7429-90-5) – max. 2 mg/kg Calcium silicide - max. 5 mg/kg		2010	10
Maxam (ES)	Electric detonators Riodet®, Seismic Riodet®	Not given	Primary explosive: lead azide (and lead styphnate) Secondary explosive: pentaerythritol tetranitrate (PETN) Pyrotechnic composition: lead peroxide, potassium permanganate, silicon, antimony		2009	11
Maxam (ES)	Riodet®, Seismic Riodet® , RIODET IZ, RIODET IEP	6%	Lead azide (CAS No. 13424-46-9) – 10% Pentaerythritol tetranitrate (PETN) (CAS No. 78-11-5) – 64% Lead peroxide (CAS No. 1309-60-0) – 5% Potassium permanganate (CAS No. 7722-64-7) – 5% Silicon (CAS No. 7440-21-3) – 5% Antimony (CAS No. 7440-36-0) – 5%		2010	12

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	**Description of product**	**Lead styphnate content**	**Other ingredients**	**Notes**	**Year**	**Source**
Orica (AUS)	Electric instantaneous detonators Initiators for explosive charges Metal tubes (aluminium or copper), closed at one end and capped at the other with plastic closure plug ending in plastic covered electric lead	<1%	Metal and plastic components - >60% Pentaerythritol tetranitrate (PETN) (CAS No. 78-11-5) - <1% Lead azide (CAS No. 13424-46-9) - <1% Aluminium (CAS No. 7429-90-5) - <1% Tetryl (N-Methyl- N,2,4,6-tetranitroaniline) (CAS No. 479-45-8) - <1%		2009	13
Special Devices (US)	1.4B UN0255 Electronic Detonators Aluminium or copper shells with attached PVC or polyethylene coated copper or iron leg wires	Not given	Zirconium (CAS No. 7440-67-7) Potassium perchlorate (CAS No. 4778-74-7) Viton (CAS No. 25190-89-0) PETN, Pentaerythritol tetranitrate (CAS No. 78-11-5) Lead azide (CAS No. 13424-46-9)		2005	14
UEB-Maxam (ES)	Electric detonators for blasting	<0.5%	Lead azide (CAS No. 13424-46-9) - <1.5% Lead picrate (CAS No. 6477-64-1) - < 0.1% Pentaerythrythol tetranitrate, PETN (CAS No. 78-11-5) - < 5% Lead Peroxide (CAS No. 1309-60-0) - <0.1% Potassium permanganate (CAS No. 7722-64-7) - <0.1% Silicon (CAS No. 7440-21-3) - <0.1% Antimony (CAS No. 7440-36-0) - <0.1% Metal and plastic components - >90%		2008	15

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	**Description of product**	**Lead styphnate content**	**Other ingredients**	**Notes**	**Year**	**Source**
Raikka Oy (FI)	SHOCK TUBE - including detonating cord, primer and detonators	Not given	Detonator: RDX and PETN hexogen PETN, about 1 g / pc Detonating cord: oktogen HMX 10-20 g/m, aluminium 1-5 mg/m Primer: lead styphnate, barium nitrate, antimony sulphide, aluminium, nitrocellulose, nitroglycerol, tetrazene, about 25 mg / pc		2009	16
Hilti (UK)	Cartridges for technical purpose – Powder actuated fasting tools	20-60%	Tetrazene (CAS No. 109-27-3) – 0-15% Barium nitrate (CAS No. 10022-31-8) – 0-40% Lead dioxide (CAS No. 1309-60-0) – 0-40%	Also contains cellulose nitrate, glycerol trinitrate and diphenylamine	2008	17
ITW (UK)	Spit 6.30/12 Red Plug Cartridges Cartridges for pyrotechnical device	45%	Not given (contains primer and propellant powder)		N/A	18
JCP (UK)	Cartridges for powder actuated cartridge tools	0.1-1%	Zinc powder (pyrophoric) (CAS No. 7440-66-6) – 15-32% Nitrocellulose (CAS No. 9004-70-0) – 7-13% Glycerol trinitrate (CAS No. 55-63-0) – 0.5-2% Dibutyl phthalate (CAS No. 84-74-2) – 0.5-2% Copper (CAS No. 7440-50-8) – 50-<100%		2009	19

Sources:

[1] *http://glarp.atk.com/2008/msds/525_Small_Pistol_Comp.pdf*

[2] *http://www.remington.com/~/media/Files/MSDS/cfssprim.ashx*

[3] *http://www.winchester.com/SiteCollectionDocuments/pdf/msds/msds_w71.pdf*

Table 4.4:Examples of Lead Styphnate-based Articles – Safety Data Sheets

Producers	Description of product	Lead styphnate content	Other ingredients	Notes	Year	Source

[4] *http://www.winchester.com/SiteCollectionDocuments/pdf/msds/msds_w71.pdf*

[5] *http://www.parbst.dk/GB/sds/gb_steel.pdf*

[6] *http://www.bt-ag.ch/pdf/PSDS_Ballistic_Smoke.pdf*

[7] *http://www.austinpowder.com/blastersguide/docs/msds/Electric%20Detonators,%20ED1.PDF*

[8] *http://www.austinpowder.com/BlastersGuide/docs/msds/Non-Electric%20Detonators,%20ED5.PDF*

[8] *http://www.austinpowder.com/blastersguide/docs/msds/Oil%20Star%20Electric%20Detonators,%20ED2.PDF*

[10] *http://www.austin.cz/download/produkty/MSDS_EF_ENG.pdf*

[11] *http://www.nordexexplosives.com/PDF/Products/MSDS/MSDSDetonatorsElectric.pdf*

[12] *http://www.maxam-na.com/pdfs/RIODET%20MSDS12.pdf*

[13] *http://www.oricaminingservices.com/download/file_id_5598/*

[14] *http://www.lectronics.com/images/Accudet%20MSDS.pdf*

[15] *http://www.maxam-corp.com.au/LinkClick.aspx?fileticket=FDfHTg_VEQw%3D&tabid=188&mid=767*

[16] *http://www.forcit.fi/archives/liitetiedosto/shock-tube-ja-nallit-ktt*

[17] *http://www.hilti.co.uk/fstore/holuk/techlib/docs/DX-Cartridges_12%2008_GB%20(2).pdf*

[18] *http://www.paslode.co.uk/Technical/COSHH%20Datasheets/PDF/Red_Cartridges.pdf*

[19] *http://www.jcpfixings.co.uk/data%20sheets/Strip%20Cartridges.pdf*

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
Manufacture	**PROC 3**: Use in closed batch process (synthesis or formulation) **PROC 4**: Use in batch and other process (synthesis) where opportunity for exposure arises **PROC 15**: Use as laboratory reagent	**ERC 1**: Manufacture of substances	As a substance	**PC 11**: Explosives	**SU 9**: Manufacture of fine chemicals **SU 0**: Other: SU 3 (industrial uses) with end use **SU 10** (NACE 20.51 - Manufacture of explosives)	Not relevant	C20.51 - Manufacture of explosives
			Formulation of mixtures				
Formulation of lead styphnate as component of primer mixtures (explosives)	**PROC 2**: Use in closed, continuous process with occasional controlled exposure **PROC 5**: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact)	**ERC 2**: Formulation of preparations **ERC 5**: Industrial use resulting in inclusion into or onto a matrix	As a substance	**PC 11**: Explosives	**SU 10**: Formulation [mixing] of preparations and/or re-packaging (excluding alloys)	Not relevant	C20.51 - Manufacture of explosives

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
Fabrication of articles – Applications confirmed as relevant to the EU							
Use of primer mixtures in fabrication of ammunition for civilian (hunting/ sport) firearms	**PROC 5**: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact) **PROC 8a**: Transfer of substance or preparation (charging /discharging) from/ to vessels/ large containers at non-dedicated facilities **PROC 9**: Transfer of substance or preparation into small containers (dedicated filling line, including weighing)	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C25.4.0 - Manufacture of weapons and ammunition C32.3.0 - Manufacture of sports goods
Use of primer mixtures in fabrication of ammunition for military firearms	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C25.4.0 - Manufacture of weapons and ammunition

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
Use of primer mixtures in fabrication of detonators for civil applications (quarries, mining, construction)	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.5.1 - Manufacture of explosives
Use of primer mixtures in fabrication of detonators and pyrotechnics for military explosives and munitions (incl. aerospace)	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C25.4.0 - Manufacture of weapons and ammunition

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
Use of primer mixtures in fabrication of powder actuated cartridges for power tools	**PROC 8a**: Transfer of substance or preparation (charging /discharging) from/ to vessels/ large containers at non-dedicated facilities **PROC 9**: Transfer of substance or preparation into small containers (dedicated filling line, including weighing) **PROC 14**: Production of preparations or articles by tabletting, compression, extrusion, palletisation	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.5.1 - Manufacture of explosives
Use of primer mixtures in fabrication of igniters for automotive airbags and seat pre-tensioners	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.5.1 - Manufacture of explosives

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
Use of primer mixtures in fabrication of Cartridge Actuated Devices	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.5.1 - Manufacture of explosives
Use of primer mixtures in fabrication of cattle killer cartridges	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**SU 0**: Other **SU 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.5.1 – Manufacture of explosives

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
End-use of articles							
Firing of ammunition for civilian (hunting/ sport) firearms	Use of articles containing lead styphnate as a primary explosive	**ERC 8f**: Wide dispersive outdoor use resulting in inclusion into or onto a matrix **ERC 10a**: Wide dispersive outdoor use of long-life articles and materials with low release Substance consumed during use	Article	**PC 11**: Explosives	**SU1**: Agriculture, forestry, fishery **SU21**: Private households	Not relevant	A1.7.0 - Hunting, trapping and related service activities R93.1 - Sports activities
Firing of ammunition for military firearms	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU22**: Professional uses: Public domain	Not relevant	O84.2.2 - Defence activities
Detonation of detonators for civil applications	Use of articles containing lead styphnate as a primary explosive	**ERC 10a**: Wide dispersive outdoor use of long-life articles and materials with low release Substance consumed during use	Article	**PC 11**: Explosives	**SU2a**: Mining (without offshore industries)	Not relevant	F43.1.1 - Demolition B5 - Mining of coal and lignite B7 - Mining of metal ores

Table 4.5: Identified Uses and Process Categories for Lead Styphnate

Identified use	**Process category**	**Environmental release category**	**Substance supplied to that use in the form of…**	**Market sector by type of chemical product**	**Sector of end use**	**Subsequent service life relevant for that use?**	**Relevant NACE code(s)**
Detonation of detonators for military explosives and munitions	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU22**: Professional uses: Public domain	Not relevant	O84.2.2 - Defence activities
Detonation of detonators for aerospace blade-off tests	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU24**: Scientific research and development	Not relevant	C30.3.0 - Manufacture of air and spacecraft related machinery
Use of powder actuated cartridges	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU19**: Building and construction work	Not relevant	F - Construction
Deployment of automotive airbags and seat pre-tensioners	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU21**: Private households **SU22**: Professional uses: Public domain	Not relevant	H49.3.1 - Urban and suburban passenger land transport
Deployment of Cartridge Actuated Devices	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU22**: Professional uses: Public domain	Not relevant	H51 - Air transport
Use of cattle killer cartridges in slaughter houses	Use of articles containing lead styphnate as a primary explosive	As above	Article	**PC 11**: Explosives	**SU22**: Professional uses: Public domain	Not relevant	A1.4 - Animal production

Source: REACH Registration dossiers, literature and consultation

5 RELEASES FROM USES

5.1 Releases to the Environment

5.1.1 Releases from Formulation of Mixtures and Production of Articles

Lead styphnate is added to mixtures (primers) and mixtures are used to fabricate articles (primer caps, detonators, igniters, pyrotechnic devices) on the same site where the substance is manufactured. The substance is primarily used in its ‘wet’ form (‘wet’ applications account for more than 90% of the total EU consumption of lead styphnate) but in some minor uses as a dry crystalline solid. Releases from the ‘first use’ of the substance in formulation and article fabrication are included in releases from manufacture.

Articles containing lead styphnate-based mixtures may subsequently be used in the production of larger, more complex articles, e.g. a primer cap is used in the production of an ammunition cartridge, a detonator/fuze becomes a component of an artillery shell, an ignite becomes a component of an automotive airbag system and so on. Lead styphnate is captive within the component (e.g. primer cap), it is not intended for release during these fabrication processes and it is conceivable that any releases may occur only as a result of an accident or misuse.

5.1.2 Releases from End Use of Lead Styphnate Articles

Fate of Lead Styphnate during Firing/Detonation

Being a primary explosive, lead styphnate essentially has to be consumed (burnt) during the active use of articles that contain it, i.e. during the firing of ammunition/munitions or the detonation of detonators and other pyrotechnic devices. We have enquired among consultees on the fate of the substance during such use. Testimonies from individual companies are consistent in suggesting no or very low release of the substance. Instead, the decomposition products will include lead monoxide, lead carbonate, soot, CO, CO2, NOX and water.Under these conditions, , an issue arises with the release of lead to the environment. Nevertheless, some literature sources suggested that unreacted lead styphnate might also be released (see Clausen et al, 2007; ITRC, 2003).

If it assumed that <100 t/y of lead styphnate used in the production of articles each year in the EU, then we can estimate the amount of lead present in these products. Assuming 20% presence of water in the vast majority of products (small calibre ammunition) and a lead content in the molecule of 46% (normal type), the use of <100 tonnes of lead styphnate would mean use of <37 (100 x 0.80 x 0.46) tonnes of lead. It cannot be assumed that the entire amount of articles sold within a year will be consumed in the same year – ammunition and defence munitions, at least, may remain in storage for years before they are used in firing ranges or at wartime.

While this calculated tonnage of lead is not negligible, it is only a small fraction of overall lead releases in Europe[22.] Huynh (2006) suggests that the long-term use of lead azide and lead styphnate

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[22] A recent UNEP document provides some detail on atmospheric releases of lead in Europe (see Table 5-5 and Figure 5-2 of this document: http://www.unep.org/hazardoussubstances/Portals/9/Lead_Cadmium/docs/Interim_reviews/UNEP_GC26_INF_11_Add_1_Final_UNEP_Lead_review_and_apppendix_Dec_2010.pdf).

as primary explosives has resulted in lead contamination at artillery and firing ranges, becoming a major health hazard for civilian and military personnel. On the other hand, the presence of lead styphnate in individual articles is very small, at the milligram level, hence the release from individual articles will be very small.

The following paragraphs discuss the releases of lead from certain end uses of lead styphnate articles.

Lead Releases from Firing of Ammunition containing Lead Styphnate Primers

Lead is known to be released from the firing of small arms ammunition shells. Landrigan et al, 1975; Fischbein et al, 1979; Muskett & Caswell, 1980; Dams et al, 1988; Heider (undated); and the Texas Department of Health (1996) summarise the sources of airborne lead particles from the firing of ammunition:

- combustion of lead styphnate in primers;
- exposure of the projectile base to hot gases;
- friction of the projectile and the barrel itself;
- impact against the bullet/target impact area;
- spent bullets and settled dust;
- improper range-cleaning methods disturbing settled dust; and
- poor indoor range ventilation.

According to Clausen et al (2007), once a projectile ejects from the bore of the weapon, it travels towards the target. Due to scouring of the projectile in the weapon barrel, a small amount of copper (if the bullet is copper-jacketed) and/or lead (unjacketed projectile) may be deposited near the firing point. In addition, small quantities of propellant powder and lead styphnate used in the primer may also be released. Where a primary berm backstop exists, the projectile impacts the berm in a heads-on manner. Two mechanisms scrub energy to stop the projectile: displacement of soil particles and fragmentation. Eventually, all of the energy is dissipated, and the projectile comes to rest.

According to Fronabarger et al (2010), more than 95% of all shooting, missile launches and explosions within the military or police force (at least in the USA) are done exclusively for training purposes in “friendly” areas. Lead styphnate contributes to the levels of lead found at some firing ranges butis not the only source of lead relevant to environmental releases of lead from ammunition. MIDAS (2007) suggests that common military primer formulations (FA-956 and FA-70 used in the USA), igniters, and propellants contain several organo-lead compounds (lead thiocyanate, lead styphnate, lead stearate, and lead salicylate) at approximately 0.1 to 0.2 g per bullet. Lead carbonate is also added to inhibit corrosion of gun barrels. ITRC (2003) further notes that, in the USA, bullet masses range from 32 to 86 grams per bullet, of which 96.4% by weight is lead. The primary sources of lead at training ranges are spent bullet projectiles and shot pellets. However, residues from unignited propellant and explosives from artillery, rockets, etc. may also exist.

The US National Bureau of Statistics states that when lead-based primers are used, 80% of airborne lead on firing ranges comes from the projectile and 20% comes from the priming composition. These percentages depend on whether the bullet is in plain lead or jacketed. In the case of a non-jacketed bullet, the rifling will strip the lead from the bullets surface, this dramatically increasing the percentage of non-primer-based airborne lead (Heard, 2008). It is clear that lead styphnate may be responsible for only (a small) part of the releases of lead to the environment from the use of ammunition.

Several sources of information exist on the presence of lead in the environment as a result of the use of ammunition, for example the Voluntary Risk Assessment for lead compounds undertaken by industry or Tranel & Kimmel (2009) or FERA (2010). However, these reports focus on the impacts of lead shot and projectiles rather than the impacts from the small amount of lead primary explosives present in ammunition cartridges.

Lead Releases from Automotive Igniters

Ökopol (2001) evaluated the use of lead-based pyrotechnics in automobile safety systems. The report noted that, at the end of a vehicle's life, lead from pyrotechnic initiators is expected to end up in the shredder light fraction or as dust when airbags are initialised before shredding. The impact on the environment is expected to be relatively low due to the small quantities involved. Any lead compounds may be formed upon the detonation of lead styphnate in the airbag igniter are expected to remain within the inflator.

Lead Releases from Bullet Hit Squibs

With particular regard to bullet hit squibs containing lead styphnate, Kohler (2005) suggests that the sequential serial triggering of sometimes more than a thousand bullet hits of this type could lead to the objects "shot" becoming contaminated with lead and to consequent releases of lead to the environment.

5.2 Releases to the Working Environment

5.2.1 Overview

A 2003 report from the USA presents an overview of the categories of exposed workers split into groups according to the patterns of exposure to lead. This is reproduced in **Table 5.1**.The entries relevant to the applications of lead styphnate are given in bold, however, it should be noted that the table refers to lead, not specifically to lead styphnate; therefore, it should not be assumed that the substance is responsible for the majority of the perceived high occupational exposure.

Table 5.1: Patterns of Occupational Exposure to Lead for Different Worker Groups

Exposure category	**Occupational exposure groups**
Category 1: High on-going exposure	Battery-production workers Battery-recycling workers Foundry workers Lead chemical workers Lead smelter and refinery workers Leaded-glass workers Pigment workers Radiator-repair workers

Table 5.1: Patterns of Occupational Exposure to Lead for Different Worker Groups

Exposure category	**Occupational exposure groups**
Category 2: High exposure, moderate frequency	**Firing-range instructors** House renovators Lead miners Newspaper printers Plastics workers Rubber workers Steel welders and cutters
Category 3: High exposure, low frequency	Automobile-repair workers Cable-production workers **Construction workers** **Demolition workers** **Firing-range participants** Flame-solder workers Plumbers and pipefitters Pottery-glaze producers Ship-repair workers Stained-glass producers

Source: Technology Planning and Management Corporation (2003)

The absence of the explosives industry (manufacture of the substance and of mixtures for subsequent inclusion in articles) is telling and supports the argument that worker exposure to the substance is limited. It should also be acknowledged that the nature of the substance is such that precautions need to be taken to prevent exposure during routine handling and by accident. These include the use of wet chemistry (primarily) or of conductive additive materials (such as graphite) when dry lead styphnate is handled, minimisation of exposure by use of automated procedures where possible (for activities such as filtering, washing, drying, weighing, mixing, sieving, pressing) and the absence of workers from several of the fabrication steps which are undertaken in closed reinforced spaces.

A leading manufacturer of the substance (one who is involved in the production of small calibre ammunition) suggests that contact of workers with the substance, even in its ‘wet’ form, is avoided at all costs. Activities are typically undertaken in a remote room and mixing with other components is done remotely. The transfer of the material is undertaken in rubber containers with a suitable wooden shove. When the primer mixture arrives to the primer charging department, workers charge it into the primer caps or rimfire shells with a wooden tampon. If something goes wrong, the primers are put in a pail containing water and then sent to incineration.

5.2.2 Releases and Exposure during the Production of Articles

Information is available from a number of companies; as this was provided in confidence, it appears in the Confidential Annex (Section A5.2). In general, producers of articles claim that there is very low, if any at all, worker exposure to lead styphnate.

Two companies have provided non-confidential information, one manufacturing detonators after manufacturing lead styphnate and another which purchases primer caps and pyrotechnic devices and uses those to production military ammunition and munitions. This is reproduced in Table 5.2.

Table 5.2: Worker Exposure during the Production of Articles – Company 20

Worker exposure parameter	Company 2	Company 20
Production process	***On-site production of detonators***	***Use of purchased primer caps and pyrotechnic devices in ammunition and large calibre munitions***
Type of product handled	Mixture containing lead styphnate 20%	Closed article containing lead styphnate
Relevant process step where exposure occurs	Pressing	None. Article is dust & vapour free. Article loaded to hopper from transport container; assembly into ammunition is done by automated or manual assembly
Route of occupational exposure	Skin, inhalation	Not applicable
Exposure level (lead mg/m^3)	<0.05 mg lead/m^3	Nil
Ventilation conditions	Ventilation present	LEV for removal of other vapours in assembly area, but not specifically designed to remove primary explosive materials
Other exposure control measures	Textile gloves coated with PVC and ordinary respirators	Gloves to protect workers from other materials used in manufacturing process. These are not used to prevent exposure to lead styphnate
Frequency of exposure (days per year)	22	Varies depending on contract need
Duration of exposure per day (minutes per day)	300	Varies depending on contract need
Number of employees exposed	6	Varies depending on contract need

Source: Consultation

5.2.3 Releases and Exposure during End Use of Articles

Releases and Exposure from the Use of Ammunition

The release of and associated exposure to the substance itself during the end use of articles is considered to be minimal. Articles cannot be opened by the user under normal use of ammunition articles.

Literature only addresses exposure to lead rather than lead styphnate due to the limited presence of the substance in the primer, the small likelihood of significant releases of the substance itself (as opposed to lead/lead oxide) and the simultaneous presence of much more significant sources of lead releases and exposure within ammunition articles.

It is suggested that outdoors exposure to the cloud of lead fume and dust near the breach of the weapon or the lead dust generated upon the impact of the bullet around the target does not pose a significant risk to the weapon shooter; in most cases, natural ventilation will either blow away or dilute both clouds. However, in indoor firing ranges, such ventilation and dilution often do not occur, and the potential for exposure to lead could be significant (Lachiver, undated).

Several literature sources provide details of exposure of instructors and users of fire ranges dating back into the 1970s (for example, Anania & Seta, 1975). Results from several studies on exposure to lead are summarised in IARC (undated). A positive correlation was reported between exposure of firearms instructors to elemental lead at covered outdoor firing ranges and increased blood lead concentrations (Tripathi et al, 1991). Concentrations of airborne lead can be significantly reduced (97-99%) by using a lead-free primer and bullets jacketed with nylon, brass or copper (CDC, 1983; Valway et al, 1989; Robbins et al, 1990; Tripathi et al, 1990, 1991; Goldberg et al, 1991; Löfstedt et al, 1999; Bonanno et al, 2002). Other sources of relevant information include Abudhaise et al (1996) (they studied lead exposure in users of military indoor firing ranges in Amman, Jordan), White & Narula (1996) (described a case of lead poisoning in a 37-year old car mechanic who was a recreational user of a UK indoor firing range), Shannon (1999) (reported a case series of four adolescent females who were competitive ‘marksmen’ at the same US indoor firing range with elevated blood lead levels), and Tumpowsky et al (2000) (reported data collected by the Massachusetts Occupational Lead Registry on adults with elevated blood lead levels between 1991 and 1995).

Results from these studies show that lead projectiles are the main source of lead exposure (rather than the primer) where high exposure levels occur. In any case, the amount of lead styphnate per bullet is very small, thus its contribution to lead exposure will be only a fraction of the total.

Releases and Exposure from the Use of Military Munitions

As for small calibre ammunition, literature only addresses exposure to lead rather than lead styphnate. It is suggested thatwhen munitions containing lead styphnate are used inside certain artillery and infantry vehicles with closed hatches and ventilation and dilution of lead aerosols is limited, the potential for exposure to lead could be significant. In addition, soldiers involved in outdoor munitions training (such as tank or howitzer crews) and observers in close proximity to the firing operations may be significantly exposed to aerosolised lead. Although these exposures may not be as consistent as other occupational lead exposures, gunners may experience very high airborne levels for very brief periods of time. Gunners in training will not often be subjected to these levels for more than 30 days per year (Lachiver, undated). Again, lead styphnate is unlikely to be a significant source of lead exposure.

Releases and Exposure to Lead from the Use of Powder Actuated Cartridges

Hilti (2003) suggests that during the use of powder actuated cartridges, lead styphnate is converted to metallic lead and lead oxide (Hilti, 2003). A US insurance company, Liberty Mutual, undertook a study on lead exposure arising from the lead primer contained in powder actuated cartridges. The study found that when as few as 50 to 90 loads are used per shift, the US Occupational Health and Safety Administration (OSHA) Action Limit[23] of 30 µg/m^{3}could be exceeded. This depends upon the type of load, where work is being done (location), and the type of work (overhead, etc.). The report also suggests that the airborne exposure can be estimated based upon the number of rounds. The report goes on to suggest that there are many alternatives to minimising this exposure including: using battery-operated, or pneumatic anchoring tools, loads without lead, decreasing the frequency of use, and finally- respirators. A half-face, tight fitting negative pressure respirator is suggested to be adequate (Industrial Hygiene in Construction, 2010).

Releases and Exposure from the Use of Automotive Pyrotechnics

Consultation with Company 1, an airbag producer, indicates that some lead compounds may be formed upon the detonation of lead styphnate in the airbag igniter. However, such compounds are expected to remain within the inflator.

Releases and Exposure to Lead from the Use of Bullet Hit Squibs

With particular regard to bullet hit squibs containing lead styphnate, Kohler (2005) suggests that a permissible concentration for lead of 0.1 mg/m^3 is easily exceeded multiple times, even inside large spaces, through the sequential serial triggering of sometimes more than a thousand bullet hits of this type. The objects “shot” are also contaminated with lead.

5.3 Worker Exposure Modelling Estimates

5.3.1 Production of Articles

Overview

Exposure during production of articles is considered similar as the exposure during manufacturing of the compound lead styphnate. Manufacturing of articles is commonly done on the same site as the manufacturing of lead styphnate hence similar operational conditions and risk management measures. The articles containing lead styphnate commonly contain very low concentrations of the substance; however, the reasonable worst-case situation during the production process of articles containing lead styphnate is with the pure substance. Besides the pure substance exposure to mixtures containing 20-50% of lead styphnate during transfer has been indicated by the manufactures as situations with high exposure potential. For those mixtures containing up to 50% of lead styphnate we could apply a linear correction for the concentration on the exposure estimated. This would result in the exposure presented in **Table 5.3** and **Table 5.4**.

Scope of Exposure Estimates

For the process steps in closed systems or for remotely controlled activities no calculations are made, as exposure is expected to be negligible.

Exposure estimates with exposure models are made for the activities with potential for exposure:

- transfer of wetted material for further processing either during or after the production process, incl. transfer to the drying trays. Both an “automated transfer” (not remote controlled) and

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[23] “Action level” means employee exposure, without regard to the use of respirators, to an airborne concentration of lead of 30 micrograms per cubic meter of air averaged over an 8-hour period.

"manual transfer" have been assessed up to kilogram amounts. The material is blended with at least 50% other components. For higher percentages of lead styphnate we refer to the estimation made for manufacturing;

- manual transfer of dry material into or from the closed vessels/drying trays. The material is blended with at least 50% other components. For higher percentages of lead styphnate we refer to the estimation made for manufacturing;
- manual transfer of the dry material of small quantities (milligrams) into devices. The material contains up to 100% of lead styphnate; and
- cleaning (final cleaning of equipment and cleaning of the workplace). The spilled material was blended with at least 50% other components. For higher percentages of lead styphnate we refer to the estimation made for manufacturing.

Inhalation Exposure Estimates

Inhalation exposure was estimated using the Stoffenmanager 4.0. The considerations regarding the input parameters are the same as during manufacturing with a few exceptions:

- companies indicated that although the transfer of the milligrams of dry material is performed in well ventilated rooms no local exhaust ventilation is present;
- the material is blended with at least 50% water; and
- manual transfer of the dry material, both has been specifically indicated by a company not to exceed 1 hour of exposure. Other companies indicate transfer of the dry material is only once a day and 200-300g, which is also unlikely to take longer than 1 hour. We assume this duration is both applicable for the transfer of several hundred grams of material as for the transfer of dry material into devices (up to 250 mg per device).

The results are shown in **Table 5.3**. The bottom of the table shows the results expressed in mg of lead per cubic metre (lead accounts for 46% of the molecular weight of lead styphnate).

We will use here the approach followed for the modelling estimates for inhalation exposure during manufacture of lead styphnate (see Section 3.5.3). Therefore, we compare the inhalation exposure estimates to the notional organic lead inhalation exposure limit of 0.05 mg/m^3.

Overall, none of the exposure scenarios with or without the use of PPE would appear to result in the selected OEL value of 0.05 mg/m^3 being exceeded. Therefore, based on the assumptions and calculations made, the inhalation risks for workers are low. The measures taken by producers of articles containing lead styphnate (including PPE) are also noted.

Table 5.3:Input and Results - Inhalation Exposure Estimates during the Production of Articles

Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-several hundred grams**	**Transfer of dry material-manual-filling devices**	**Sampling**	**Cleaning**
Product and substance data						
Physical state of the substance	Solid (wetted)	Solid (wetted)	Solid-dry	Solid (dry)	Solid (wetted)	Solid
Concentration	Up to 50%	Up to 50%	Up to 50%	Up to 100%	Up to 50%	Up to 50%
Dustiness (category)	Solid granules/grains/flakes	Solid granules/grains/flakes	Granules/grains/flakes	Granules/grains/flakes	Solid granules/grains/flakes	Coarse dust
Handling data						
Handling category	Handling of product with low speed or with little force or in medium quantities	Handling of product in very small amounts or in situations where release is highly unlikely	Handling of product in small amounts or in situations where only low quantities of product can be released.	Handling of products in negligible amounts	Handling of product in very small amounts or in situations where release is highly unlikely	Handling of products in negligible amounts
Duration of task or process (hour)	2	2	1	1	1	1
Exposure control data						
Local controls used to limit emission from the source	Containment of the source with local exhaust ventilation	No control measures at the source	Local exhaust ventilation	No control measures at the source	Local exhaust ventilation or containment of the source.	Use of a product that reduces the emission: wetting of product
Source in the near field:	Yes	No	Yes	Yes	Yes	Yes
Other sources of Lead Styphnate in the same room:	Yes	Yes	Yes	Yes	Yes	Yes

Table 5.3:Input and Results - Inhalation Exposure Estimates during the Production of Articles

Task or process assessed		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-several hundred grams**	**Transfer of dry material-manual-filling devices**	**Sampling**	**Cleaning**
Room volume:		Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3	Volume 100-1000 m^3
General ventilation:		General ventilation (mechanical or natural)	General ventilation (mechanical or natural)	General ventilation (mechanical or natural)	General ventilation (mechanical)	General ventilation (mechanical or natural)	General ventilation (mechanical or natural)
Immission controls:		The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin	The employee does not work in a cabin
Work area regularly cleaned:		Yes	Yes	Yes	Yes	Yes	Yes
Equipment regularly inspected and well maintained:		Yes	Yes	Yes	Yes	Yes	Yes
Resulting exposure level estimate							
Worst case (90%) estimation of exposure level (mg/m^3) per task	Without PPE	0.10	0.09	0.47	0.44	0.10	0.22
	With PPE	0.04	0.03	0.19	0.18	0.04	0.09
Worst case (90%) estimation of exposure level (mg/m^3)-8 hours' time average	Without PPE	0.03	0.02	0.06	0.06	0.01	0.03
	With PPE	0.01	0.01	0.02	0.02	0.01	0.01
Worst case (90%) estimation of exposure level (**mg Pb/m^3**) per task	Without PPE	**0.05**	**0.04**	**0.22**	**0.20**	**0.05**	**0.10**
	With PPE	**0.02**	**0.01**	**0.09**	**0.08**	**0.02**	**0.04**

Table 5.3:Input and Results - Inhalation Exposure Estimates during the Production of Articles

Task or process assessed		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-several hundred grams**	**Transfer of dry material-manual-filling devices**	**Sampling**	**Cleaning**
Worst case (90%) estimation of exposure level (**mg Pb/m³**)-8 hours' time average	Without PPE	**0.014**	**0.009**	**0.028**	**0.028**	**0.005**	**0.014**
	With PPE	**0.005**	**0.005**	**0.009**	**0.009**	**0.005**	**0.005**

Source: TNO calculations

Dermal Exposure Estimates

Dermal exposure was estimated using the RISKOFDERM version 2.1 model. The considerations regarding the input parameters are the same as during manufacturing with a few exceptions:

- the substance is generally wetted with water up to 50% this results in a not highly dusty type of product (input in RISKOFDERM: Light or moderately dusty solid). Only for manual transfer of the dry material of small quantities (milligrams) into devices up to 100% has been calculated as this has not been assessed during manufacturing and could also be applicable during manufacturing of articles;
- manual transfer of the dry material has been specifically indicated by a company not to exceed 1 hour of exposure. Other companies indicate transfer of the dry material is only once a day and 200-300g, which is also unlikely to take longer than 1 hour; and
- manual transfer of the dry material is performed when transferring several hundreds of grams and few milligrams into the devices. These small batches were indicated to be approximately 300g (during 1 hour), the transfer into the devices were indicated to be few milligrams up to a few grams but overall approximately 200g (during 1 hour). This results in an application rate of product of respectively 0.005 kg/min and 0.00333 kg/min.

The results are shown in **Table 5.4**. The bottom of the table shows the results expressed in mg of lead per task and per kilogram of bodyweight per day (lead accounts for 46% of the molecular weight of lead styphnate).

Table 5.4:Input and Results – Dermal Exposure Estimates during the Production of Articles

Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-several hundred grams**	**Transfer of dry material-manual-filling devices**	**Sampling**
Product and substance data					
Type of product	Light or moderately dusty solid	Light or moderately dusty solid	Light or moderately dusty solid	Light or moderately dusty solid	Light or moderately dusty solid
Concentration	Up to 50%	Up to 50%	Up to 50%	Up to 100%	Up to 50%
Handling data					
Handling category	Filling, mixing or loading	Filling, mixing or loading	Filling, mixing or loading	Filling, mixing or loading	Filling, mixing or loading
Duration of task or process (hour)	2	2	1	1	1

Table 5.4:Input and Results – Dermal Exposure Estimates during the Production of Articles

Task or process assessed		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-several hundred grams**	**Transfer of dry material-manual-filling devices**	**Sampling**
Exposure control data						
Quality of the ventilation:		Normal or good	Normal or good	Normal or good	Normal or good	Normal or good
Frequency of skin contact:		rare contact	rare contact	rare contact	rare contact	rare contact
Kind of skin contact:		Light contact	Light contact	Light contact	Light contact	Light contact
Significant amount of aerosols:		No	No	No	No	No
Level of automation		Manual	Automated or semi-automated	Automated or semi-automated	Manual	Manual task
Application rate of product (kg/min)		0.5	1.3	5.00E-03	3.33E-03	2.00E-04
Resulting exposure level estimate						
Worst case (90%) estimation of exposure level hand loading (mg/shift)	Without PPE	9.40	15.75	6.50E-02	8.90E-02	3.50E-03
	With PPE	0.94	1.58	6.50E-03	1.00E-02	3.50E-04
Worst case (90%) estimation of exposure level hand loading (mg/kg bw/day)-full shift	Without PPE	0.13	0.23	9.29E-04	1.27E-03	5.00E-05
	With PPE	0.01	0.02	19.29E-05	1.27E-04	5.00E-06
Worst case (90%) estimation of exposure level hand loading (**mg Pb/shift**)	Without PPE	**4.3**	**7.2**	**2.99E-02**	**4.10E-02**	**1.61E-03**
	With PPE	**0.43**	**0.72**	**2.99E-03**	**4.10E-03**	**1.61E-04**
Worst case (90%) estimation of exposure level hand loading (**mg Pb/kg bw/day**)-full shift	Without PPE	**0.06**	**0.11**	**4.27E-04**	**5.84E-04**	**2.30E-05**
	With PPE	**5.98E-03**	**1.06E-02**	**8.88E-05**	**5.84E-05**	**2.30E-06**

Source: TNO calculations

Following the approach taken in Section 3.5.3 for the manufacture of the substance, we will assume that the absorption of the substance through the skin occurs readily, as expected for an organic lead compound and, following a precautionary approach, the intake rate is 100%. Thus, the estimate intake of lead under the scenarios of dermal exposure is as shown in the above table, expressed in mg Pb/shift with and without PPE.

We consequently compare these figures with the lead uptake of 0.05 x 10 x 100% = 0.5 mg per day which can be derived from the inhalation exposure OEL of 0.05 mg/m^3. The table shows that for two scenarios, "*Transfer of wetted material-manual*" and "*Transfer of wetted material-automated*" the 'baseline' intake figure of 0.5 mg/day would be exceeded even with the use of PPE. As before, it is acknowledged that this comparison to inhalation intake is for illustrative purposes only and the estimates are based on a series of assumptions on the processes used and on the behaviour of the substance. If a behaviour akin to inorganic lead compounds was assumed (0.01% absorption rate), the estimated intake would be minimal. Again, we note the engineering and worker protection measures taken by the relevant companies, especially given the nature of the substance which requires that worker contact with the substance be minimised to the degree possible.

5.3.2 Use of Articles

Lead styphnate is used in articles because of its easily triggered explosive decomposition. Consequently, exposure to lead styphnate during the use of the articles is considered negligible, as the substance theoretically, completely decomposes during the use. Products of decomposition contain lead oxides and nitrogen oxides. To prevent preliminary decomposition, lead styphnate needs to be in a completely closed system before the actual use. The closed system also prevents exposure during handling the articles before use.

5.4 Exposure of Consumers

Some of the exposures discussed above, namely exposure to lead arising from the firing of firearms could be relevant to consumers (recreational shooters). Indoor exposure will evidently be more prominent than outdoor exposure. Exposure to lead styphnate is expected to be very limited if any at all.

It is considered unlikely that consumers will have access to 'nail guns' hence lead exposure from the use of powder actuated cartridges is not foreseen.

6 CURRENT KNOWLEDGE OF ALTERNATIVES

6.1 Literature Review ofAlternative Primary Explosives

6.1.1 Alternative Primary Explosives

Multi-component compositions of lead primary explosives with improved performance have been developed for specialised applications in military and civilian ammunition, but long-term environmental contamination, health effects and hazards from extreme sensitivities have made their replacement desirable (Huynh et al, 2006). Work on lead replacements, especially in the USA, has focused on identifying substances that retain energetic properties upon exposure to the atmosphere and must have the following qualities (Huynh et al, 2006):

- insensitivity to light;

- sensitivity to detonation but not too sensitive to handle and transport;
- thermal stability to at least 200°C;
- chemical stability for extended periods;
- absence of toxic metals such as lead, mercury, silver, barium, or antimony; and
- absence of perchlorate, which may be a possible teratogen and has adverse effects on thyroid function.

There are a great variety of primary explosives identified in the open literature. In short, primary explosives may include (Ledgard, 2007; Huynh et al, 2006):

- ammonium and metal salts of nitrophenyls;
- azonitriphenyls;
- ammonium or metal salts of nitrotriazoles and tetrazoles;
- metastable interstitial composites (MICs); and
- co-ordination complexes.

Examples of potential substitute primary explosives include the substances shown in **Table 6.1**. Where detailed information is available, this is presented in the remainder of Section 6. Mercury fulminate (and other fulminates) is not considered a potential alternative as it represents obsolete technology.

Table 6.1: Examples of Alternative Primary Explosives

Alternative	**EC Number**	**CAS Number**
Diazodinitrophenol or 2-diazo-4,6-dinitrobenzene-1-oxide (DDNP)	225-134-9	4682-03-5
Tetrazene or tetracene or 1-(5-tetrazolyl)-4-guanyltetrazene hydrate	*608-603-6	31330-63-9
Triazine triazide (TTA) or 2,4,6-azido-1,3,5-triazine or cyanuric triazide (CTA)	-	5637-83-2
Potassium 4,6-dinitro-7-hydroxy-7-hydrobenzofuroxan (KDNBF) and potassium or sodium 7-hydroxy 4,6-dinitrobenzofuroxan (KDNP)	-	See note below
Mixtures of aluminium nanoparticles and heavy metal oxides such as molybdenum trioxide and bismuth trioxide	215-204-7 (MoO_3) 215-134-7 (Bi_2O_3)	1313-27-5 (MoO_3) 1304-76-3 (Bi_2O_3)
Complex metal dianions and environmentally benign cations, $(cat)_2[M^{II}(NT)_4(H_2O)_2]$ (where cat is NH_4^+ or Na^+, M is Fe^{2+} or Cu^{2+}, and NT^- is 5-nitrotetrazolato-N^2)	N/A	N/A
Zirconium/potassium perchlorate	231-176-9 (Zr) 231-912-9 ($KClO_4$)	7440-67-7 (Zr) 7778-74-7 ($KClO_4$)

Source: Huynh et al (2006); Mayer et al (2007); Agrawal (2010); Mehta et al (undated); Fronabarger et al (undated)

Note: a CAS/EC number has not been found for KDNBF but the CAS Number of the apparent isomer potassium 4-hydroxy-5,7-dinitro-4H-2,1,3-benzoxadiazol-1-ide3-oxide is 42994-94-5

It is of note that efforts to find alternatives to lead styphnate and lead azide in the USA have been made over several decades, especially in the military field. Fronabarger *et al* (2010) indicate that under NAVSEA Instruction 8020.3A (1986), limits on the use of lead azide in US Navy ordnance were imposed. In non-hermetic systems, lead azide may generate hydrazoic acid, a gas which can migrate and react to form unstable copper azide; fatalities have occurred in the USA. Also, under

Executive Order 12856 (1993), the procurement of hazardous substances and chemicals by US federal facilities had to be reduced/eliminated.

There are also substances with similarities to lead styphnate which may be considered alternative substance. These include salts of picric acid such as lead picrate (2,4,6-trinitrophenol, lead salt) and ammonium picrate as well as other styphnate salts. These are discussed in Section 6.2.

6.1.2 Individual Alternatives to Lead Styphnate

Diazodinitrophenol (DDNP) and SINTOX Primer Compositions

DDNP is less sensitive to impact than mercury fulminate, lead styphnate or lead azide. It is more stable and brisant than mercury fulminate and is used in blasting caps, loading fuse detonators and in priming compositions for civilian and military use. Some investigators are of the opinion that DDNP alone is not suitable as an initiating material for detonators because it requires too long a path to change from burning to detonation and hence it is necessary to add another initiating material such as lead azide. DDNP does not become dead pressed even under a pressure of 9,140 kg/cm^2 which is considered a great advantage for an initiating material. It has good storage properties and is a preferred initiating explosive particularly in the USA and Japan as it is relatively insensitive to impacts and friction compared to other initiating explosives (Agrawal, 2010).

A company has suggested that the synthesis of DDNP has poor reaction yield (resulting in increased production of waste) and involves several toxic raw materials and intermediates. The company has argued that issues of reaction yields and of toxicity of raw materials and of produced wastewater have been examined in a recent paper by Zong-Wei et al (2010).

Use of DDNP in SINTOX Lead-Free Primers

To solve the issue of lead, antimony and barium emissions when ammunition is discharged, Dynamit Nobel AG developed a non-toxic primer composition called SINTOX. Lead styphnate is replaced by DDNP and the barium nitrate and antimony sulphide are replaced by a mixture of zinc peroxide and titanium metal powder. The SINTOX primer mixture contains tetrazene, diazole, zinc peroxide/titanium powder, and nitrocellulose ball powder (Smyth Wallace, 2008).

A company placing on the market SINTOX primers claims that SINTOX offers reliability and functional stability under extreme conditions and retains stability in storage also under critical storage conditions. SINTOX has extraordinary ignition sensitivity without formation of corrosion or erosion in the barrel and has successfully been marketed for more than twenty years and is used with several NATO-qualified cartridges (RUAG, 2011).

Use of DDNP in MEMS Propellants

DDNP has also been considered as a propellant for MEMS. Recently Kyushu University in Japan proposed a DDNP application for MEMS rockets. DDNP can be synthesised to a round shape of 80 to 500 micrometers in diameter, which remarkably improves its handling. The ideal specific impulse of DDNP is 69.5s, which is lower than glycidyl azide polymer (97.9s) but higher than gunpowder (57.1s). The low ignition point (180°C) is another advantage. A 200μm order rocket using DDNP has successfully fired in atmospheric pressure (Takahashi, 2006)[24].

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[24] Notably, other potential propellants for MEMS under testing mentioned by Takahashi (2006) (beyond DDNP and lead styphnate) include glycidyl azide polymer, boron/potassium Nitrate B/KNO3), lead rhodanide (thiocyanate)-

Tetrazene (Tetracene)

Despite the fact that lead azide, lead styphnate and tetrazene suffer from serious drawbacks, they are still being used in detonators and cap compositions for military and civil applications. Thus, lead azide, lead styphnate and tetrazene are the most commonly used primary explosives (Agrawal, 2010).

Tetrazene explodes when subjected to a temperature of 160°C for 5 seconds and is not stable at temperatures above 75°C. It is as sensitive to impact as mercury fulminate and DDNP. When exposed to a flame, it undergoes a mild explosion with the production of black smoke. When subjected to high pressure, it becomes 'dead-pressed'. As the density increases, its brisance declines. Its power is slightly higher than that of mercury fulminate but it does not have sufficient initiating efficiency to permit its use alone as an initiatory explosive. It can, however, act as a good sensitising agent to other initiatory explosives and mixtures and, therefore, finds extensive use in cap compositions. It is used in primer cap compositions where as little as 2% in the composition results in an improved uniformity of percussion sensitivity (Agrawal, 2010).Tetrazene cannot be considered as a direct replacement for lead-based primary explosives.

High Nitrogen Compounds

Oyler et al (undated) report that a current focus in the field of new energetic discovery is the area of high-nitrogen molecules. Although not strictly defined, these compounds are generally considered to be molecules which contain 50% or more nitrogen content by atom. As a result, the major detonation product formed from energetic high nitrogen compounds is diatomic N_2, which is both non-toxic and gaseous, meaning it is less likely to give off unwanted solid residues. Also of great importance, the high stability, low-energy state of the N_2 product results in potentially large energy output during detonation – high nitrogen compounds typically possess high heats of formation. Typically, high nitrogen systems take the form of heterocyclic rings such as substituted tetrazines or tetrazoles.

One high nitrogen compound that has been investigated extensively as a replacement for lead azide is triazine triazide (TTA), also referred to as 2,4,6-azido-1,3,5-triazine or cyanuric triazide (CTA). TTA is a known energetic material with high impact and friction sensitivity and energy performance comparable to lead azide. It was preliminarily investigated in the mid-1900s but was abandoned over concerns regarding its high sensitivity. Recent recrystallisation efforts have been successful in producing the material in a safer to handle form and allowed it to be synthesised at the 50 g level, possibly allowing for its use as a lead-based explosive replacement (Oyler et al, undated). Mehta et al (undated) discuss how CTA may be used in the fuses of grenade detonators where it may replace the combined use of lead styphnate and lead azide.

Dinitrobenzofuroxans

Investigation of dinitrobenzofuroxans such as the known potassium 4,6-dinitro-7-hydroxy-7-hydrobenzofuroxan (KDNBF) and experimental potassium or sodium 7-hydroxy-4,6-dinitrobenzofuroxan (KDNP) as lead styphnate replacements has reportedly indicated that the furoxan group effectively serves as a sensitising group for these materials. In addition, the presence of a phenoxide group in KDNP allows for facile non-heavy metal salt formation, and thus a higher melting point and ignition temperature (271ºC). It is believed that KBFNP may find uses in actuators or unconfined micro-propulsion applications (Fronabarger et al, undated).

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based explosive, nitrocellulose, HMX, RDX, HTPB/AP/AL, PETN, zirconium perchlorate potassium and gunpowder (KNO3/C/S/NH4ClO4/Al).

Fronabarger et al (2010) suggest that, like lead styphnate, KDNP is a fast deflagrating material with good thermal stability and safe handling characteristics. It appears suitable as a drop-in replacement for lead styphnate and it offers high performance. It was approved as "safe and suitable for service use and qualified for weapons development" in the USA in February 2009.The same source provided details of official documentation by the US Navy confirming that KDNP is a green replacement for lead styphnate and that the US Naval Sea Systems Command qualified KDNP as a primary explosive in accordance with the requirements of NAVSEAINST 8020.5C.

KDNP has been evaluated versus lead styphnate successfully in a variety of applications including (Fronabarger et al, 2010):

- CCU-63 Impulse Cartridge – in a bridgewire slurry mix;
- TOW Missile Initiator Units – pressed onto bridgewire;
- PVU-12/A Percussion Primers;
- Reactive Semi-Conductor Bridge (RSCB) technology to interface between the electrical circuit and the energetic material output charge – as consolidated/unconsolidated output; and
- various pressure-time (closed bomb) tests – it reportedly has higher impetus, equivalent ignition time and faster rise time compared to lead styphnate.

Mixtures of Nanoparticles and Heavy Metal Oxides

Metastable Intermolecular Composite (MIC) materials have the potential to replace the current conventional energetic compositions in percussion primers used in munitions and cartridge actuated devices. These materials, being comprised of nano-sized particles, offer the possibility of tuneable energy release and high temperatures without appreciable gas generation and attendant high pressures. One unique feature of MIC materials is their ability to produce particles hot enough to ignite a bed of propellant. Additionally, the MIC materials are impact-sensitive which makes them good percussion primer mix candidates (Allen, undated). On the other hand, instability toward atmospheric oxygen and moisture, safety concerns during large-scale production and residual heavy metal contaminations have so far prevented the adoption of MICs as lead salt replacements (Huynh ***et al, 2006).***

Literature suggests that the US Navy has in place a lead styphnate replacement programme under which the Los Alamos National Laboratory has developed nano-scale thermite-like mixtures. One in particular, a 55/45 weight per cent Al/MoO3 composition had been loaded into commercial No. 41 percussion primers for evaluation for use in small arms ammunition. Given the similarity between the No. 41 and the PVU-1/A primers that are used by the US armed forces, several lots of PVU-1/A hardware were also loaded with the Al/MoO3 MIC composition and evaluated. The next table shows the composition of these two key traditional primers used by the US military.

Table 6.2: Composition of Lead Styphnate Primers in Small/Medium Calibre Ammunition and CAD/PAD that may be Replaced by Nano-mixture Primers

FA-956 Primer Mix (No. 41 Primer) for small and medium calibre ammunition		**5086 Primer Mix (PVU-1/A Primer) for CAD/PAD**	
Ingredient	**Weight (%)**	**Ingredient**	**Weight (%)**
Normal lead styphnate	37.0	Normal lead styphnate	26.0
Barium nitrate	32.0	Barium nitrate	41.5
Antimony sulphide	15.0	Antimony sulphide	20.0
Tetrazene	4.0	Tetrazene	2.0

Aluminium powder	7.0	Calcium silicide	10.5
PETN	5.0		
Source: Allen (undated)			

In the course of the evaluation, Bi2O3 oxidiser was also used. The results have been promising (Ostrowski et al, undated).

Allen (undated) supports the view that Al/MoO3 mixtures can be used in small and medium calibre arms ammunition primers but also in Cartridge Actuated Devices and Propellant Actuated Devices (CAD/PAD) used in US Navy aircraft ejection systems, countermeasure applications and stores release systems. These can be used in preference to DDNP which Allen claims show poor performance in cold temperatures (the required temperature range is -54°C to +93°C).

Dixon (2004) further suggests that the US Navy holds a key patent in the area of substituting MICs for the lead styphnate and barium nitrate normally used in electric primers for medium calibre gun munitions. As above, the various MIC compositions are fundamentally a mixture of nano-aluminium and MoO3 as an oxidiser. The general configuration of an experimental primer based on such a mixture can be virtually identical to that used in the fabrication of the currently operational M52A3B1 electric primer used in US military 20mm munitions.

Finally, Oyler et al (undated) indicate that nano-porous silicon composites may also be used as alternative primers. In 2001, Kovalev et al reported the observation of explosive reactions even at cryogenic temperatures when porous silicon was immersed in liquid oxygen (Kovalev et al, 2001). This discovery was extended to more conventional composites in 2002 when Mikulec et al incorporated gadolinium nitrate into porous silicon, which was observed to explode when triggered by friction or an electric spark (Mikulec et al, 2002). Additionally, porous silicon composites have also been studied by researchers at the US Army Research Laboratory as initiators for devices such as MEMS. Solution-based incorporation of various inorganic oxidisers was carried out by Clément et al (2005). An advantage of the silicon framework is that it provides large potential as a fuel in energetic systems. The theoretical energy yield from the oxidation of Si is 14 kJ/g (compared to 9 kJ/g for carbon and 16 kJ/g for aluminium). Although the yield from Al is slightly higher, aluminium particles readily form a coating of energetically useless Al2O3 at their surface – this becomes a particular problem when dealing with small particle sizes, as a significant portion of each particle will be oxide (Oyler et al, undated).

Explosive Complexes

Huynh et al (2006) report on green primary explosives based on complex metal dianions and environmentally benign cations, (cat)2[MII(NT)4(H2O)2] (where cat is NH4+ or Na+, M is Fe2+ or Cu2+, and NT- is 5-nitrotetrazolato-N2). These have been tested and found to be safer to prepare, handle and transport than lead compounds, have comparable initiation efficiencies to lead azide, and offer rapid reliable detonation comparable with lead styphnate. They possess all current requirements for green primary explosives and are suitable to replace lead primary explosives in detonators.

The researchers describe the (cat)2[MII(NT)4(H2O)2] salts as follows (Huynh et al, 2006):

"*the only technologically advanced materials that meet all current criteria for green primary explosives and hold great promise as lead replacements in detonators because they (i) are synthesised by a green process that generates innocuous waste by-products (H2O, NaCl, or NH4Cl,* *and NaNO3 or NH4NO3), (ii) have controllable explosive sensitivities allowing for mitigation of unexpected accidents, and (iii) deposit undisruptive decomposition products (iron or copper, N2, CO2, H2O, 2% of NO2, and 3% of CO) to the environment, avoiding the heavy metal contamination".*

Other recent examples of coordination complex primaries are tetraammine and pentaammine cobalt(III) complexes, e.g., tetraamminedi (5-nitrotetrazolate-N2) cobalt(III) perchlorate ([CoIII(NH3)4(NT)2]ClO4), pentaammine(5-cyanotetrazolateN2)cobalt(III) perchlorate ([CoIII(NH3)5(CAT)](ClO4)2), and pentaammine (5-aminotetrazolate-N2) cobalt(III) perchlorate ([CoIII(NH3)5(DAT)](ClO4)3). Their sensitivity and performance can be varied with the number of perchlorate groups; however, perchlorate is a possible teratogen and has adverse effects on thyroid function (Huynh et al, 2006b).

Zirconium/Potassium Perchlorate

Numerous references are made in literature of the use of mixtures of zirconium and potassium perchlorate as primers in igniters for automotive airbags and other devices (Erjavec, 2005; Katsuda et al, 2002; Miyake et al, 1994).

Mixtures for Bullet Hit Squibs

Kohler (2005) explains why individual alternative primers may not be suitable to replace lead styphnate in bullet hit squibs (for example, DDNP has an unsatisfactory detonation reaction when uncompressed and, when compressed, it is much too brisant at quantities of more than 40 mg; tetrazene results in very strong smoke formation and its thermal long-term stability is unsatisfactory).

Pyrotechnic bodies meet all requirements for detonating compositions if they contain (Kohler, 2005):

- at least one primary explosive selected from a first group consisting of non-toxic metal cations of a mono- and a dinitrohydroxydiazobenzene ("diazinate");and
- at least one primary explosive selected from a second group consisting of a ditetrazole compound of highly nitrated organic compounds from salts of the ditetrazole and aromatic nitro bodies having easily replaceable molecule groups and non-toxic metal cations of a dinitrobenzofuroxan.

By varying the proportions of these primary explosives in their mixture, with the optional use of other primary and/or secondary explosives (also free of heavy metals, and possibly further additives such as oxidation and binding agents), it is possible to produce pyrotechnic detonating compositions which allow complete detonation with low smoke and without forming flames at any desired tamping. Such detonating compositions may contain (Kohler, 2005):

- the non-toxic metal cations of 4,6-dinitrobezofuroxan, diazodinitrophenol (2-diazo-4,6-dinitrophenol), 4-diazo-2,6-dinitrophenol, tetrazene, diazodinitrobenzene (styphnic diazide), triazidotrinitrobenzene, 2-picryl-5-nitrotetrazole, 2-methyl-5-nitrotetrazole; and
- the non-toxic metal cations of 5-nitraminotetrazole, 4-hydroxyamino-5,7-dinitrobenzofurazine-3-oxide, 5,5-diazoaminobitetrazole, 5,5-azotetrazole, azidodinitrophenol, and polynitrophenolates as further primary explosives.

Past Attempts to Develop Alternatives for Priming Mixtures

Smyth Wallace (2008) provides an extensive account on the efforts made since the 1920s to identify alternatives to lead-based primers (apparently without success). Examples have included:

- hypophosphite salts, such as calcium hypophosphite;
- mixtures of stabilised red phosphorus (18%) and barium nitrate (82%) which was later on supported by PETN, RDX or TNT;
- basic lead picrate-clathrate inclusion compounds which did not have the static electricity hazard of lead styphnate; and
- pyrophoric metal alloys, such as “mischmetal” (cerium 50%, lanthanum 40%, other rare earth elements 3% and iron 7%).

6.2 Possible Replacement of Lead Styphnate by Similar Substances

6.2.1 Identities of Potential Alternatives

We have examined whether there any substances similar to lead styphnate (isomers, technical grades, reaction masses, derivatives with different substituents) which could potentially replace the substance in one or more of its known applications. The obvious candidates are picrates and styphnates such as barium styphnate, potassium styphnate and calcium styphnate. Azides such as silver azide may be considered as potential alternatives for lead azide (and are discussed in the lead azide report) but not for lead styphnate.

6.2.2 Hazard Profile of Potential Alternatives

Table 6.3 shows the classification and labelling for salts of picric acid according to the CLP Regulation. Whilst the salts are not without hazards, their hazard profile is apparently much more benign than lead azide. On the other hand, if classification of lead compounds is considered instead (also available in Table 6.3), this appears to not substantially differ to that of lead styphnate, with the exception of the explosive properties that lead styphnate is classified for.

Table 6.3: Classification of Salts of Picric Acid and of Lead Compounds according to the CLP Regulation

Chemical	Classification		Pictograms
	Hazard Class and Category Codes	Hazard Statement Codes	
Salts of picric acid	Unst. Expl Acute Tox. 3 * Acute Tox. 3 * Acute Tox. 3 *	H201 H331 H311 H301	Exploding bomb Skull and crossbones

Lead compounds with the exception of those specified elsewhere in Annex VI of the CLP Regulation	Repr. 1A	H360Df	
	Acute Tox. 4 *	H332	
	Acute Tox. 4 *	H302	
	STOT RE 2 *	H373 **	
	Aquatic Acute 1	H400	
	Aquatic Chronic 1	H410	

Source: ESIS Internet site, http://ecb.jrc.ec.europa.eu/esis/index.php?PGM=cla

** indicates that the classification corresponds to the minimum classification for a category*
*** the classification under 67/548/EEC indicating the route of exposure has been translated into the corresponding class and category according to this Regulation, but with a general hazard statement not specifying the route of exposure as the necessary information is not available*

With regard to barium styphnate and potassium styphnate, classification and labelling details have not been identified in the CLP or indeed from other sources, although hazards similar to lead styphnate might arise. They are given a hazard Class of 1.1A and a transport identification number of UN0473 (CAMEO Chemicals, 2011; US DoT, 2011). Ledgard (2007) notes that barium styphnate crystals are stable, but may detonate if strongly heated and they deflagrate on ignition.

6.2.3 Technical Suitability of Potential Alternatives

Picrates

Lead picrate is more sensitive than any other metal picrate and, due to this hazard, it has now been replaced by more modern and superior explosives. Lead picrate is extremely sensitive to impact and is considered dangerous for practical use (Agrawal, 2010). Picrates are known for decades and still have not been as widely used as lead styphnate (or lead azide) in the applications discussed in this report. Moreover, the SIC BREF Document would suggest a very low production capacity for lead picrate compared to lead styphnate (<0.3 t/y in 2004) which could make replacement difficult. Of note is the presence of lead picrate (as well as lead azide) in one of the detonator mixtures presented in Table 4.4 (Reference 15). Lead picrate is present at very low levels, much lower than lead styphnate or lead azide.

Styphnates

Ledgard (2007) suggests that barium styphnate is “well suitable” for use in priming compositions for bullets, pyrotechnic compositions and rocket propellants. However, it is primarily used as a substitute for lead styphnate in initiation compositions. The same source claims that barium styphnate should be stored submerged in kerosene.

A very recently published US patent also discusses the suitability of styphnate salts as primary explosives in a variety of applications. Bley et al (2011) start from the premise that conventional primer substanceshave the disadvantage that, owing to low decomposition temperatures, cannot be used in the engine compartment of motor vehicles. In the engine compartment of a motor vehicle, temperatures of 140°C and higher are reached, which requires a decomposition temperature of a primer substance of over 300°C. Potassium dinitrobenzofuroxanate KDNP, for example, has a decomposition temperature of ca. 220°C and is therefore unsuitable for this purpose. The researchers investigated the development of substancesthat are suitable as primer substanceswith a decomposition temperature of over 300°C, which are free from heavy metals, are suitable for both mechanical and electrical ignition systems (thus can be used in vehicle safety systems, ammunition and propellant cartridges for powder actuated tools), and/or the preparation of which is possible by simple industrial processes. The patent refers to a salt of styphnic acid that is selected from the group consisting of potassium-calcium styphnate, basic potassium-calcium styphnate and basic calcium styphnate. These styphnates can be used according to the invention as a primer substance both individually and in a mixture with one another and/or optionally in a mixture with the conventional additives, such as e.g. oxidising agents, reducing agents, sensitising agents, binders, high-energy additives and combustion modifiers and processing auxiliaries (Bley et al, 2011). Examples of the types of additives are provided in the patent document.

The patent also suggests that the new primers, apart from absence of heavy metals and high thermal stability, in the case of calcium styphnate and potassium-calcium styphnate, contain calcium, which is advantageous for weapons systems through the formation of calcium carbonate in the combustion residues, as a result of the favourable tribological properties of calcium carbonate (Bley et al, 2011).

For completeness, Table 6.4 is provided overleaf. This presents a summary of primary explosives with some structural similarities to lead styphnate and compares some key technical characteristics as well as their stability, toxicity and overall perceived value as primary explosives, as presented by Ledgard (2007).

The table shows that some of these primary explosives may not necessarily be less hazardous (or sensitive) than lead styphnate. However, the table only provides a quick overview and cannot be assumed to provide a conclusive comparison or properties or a clear assessment of technical suitability. In any case, lead-based alternatives are not considered to be ‘green explosives’ and it is doubtful that they may be considered to be suitable alternatives to lead styphnate.

Table 6.4: Key Properties of Primary Explosives with Structural Similarities to Lead Styphnate

Substance Name	CAS Number	Properties						
		Molecular Weight	**Detonating Velocity (m/s)**	**Sensitivity**	**Stability**	**Flammability**	**Toxicity**	**Overall value (as a primary explosive)**
Lead azide	13424-46-9	291.242	5,000 (± 15)	Easily detonated	Moderate	Explodes when ignited	Moderate	High
Lead styphnate (2,4,6-trinitro-lead-II-resorcinate)	15245-44-0	691.501 (basic lead styphnate) 450.287 (normal lead styphnate)	7,300 – 7,600	High	Moderate	Explodes when ignited	Moderate	Very high
Lead-TNP – (Trinitrophloroglucinol lead salt)	51325-28-1	1065.69	Not calculated	High	Moderate	Explodes when ignited	Moderate	Moderate
Barium styphnate	20236-55-9	253.898	Not calculated	Moderate	Good	Flashes when ignited	Moderate	Moderate
Ammonium picramate (Ammonium 2-amino-4,6-dinitro phenolate; Ammonium-2-amino-4,6-dinitro picrate)	-	216.153	Not calculated	High	Moderate	Highly flammable (deflagrates)	Moderate	High
Ammonium picrate	131-74-8	246.135	6,500	High	Moderate	Flammable – may flash when ignited	Low	High
Lead picrate (2,4,6-trinitro-lead-phenolate basic)	25721-38-4	452.303	Similar to Ammonium picrate	High	Moderate	Explodes when ignited	Moderate	Moderate
Sodium picramate (Ammonium 2-amino-4,6-dinitro phenolate; Ammonium-2-amino-4,6-dinitro picrate)	831-52-7	221.104	Not calculated	High	Moderate	Highly flammable (deflagrates)	Moderate	Moderate

Source: Ledgard (2007)

6.2.4 Substitution of Lead Styphnate by Lead Azide

Finally, there is no evidence that lead styphnate can be interchanged with lead azide in its known applications. Both substances are frequently jointly present in primer mixtures but lead styphnate is the main primary explosive in primers for small calibre (military/sport/hunting) ammunition while lead azide is mostly used in detonators. There has been no suggestion by any consultee that one can successfully act as a replacement for the other. The initiating and ignition characteristics of the two substances are different; thus, the replacement of the styphnate by the azide is unrealistic.

6.3 Experiences of EU Industry with Alternatives

6.3.1 Overview of Consultation Responses

Four alternative substances and one alternative technology have been named by consultees as potential alternatives but without having the ability to fully replace lead styphnate in its applications. These confirm some of the information identified in the open literature. Companies submitting the relevant information have requested that this be treated as confidential; therefore, the identities of these alternatives cannot be revealed here but are given in the Confidential Annex (Section A6). In short, the information submitted in confidence by companies indicates that:

- not all companies are currently working on alternatives and several of them could not name any substance/technique as a possible alternative;
- there is significant concern among companies with regard to the qualification and certification of alternative primer mixtures. In particular, articles intended to be used by military personnel (ammunition, detonators, munitions, CADs) need to meet specific requirements typically set by relevant authorities/defence agencies. It is not possible for the ammunition producer to unilaterally change an approved composition;
- R&D work will definitely be required and changes to products and processes to accommodate alternative substances would be very likely; and
- suggestions on the timeframe of R&D required for the development and qualification of alternative compositions range from 5 years to more than 25 years without a clear indication (at present) that efforts might be fruitful for all applications of lead styphnate.

The Federation of European Explosives Manufacturers has also made an input in relation to alternatives. The Federation notes that DDNP has been used as alternative primary explosive since end of the 19th Century. However, it has unpleasant aspects – dermal effect issues and unclear toxic consequences; DDNP is much less known substance compared to lead styphnate. In addition, DDNP is a part of nitro-aromatic substances, which do not have a good toxicological profile. The fact that there is no European producer of detonators who uses DDNP in industrial detonators is, according to the Federation, proof that DDNP is not a suitable alternative to lead styphnate (Federation of European Explosives Manufacturers, 2011b).

6.3.2 Potential Cost of Alternatives

In respect of the cost of replacing lead styphnate (and lead azide), one consultee has noted that it is very difficult to individually assess the costs for qualifying and approving a new detonator or primer cap containing alternative primary explosives. The explosive would have to be fully tested to confirm all aspects of safety in manufacture and filling of the new design. Each design of cap/detonator would have to undergo a series of tests to prove it is safe, and to qualify for use. Its use in every specific type of article would also have to be tested to ensure that throughout the article's service life it remains safe and functions reliably in all environmental conditions that it will be used in. Moreover, ammunition for military use can have a long life (possibly up to 20 years) before it is used.

The cost of testing depends on the requirements of the customer, which in turn may be dictated by military specification and national/international legislation. As a very rough assessment, the qualification of a new primer cap or detonator would cost several hundred thousand Euros for each new design. The qualification of the new article in its use would also cost money, though it is more difficult to assess this, as costs depend on the complexity of the nature of munition. These could vary from several hundreds of thousands of Euros to millions of Euros. There are many hundreds of ammunition/detonator/munition designs in production within the EU and every one in which a new detonator is used would have to be tested.

6.3.3 Views of Industry Stakeholders on the Suitability of Picrates and Lead Azide

Views of consultees on the suitability of picrates as a replacement for lead styphnate and on the potential for replacement of lead styphnate by lead azide are provided in the Confidential Annex (Section A6.4). Consultees generally do not believe that replacement of lead styphnate by these substances is possible.

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ANNEX 1. GLOSSARY

Term	**Description**
ANFO	Ammonium Nitrate/Fuel Oil. ANFO is a widely used explosive mixture
ASA	Lead Azide, Lead Styphnate and Aluminium. ASA compound is a primary explosive used in many detonators
$BKNO_3$	Boron Potassium Nitrate
Brisance	Brisance is the shattering capability of an explosive. It is a measure of the rapidity with which an explosive develops its maximum pressure
CAD	Cartridge-Actuated Device. A CAD is a small explosive device used to eject stores from launched devices, actuate other explosive systems, or provide initiation for aircrew escape devices
COD	Chemical Oxygen Demand. Quantity of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD is expressed in mg/L O2
CTA	Cyanuric Triazide. It is also known as ,4,6-azido-1,3,5-triazine, triazine triazide (TTA) or cyanuric triazide (CTA)
DDNP	Diazodinitrophenol. DDNP is often used as an initiating explosive in propellant primer devices and is a substitute for lead styphnate in what are termed “non-toxic” (lead free) priming explosive compositions
DDT	Deflagration-to-Detonation Transition. DDT refers to the transition between a deflagration type of combustion to a detonation type of combustion
FCDC	Flexible Confined Detonating Cord. FCDC is mild detonating cord that has various layers such as polyethylene, fiberglass, kevlar, stainless steel and copper wire braiding to ensure confinement of the products of detonation once the material has been incorporated into a complete assembly
Hexogen	RDX, see below
HMTD	Hexamethylene tirperoxide, a high explosive organic compound
HMX	HMX (also called octogen) is a powerful and relatively insensitive nitroamine high explosive, chemically related to RDX

Term	Description
HNS	Hexanitrostilbene. HNS (also called JD-X) is a heat resistant, nitro-aromatic, insensitive secondary explosive.Other names include 1,1’-(1,2-ethenediyl)bis[2,4,6-trinitrobenzene];1,2-bis-(2,4,6-trinitrophenyl)-ethylene; hexanitrodiphenylethylene. It is commercially produced by oxidizing trinitrotoluene (TNT) with a solution of sodium hypochlorite. HNS boasts a higher insensitivity to heat than TNT, and like TNT it is very insensitive to impact
KDNBF	4,6-dinitro-7-hydroxy-7-hydrobenzofuroxan
KDNP	Sodium 7-hydroxy-4,6-dinitrobenzofuroxan
LEV	Local exhaust Ventilation, a ventilation system that takes dusts, mists, gases, vapour or fumes out of the air so that they cannot be breathed in
MEMS	Microelectrical Systems
MIC	Metastable Interstitial Composites are materials comprised of nanoscale composite energetic materials, often a metal and an oxidiser. These materials have found a variety of applications including as electric and percussion igniters or primers
Micro gas generator	A micro gas generator generates gas for a seatbelt pre-tensioner device, which winds up the seatbelt and instantly restrains the occupant’s body when a vehicle collision occurs. A sensor detects the collision, and an electrical signal is sent to the micro gas generator. The squib (igniter) inside the micro gas generator ignites the gas-generating agent. The generated gas pressure becomes the dynamic force that winds up the seatbelt
NACE codes	NACE Codeis a pan-European classification system which groups organisations according to their business activities. It assigns a unique 5 or 6 digit code to each industry sector
Nitropenta	PETN, see below
NOL-130	NOL-130 is a primer mix. It is comprised of lead styphnate (basic) 40%, lead azide (dextrinated) 20%, barium nitrate 20%, antimony sulphide 15%, and tetrazene 5%
PAD	Propellant Actuated Devices
PETN	Pentaerythritol Tetranitrate. PETN (also known as PENT, PENTA, TEN, corpent or penthrite) is the nitrate ester of pentaerythritol, a polyol. It is one of the most powerful high explosives known
RDX	Research Department Explosive. RDX (also known as cyclonite or hexogen) is an explosive nitroamine widely used in military and industrial applications. As an explosive, it is usually used in mixtures with other explosives and plasticisers, phlegmatisers or desensitisers. It is stable in storage and is considered one of the most powerful and brisant of the military high explosives
RSCB	Reactive Semi-Conductor Bridge, fast acting, low energy electro-explosive devices. SCB initiators are extremely efficient at converting electrical energy to explosive energy to produce a squib or detonation output

Term	**Description**
SIC	Speciality Inorganic Chemical (SIC) is taken to mean an inorganic substance manufactured industrially by chemical processing, generally in relatively small quantities, according to specifications (i.e. purity) tailored to meet the particular requirements of a user or industry sector
SINTOX	A non-toxic primer composition developed by Dynamit Nobel AG. Lead styphnate is replaced by DDNP and the barium nitrate and antimony sulphide are replaced by a mixture of zinc peroxide and titanium metal powder. The SINTOX primer mixture contains tetrazene, diazole, zinc peroxide/titanium powder and nitrocellulose ball powder
TATNB	1,3,5-traizido-2,4,6-trinitrobenzene. TATBNB is an aromatic high explosive composed of a benzene ring with three azido groups (N_3) and three nitro groups (NO_2) alternating around the ring. It has the chemical formula $C_6(N_3)_3(NO_2)_3$. Its velocity of detonation is 7,350 meters per second, comparable to TATB and CPN (CycloPropenium Nitrate)
TATP	Triacetone triperoxide. This is an organic peroxide and a primary high explosive. It takes the form of a white crystalline powder with a distinctive acrid odour
Tetryl	2,4,6-trinitrophenylmethylnitramine commonly referred to as tetryl ($C_7H_5N_5O_8$) is a sensitive explosive compound used to make detonators and explosive booster charges. Tetryl has been largely superseded by RDX
TGTH	Tetrazene or tetracene or 1-(5-tetrazolyl)-4-guanyltetrazene hydrate. Used for sensitization of priming compositions
TNT	2,4,6-trinitrotoluene. TNT is one of the most commonly used explosives for military and industrial applications