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 diazide**
EC Number:	**236-542-1**
CAS Number:	**13424-46-9**

Submitted by: European Chemical Agency at the request of the European Commission

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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 diazide**
EC Number:	**236-542-1**
CAS number:	**13424-46-9**

- 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 diazide is covered by index numbers 082-003-00-7 and 082-003-01-4 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 diazide 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

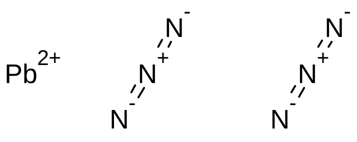
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1.1: Substance identity

EC number:	236-542-1
EC name:	lead diazide
CAS number (in the EC inventory):	13424-46-9
CAS number:	13424-46-9 69985-35-9 Lead azide (Pb(N3)) 73513-16-3 Plumbane, tetrazido-
Deleted CAS number:	85941-57-7
CAS name:	Lead azide (Pb(N3)2)
IUPAC name:	Lead(2+) diazide
Index number in Annex VI of the CLP Regulation	082-003-00-7
Molecular formula:	N_6 Pb
Molecular weight:	291.2 g/mol
Synonyms:	---

Structural formula:



1.2 Composition of the substance

Name: lead diazide

Description: not relevant

Degree of purity: 88 – 98 %

Table 1.2: Constituents

Constituents	Typical concentration	Concentration range	Remarks
Lead diazide EC number: 236-542-1		88 – 98 %	Based on the registration dossiers received

Table 1.3: Impurities

Impurities	Typical concentration	Concentration range	Remarks
See confidential Annex 2			

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 Colourless, spicular crystals	*Discussion and the value used for Chemical Safety Assessment (CSA) reported in the endpoint summary*	Bornscheuer, U.; Roempp; Georg Thieme Verlag KG, 2008
Water solubility	0.023 g /100 g at 18 °C	*idem*	O'Neil, Maryadele J.; The Merck Index; Merck & Co Inc.; Whitehouse Station, NJ, USA; 14th Edition; 2006

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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 diazide is covered by Index number numbers 082-003-00-7 and 082-003-01-4 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)**		
082-003-00-7	Lead diazide; lead azide	236-542-1	13424-46-9	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
082-003-01-4	Lead diazide; lead azide (≥ 20% phlegmatiser)	236-542-1	13424-46-9	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
082-003-00-7	Lead diazide; lead azide	236-542-1	13424-46-9	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 diazide is covered by index numbers 082-003-00-7 and 082-003-01-4 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 diazide 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 diazide is typically prepared by the reaction of lead nitrate and sodium azide. The manufacture of lead diazide takes place in at least nine locations in the EU, in the Czech Republic, France, Germany, Poland, Spain and the UK. The overall EU production is estimated at ≤15 t/y.

The substance is not imported into or exported from the EU as a substance. However, articles containing the substance (e.g. detonators, military munitions) may well be imported into or exported from the EU. Exports are believed to be larger than import and it is estimated that 2.4 tonnes of lead diazide are exported from the EU in the form of civilian detonators.

1.2 Uses

Confirmed uses of lead diazide in the EU include:

- as an initiator or booster in detonators used for both civilian and military uses; and
- as an initiator in pyrotechnic devices used in military munitions (fuzes) and space shuttles/satellites.

Another application likely to be relevant but unconfirmed is as a primer in cartridge actuated devices for aerospace/defence/safety applications.

Based on the available information and a series of assumptions, it is estimated that civilian uses may account for around 75% of total EU consumption with the remainder used in military detonators/munitions.

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[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

With regard to the lead diazide content in articles, this generally varies between 1 and 250 mg per article, although cases with much higher lead diazide content have been noted. On average, a content of 100 mg per unit appears to be realistic. Within the primer mixtures inserted into detonators and pyrotechnic igniters, lead diazide may represent 20-80% of the mixture. In respect of the final articles, some small-sized civilian detonators may contain lead diazide at concentrations >0.1% by weight in the overall article, but for military munitions, especially of a large size (e.g., artillery shells), the concentration of the substance is well below 0.1% by weight.

1.3 Releases from Manufacture and Use

1.3.1 Manufacture and First Use

Information from the IPPC BREF Document for Speciality Inorganic Chemicals indicates that lead diazide is not released to the environment during **manufacture**. Only releases to water are of relevance and these are treated according to Best Available Techniques to break down the explosive molecules by using nitric acid and sodium nitrite. Lead contained in wastewater is precipitated by adding sulphate and/or carbonate anions to obtain solid lead sulphate and/or lead carbonate. 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 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 diazide are important:

- the substance is typically manufactured in a ‘wetted’ form, but is then dried, sieved and divided into small quantities for insertion into articles (often in mixture with dry lead styphnate);
- 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, available information suggests that manual handling of the substance takes place only when small quantities are handled – in these cases, protection measures (such as the use of Personal Protective Equipment (PPE)) is the norm. Typically, the majority of activities are undertaken using automated systems behind reinforced walls with workers located in isolated, remote ‘cells’;
- protective gloves and glasses are typically used by workers, although at least one company involved in the manufacture of military detonators avoids the use of gloves when handling dry material to avoid the development of static. 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 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. 71% of the molecular weight of lead diazide). These only demonstrate exposure levels during use of PPE (calculations without PPE are given in the main part of the report).

Table 1: Modelled Occupational Inhalation and Dermal Exposure to Lead diazide 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/m^3)-8 hours' time average - With PPE		0.014	0.014	0.036	0.007	0.014
Worst case (90%) estimation of dermal **exposure** level hand loading (mg Pb/kg bw/day)-full shift - With PPE	100%	0.021	0.036	1.32E-04	7.12E-06	-
	0.01%	2.1E-06	3.6E-06	1.32E-08	7.12E-10	

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

Exposure parameters		**Transfer of dry material-manual-filling devices**
Worst case (90%) estimation of **inhalation** exposure level (mg Pb/m^3)-8 hours' time average - With PPE		0.014
Worst case (90%) estimation of dermal **exposure** level hand loading (mg Pb/kg bw/day)-full shift - With PPE	100%	9.04E-05
	0.01%	9.04E-09

To assess inhalation exposure, we have used as a benchmark value the lowest Occupational Exposure Limit (OEL) for lead and inorganic lead compounds applicable in EU Member States, i.e. 0.05 mg/m^3. Overall, when the effect of PPE is taken into account, exposure levels for all scenarios considered are below 0.05 mg/m^3. Therefore, the worker health risks via inhalation are probably low.

To assess dermal exposure, we have adjusted an initial assumption of 100% absorption rate through the skin to a more realistic rate of 0.01% which is considered appropriate for inorganic lead. Such a rate is documented in several literature sources, most notably the Voluntary Risk Assessment Report for Lead. We then 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 m^3 inhaled air volume in a workday under light activity). The intake estimates for all scenarios are well below this 'baseline' figure of 0.5 mg/day, even when PPE is not used. It is acknowledged that these estimates are based on a series of (conservative) assumptions on the behaviour of the substance and the processes used. 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.

1.3.2 Fabrication 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 fuze becomes a component of an artillery shell), the primer mixture is loaded under pressure into metal cups or sleeves and sealed after filling. The subsequent user will not get in contact with the ingredients. Thus, lead diazide is captive within the component (detonator), 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 end-product (detonators and munitions) is expected. Lead diazide is consumed during detonation and forms reaction products such as lead oxides and nitrogen oxides. On a per article basis, the quantities of lead released are generally very small. Still, the entire EU lead diazide consumption contains an estimated <9.6 tonnes of lead part of which may be released through the use of detonators.

1.4 Current Knowledge of Alternatives

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

- picrate salts;
- silver azide;
- diazodinitrophenol or 2-diazo-4,6-dinitrobenzene-1-oxide (DDNP);
- tetrazene or tetracene or 1-(5-tetrazolyl)-4-guanyltetrazene hydrate;
- triazine triazide (TTA) or 2,4,6-azido-1,3,5-triazine or cyanuric triazide (CTA);
- metal salts of 5-nitrotetrazole, e.g. the mercuric or copper salt;
- 1,3,5-triazido-2,4,6-trinitrobenzene (TATNB); and
- complex metal dianions and environmentally benign cations.

Alternative articles are also available, for example, detonators free from primary explosives or ‘non-primary explosive detonators’ (NPEDs).

Consultation with users of lead diazide has shown:

- not all companies are currently working on alternatives;
- even for the alternatives identified as promising (mainly in the USA), they would only achieve partial rather than complete replacement of lead diazide;
- it is unclear whether articles based on alternatives would be possible or easy to qualify and certify. Articles intended to be used by military personnel (detonators, munitions) need to be especially reliable and meet specific requirements typically set by relevant authorities/defence agencies;
- R&D work and changes to products and processes would be required for substitution; and
- suggestions on the timeframe of R&D required for the development and qualification of alternative compositions range from 10 years to more than 20 years without a clear indication (at present) that efforts may be fruitful for all applications of lead diazide.

In relation to the potential replacement of lead diazide by substances of similar structure such as picrates or silver azide, substitution is unlikely due to performance and compatibility issues. Moreover, these alternatives are not hazard-free and lead picrate would still pose an issue of heavy metal presence. Finally, lead diazide cannot be replaced by lead styphnate, as the latter is a relatively poor initiating agent; only because of its ease of ignition, lead styphnate is often used as a cover charge for lead diazide.

2 DIFFERENT FORMS OF LEAD DIAZIDE

Depending upon the requirements and end applications of the lead diazide a number of modifications exist, these are summarised in **Table 2.1**, below.

Table 2.1: Modified Compositions of Lead Diazide and their Development Processes

Composition of lead diazide	**Development process**
Service lead azide	Prepared by the double decomposition of lead acetate and sodium azide in the presence of sodium carbonate and acetic acid. In this process, crystals of lead azide grow around the lead carbonate nucleus (thus preventing the growth of larger and sharp needle shaped crystals). Service lead azide is still sensitive to friction and thus may cause accidents. It is used in the absence of other alternatives
Dextrinated lead diazide	Prepared via the slow addition of a slightly alkaline solution of sodium azide to a solution of lead nitrate and dextrin, this is an amorphous form of lead diazide, which was made in the USA in 1930 and found to be safer to manufacture and handle. It has poor adhesive properties and is hydroscopic. The addition of dextrin prevented the formation of large sensitive lead diazide crystals and regulated their shape. **This is the form most likely to be used in the EU, but pure lead diazide is also manufactured**
Improved lead azide	For this form of lead diazide, precipitation is carried out using sodium carboxy methylcellulose (Na-CMC). The obtained product has a lower bulk density than service lead diazide. The use of sodium amylase offers some advantages over both (Na-CMC) and dextrin. **One EU company has confirmed the manufacture of CMC lead diazide**
Gelatine, azide, molybdenum disulphide (GAM) form of lead diazide	GAM is manufactured by the precipitation of lead diazide from a solution containing gelatine and a suspension of molybdenum disulphide. MoS_2 is incorporated in the crystal agglomerate to obtain the desired combination of cohesion and electrical properties. The electrical properties of the modified product thus obtained are excellent; however, the bulk density and power of GAM are lower than those of dextrinated lead diazide
Basic lead diazide	Prepared by reacting aqueous solution of lead acetate and glycerine with a mixed aqueous solution of sodium hydroxide and sodium azide containing trinitrophloroglucinol (TNPG) at a suitable temperature and rate of stirring. Basic lead diazide is a crystalline, free flowing, non-hygroscopic and non-sticking material. It has an initiating value of 70 mg and is less sensitive to friction and impact than service lead diazide

Source: Agrawal (2010)

There is a range of legislation regulating the manufacture, storage, transport and use of lead diazide:

- the production and usage of explosives is strictly regulated by all members of EU (special licenses and permits);
- the production of primary explosives is regulated by the IPPC Directive;
- the production of explosives is regulated by the SEVESO II directive. According to the UK Health and Safety Executive, lead diazide 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);

- lead diazide comes in dry and wet forms. When wetted with at least 20% water, it is given a hazard Class of 1.1A and a transport identification number of UN0129. Transport of lead diazide (dry) is forbidden. Transport of lead diazide, wetted with <20% water is forbidden by cargo aircraft or passenger aircraft/rail (KGHM, 2011); and
- there are other legal directives such as traceability (Federation of European Explosives Manufacturers, 2011b).

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

3.1 Manufacturing Process

3.1.1 Overview

Lead diazide is prepared by the reaction of lead nitrate and sodium azide (in stoichiometric proportions) through the following reaction:

$$2\mathrm{Na}\text{–}(\mathrm{N{=}N{=}N}) + \mathrm{Pb(NO_3)_2} \rightarrow (\mathrm{N{=}N{=}N})\text{–}\mathrm{Pb}\text{–}(\mathrm{N{=}N{=}N})\downarrow + 2\mathrm{NaNO_3}$$

Solid raw materials used in the manufacture of lead diazide (e.g. lead nitrate and sodium azide) will typically be dissolved in water to prepare aqueous solutions containing anionic and cationic components of lead diazide (the proportion of water used to prepare these solutions is considered confidential information by the manufacturers).

This process is described in the 2007 IPPC Reference Document on the Best Available Techniques for the Production of Speciality Inorganic Chemicals, hereafter referred to as the SIC BREF Document (EC, 2007). The same source presents the raw and auxiliary materials that are needed in the manufacturing process. These are shown in **Table 3.1**.

Table 3.1: Raw Materials Needed for the Industrial manufacture of Lead Diazide

Substance	Use	Manufacture step	Quantity (in kg/kg of lead diazide produced)
Lead nitrate	Raw material	Reaction	1.14
Sodium azide	Raw material	Reaction	0.45
Dextrin	Crystalline modifier	Mixing with sodium azide	Confidential
Sodium hydroxide	pH adjustment	Reaction	Confidential
Ethyl alcohol	Washing of lead diazide	Purification	Confidential
Sodium nitrite	Chemical destruction (i.e. oxidation reaction) of explosive impurities in	Waste water treatment	Confidential

Table 3.1: Raw Materials Needed for the Industrial manufacture of Lead Diazide

Substance	**Use**	**Manufacture step**	**Quantity (in kg/kg of lead diazide produced)**
Nitric acid	waste water before lead removal treatment	Waste water treatment	Confidential
Ferric chloride	Verify the completeness of the above oxidation reaction	Waste water treatment	Trace quantities for chemical qualitative analysis of explosive impurities in water
Sodium carbonate	Precipitation of lead carbonate as part of the lead removal treatment	Waste water treatment	No data available
Activated carbon	Adsorption of coloured organic impurities in waste water	Waste water treatment	No data available

Source: EC (2007)

3.1.2 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 ºC. Dextrin is added to obtain a proper product grain shape and size. The reaction (i.e. precipitation) is initiated 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). Formation of crystal needles overly sensitive to shocks is to be avoided. The reaction takes place at atmospheric pressure (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 led to wastewater treatment (EC, 2007).

3.1.3 Purification, Drying and Storage

At reaction temperatures, lead diazide is always insoluble within the reacting media. Subsequently, purification is typically carried out by means of solid-liquid separation and washing with water (small quantities of ethyl alcohol or other organic solvents are also used to minimise organic impurities). The lead diazide is then loaded up on antistatic trays, each containing less than 5 kg of finished product, and manually transported to the drying area, which will be located at some distance from the reactor room for reasons of safety. The drying area typically consists of built-in closets where the trays are deposited for approximately 72 hours. In this area, air at a temperature of 65-70ºC circulates at a low rate (to avoid particulate emissions of lead diazide into the drying room) in the closets and dries the crystals in the trays (EC, 2007).

Finally, the finished lead diazide product is stored within special storage buildings that have electrical protection in addition to safety and security systems. As with the drying rooms, these storage facilities will be located at a safe distance from other buildings (EC, 2007).

3.2 Production Sites and Volumes

3.2.1 Information from Literature

The SIC BREF Document suggests that lead diazide, lead styphnate and lead picrate are SIC explosives of key industrial and economic importance to Europe. Of the three, lead styphnate appears to be used more widely than the others (EC, 2007). The reported production capacity of lead diazide in Europe in 2004 is given in **Table 3.2**.

Table 3.2: EU Production Capacity for Lead Diazide – Mid-2000s

Location (city, county)	**Production capacity in 2004 (tonnes)**
Vsetin, Czech Republic	<5
Héry, France	<5
Tarbes, France	~1
La Ferté-Saint-Aubain, France	<1
Galdácano, Spain	<15
Total	***<27***

Source: EC (2007)

The SIC BREF Document suggests that other European producers of lead-based primary explosives existed in Italy, Germany, Portugal and probably in Sweden, Austria and Poland (EC, 2007).

3.2.2 Information from Consultation

The manufacture of lead diazide in at least ten locations in the EU is confirmed in the Czech Republic, France, Germany, Poland, Spain and the UK. Additional detail is provided in the Confidential Annex (Section A2.3).

Information on the manufacturing volumes collected through consultation with individual companies is given in the Confidential Annex to this document (Section A2.2). Information provided by the Federation of European Explosives Manufacturers suggests that the tonnage of lead diazide produced in the EU is ≤15 t/y (Federation of European Explosives Manufacturers, 2011b) and is considerably lower than the respective manufacturing tonnage of lead styphnate.

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

Information from literature and consultation would suggest that mixtures and articles (detonators, munitions) containing lead diazide are formulated and manufactured 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.

On the other hand, primers based on lead diazide may well be imported into the EU as components of articles, e.g. detonators and military munitions. This is discussed further in Section 4.6.

3.4 Recent and Future Trends

3.4.1 Information from Literature

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

The two major applications of explosives are in civil works and mining; while mining has generally been in decline in Europe over recent decades, civil works (mainly road and tunnel construction) was the only market with a significant growth rate in some Member States in the mid-2000s (EC, 2007).

3.4.2 Information from Consultation

The information presented in the Confidential Annex based on consultation with individual companies would (tentatively) suggest an increase in manufacture in the last five years; however, not all EU-based manufacturers of lead diazide made an input to this study.

The collective response submitted by the Federation of European Explosives Manufacturers indicates no discernible change in manufacturing volumes in the EU for the period 2005-2010 (Federation of European Explosives Manufacturers, 2011b).

3.5 Information on Releases from Manufacture

3.5.1 Emissions of Lead Diazide

Information from Literature

<u>Releases to the Atmosphere</u>

According to the SIC BREF Document, no significant atmospheric emissions occur from the manufacture of lead diazide. 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. CO2 may be emitted to the air during the treatment of wastewater (EC, 2007).

Releases to Water

Wastewater from the production 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 (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 (see Figure 3.1) (EC, 2007).

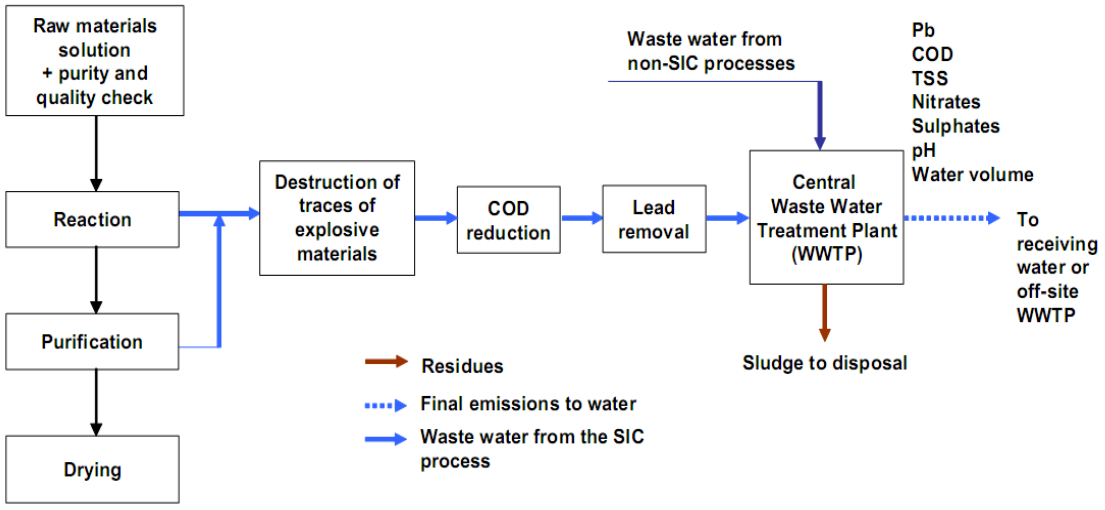

Figure 3.1: Treatment of Wastewater arising from the Manufacture of Lead Diazide

Source: EC (2007)

The first operation in the pre-treatment steps consists of destroying the traces of explosive material (i.e. lead diazide) contained in the wastewater by using nitric acid and sodium nitrite (EC, 2007). Activated carbon is used for the adsorption of organic impurities 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 adding sulphate and/or carbonate anions to obtain solid lead sulphate and/or lead carbonate. The efficiency of the lead removal pre-treatment used at a Spanish installation is shown in Table 3.3 (EC, 2007). It appears to exceed 99.5%.

Table 3.3: Total Lead Concentration in Wastewater at a Spanish Lead Diazide Production Plant

Wastewater before pre-treatment	Wastewater after pre-treatment and before discharge to a central on-site wastewater treatment plant
1,500 mg/L	5 mg/L

Source: EC (2007)

Solid Waste

In the lead diazide manufacturing process, waste arises from wastewater treatment sludge (containing lead carbonate – PbCO3) which is collected, put in metal drums and disposed of by an external contractor. Additionally, another type of waste is made of solid materials contaminated with explosive traces (EC, 2007). Table 3.4 shows the quantity of solid wastes generated at a Spanish installation - these are 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 $PbCO_3$	350 kg/tonne of lead diazide

Source: EC (2007)

Information from Consultation

Non-confidential information on releases presented in the questionnaire responses of individual companies is shown below. Confidential information is presented in the Confidential Annex (Section A4.1).

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

Manufacturer	**Details of releases**
Company 2	Releases from combined production of lead sulphate waste from both the manufacture and the on-site use of lead diazide in the fabrication of detonators. Waste arisings: 0.0045 kg of lead sulphate per kg of lead diazide manufactured each year
Company 3	No releases to any compartment (estimate)
Company 18	No losses of the substance to air, water, soil or waste during the manufacturing process. The company uses water for the manufacture of lead diazide and the cleaning of the tools but this wastewater is chemically treated to destroy lead diazide; after that, the treated water is further treated by a specialised company. No wastewater with lead diazide is released to the environment

Source: Consultation

3.5.2 Worker Exposure

During the manufacturing process, there is little opportunity for exposure to lead diazide. Lead diazide is often screened in barricaded rooms to avoid continuous exposure to the workers. Although workers could be exposed intermittently to lead diazide, whilst entering the screening room, workers should be using proper safety and respiratory equipment at this time (Deeter, 2000). It is evident that manufacturers of explosive materials such as lead diazide are required to take very strict precautions for the protection of their employees and the prevention of accidents.

Specific non-confidential information on exposure of workers is available from two manufacturers of the substance. Company 2 and Company 18 have provided the information shown in Table 3.6. The table also provides the information included in 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 diazide and the exposure 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 Diazide – Consultation

Worker exposure parameter	**Federation of European Explosives Manufacturers**	**Company 2**	**Company 18**
Type of product handled	Aqueous solution of sodium azide & lead nitrate	Substance of purity ca. 93%	Substance of purity ca. 95%
Relevant process step where exposure occurs	No exposure during manufacture – closed reactors Automated filling of metallic components into detonators Service, repair and cleaning	Synthesis - Product transfer	Synthesis - Quality testing
Route of occupational exposure	Not applicable	Skin, inhalation	Skin
Exposure level	0.001 mg/m^3	<0.05 mg lead/m^3 (measured)	1 mg/person/day of manufacture, without protection (estimate)*
Ventilation conditions	Not applicable – automated process	Ventilation present – no details	No ventilation
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	Complete mask with cartridge against acid gas (ABE1 type); no gloves
Frequency of exposure (days per year)	Approx. 100 days per year per manufacturer	100	10
Duration of exposure per day (minutes per day)	Few minutes to 120 minutes for service & maintenance	300	4
Number of employees exposed	Approx. 20 to 30 workers in the whole of Europe	4	2

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

** the company has systematically analysed lead in the blood of its employees exposed to it and so far has not noticed any level of exposure*

Accidents during the manufacture of lead diazide have been reported. For example, an employee of a California-based United States Defence contractor was seriously injured when a 5g charge of dextrinated lead diazide detonated in her hand while she was hand transporting the explosive at a facility that produced detonators for the US military. The employee lost her hand and suffered significant burn injuries to her torso and lacerations on her face (Exponent, 2010).

3.5.3 Model-based Estimates of Occupational Exposure

Overview

TNO has undertaken estimates of exposure of workers to lead diazide during its manufacture based on information in this 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 diazide has essentially three life cycle steps: (a) manufacturing of the substance, (b) production of articles containing the substance and (c) use of the articles.

Lead diazide is manufactured (and used during production 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 close reactor;
- the separation of lead diazide from the mother lye by sieving is commonly in an insulated room without operator or in a closed reactor system;
- lead diazide 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 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 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 in some cases;
- alternatively, lead diazide is not fully dried; the wetted (~ 20% water) material is then transferred for further processing (frequently automated or semi-automated).

For monitoring samples are taken during the manufacturing process. It is also further assumed that equipment and workplace are cleaned on daily basis, as accumulation of dust is very dangerous.

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 remotely 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 model[7]. 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. Manual transfers 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;
- due to the scale of the process, sampling is assumed to be at gram level with at least local exhaust ventilation or in an enclosure;
- due to the general closed systems and remotely controlled activities, cleaning involves removing at the most milligrams of lead diazide 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 is 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;
- 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 thus 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 types 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;

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

- manufacturers indicated manufacturing lead diazide 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 to be 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 just over 71% of the molecular weight of lead azide).

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).

Given that lead azide is an inorganic compound of lead, we compare the inhalation exposure estimates in **Table 3.7** to the lowest OELs for lead and inorganic lead compounds, 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 being exceeded when no PPE is used. 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 azide (including PPE) are also noted.

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

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 diazide in the same room:	Yes	Yes	Yes	Yes	Yes
Room volume:	Volume 100-1000 m3	Volume 100-1000 m3	Volume 100-1000 m3	Volume 100-1000 m3	Volume 100-1000 m3
General ventilation:	General ventilation	General ventilation	General ventilation	General ventilation	General ventilation

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

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**
		(mechanical or natural)	(mechanical or natural)	(mechanical or natural)	(mechanical or natural)	(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
Work area regularly cleaned:		Yes	Yes	Yes	Yes	Yes
Equipment regularly inspected and well maintained:		Yes	Yes	Yes	Yes	Yes
Resulting exposure level estimate						
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

Source: TNO calculations

Dermal Exposure Estimates

Dermal exposure has been estimated with RISKOFDERM version 2.1.

For dermal exposure during cleaning, no proper exposure model exists. Exposure depends a lot on the amount of lead diazide on the surfaces cleaned. Due to the general closed systems and remotely controlled activities, and the high frequency of cleaning (on a 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:

- the substance is generally pure but wetted with water to prevent preliminary decomposition, this results in a not very dusty type of product (input in RISKOFDERM: Light or moderately dusty solid);
- when the substance is dry, the material is described as more granular than powdery (input in RISKOFDERM: Light or moderately dusty solid);
- due to 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 [8];
- manufacturers indicated that manufacture of lead azide can be a full-time (8h/day) task. However, most of the process steps are in closed systems or remotely controlled. The activities assessed are therefore 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 to be 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 also initially assume dermal absorption of 100% (but see discussion below on a more appropriate absorption rate);
- 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;

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[8] "*Light contact*" corresponds with touching of contaminated surfaces and/or limited deposition of dust or aerosols. The other option is "*more than light contact*" which corresponds with splashes or drops falling onto the worker or part of the worker is in direct contact with the (stream of) product. Or when packages are clearly contaminated; for example cement bags.

- 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**. The bottom of the table shows the results expressed in mg of lead per shift and per kilogram of bodyweight per day (lead accounts for just over 71% of the molecular weight of lead azide).

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).

Table 3.8: Input and Results – Dermal Exposure Estimates during the Manufacture of Lead Azide					
Task or process assessed		**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-maximum several hundred grams**	**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
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
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	**13.4**	**22.4**	**9.25E-02**	**4.98E-03**
	With PPE	**1.34**	**2.24**	**9.25E-03**	**4.98E-04**
Worst case (90%) estimation of exposure level hand loading (**mg Pb/kg bw/day**)-full shift	Without PPE	**0.19**	**0.32**	**1.32E-03**	**7.12E-05**
	With PPE	**0.02**	**0.04**	**1.32E-04**	**7.12E-06**

Table 3.8: Input and Results – Dermal Exposure Estimates during the Manufacture of Lead Azide				
Task or process assessed	**Transfer of wetted material-manual**	**Transfer of wetted material-automated**	**Transfer of dry material-manual-maximum several hundred grams**	**Sampling**
Source: TNO calculations				

Therefore, as lead azide is an inorganic substance, we have adjusted the figures shown above by the absorption rate of 0.01% to provide the maximum daily systemic intake via the skin for any of the scenarios considered. The adjusted figures would be those shown in **Table 3.9**.

Table 3.9: Estimates of Lead Dermal Intake during the Manufacture of Lead Azide					
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	1.34E-03	2.24E-03	9.25E-06	4.98E-07
	With PPE	1.34E-04	2.24E-04	9.25E-07	4.98E-08
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 there is no obvious reason for concern for workers – even in the absence of PPE – as all intake estimates are below 0.5 mg.

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

4.1.1 Lead Diazide as a Primary Explosive

Lead diazide 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**.

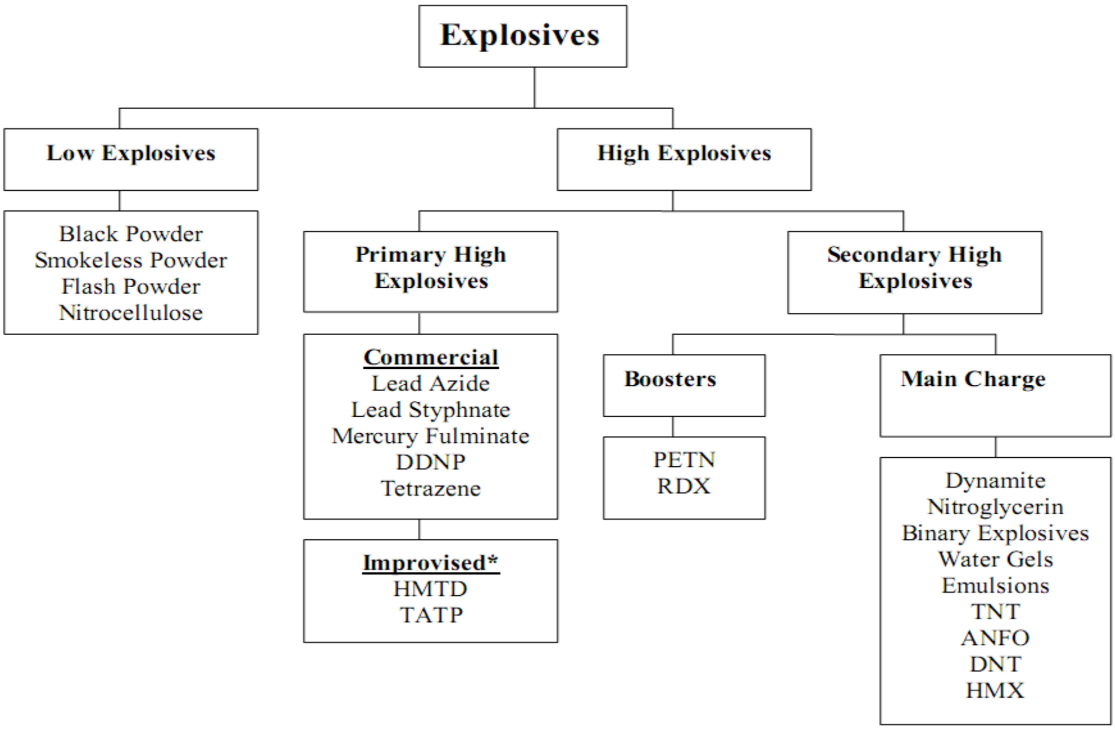

Figure 4.1: Classification of Explosives

Source: US DHS (2008)

A primary explosive is a sensitive explosive which nearly always detonates by single ignition from such means as spark, flame, impact or 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 and go from burning to detonation very quickly (Trace, 2011).

4.1.2 Range of Uses for Lead Diazide

Lead diazide is used only on-site in the manufacture of initiation devices such as civil detonators or defence products (Federation of European Explosives Manufacturers, 2011b). In summary, uses identified in literature include:

- as an initiator or booster in blasting caps/ detonators, for example in the ASA (lead diazide, lead styphnate and aluminium) mixtures, used for both civilian and military uses;
- in pyrotechnic devices used in military munitions (munition fuzes);
- as a primer in cartridge actuated devices for aerospace/defence/safety applications;
- as an initiator in primers for percussion caps for small calibre and rifle ammunition; and
- as a micro-explosive to produce shock waves for medical applications.
-

These applications are further discussed below.

4.1.3 Tonnage of Lead Diazide Consumption in the EU

Information on the consumption (in tonnes) of lead diazide in the various applications is shown in the following sub-Sections of Section 4. Company-specific, confidential, information is provided in the Confidential Annex to this report. At this point, by way of an overview, we provide details that have been submitted by the Federation of European Explosives Manufacturers (2011; 2011b).

The Federation has indicated that civilian detonators (articles used in quarries, mining and construction) account for the majority of manufacture/consumption of lead diazide in the EU. Civilian detonators are believed to account for a consumption of ≤10 t/y lead diazide[9].

Military initiators (detonators, fuze heads, relays, delay elements) used in munitions may also contain lead diazide. The Federation of European Explosives Manufacturers only represents the civilian explosives market but estimates that ≤5 t/y lead diazide is used such military uses.

These two market segments are the most important ones for lead diazide. This information has generally been corroborated by the individual submissions of companies manufacturing and consuming lead diazide.

4.2 Use in Detonators and Pyrotechnics for Military Munitions and Space Applications

4.2.1 Description of Use

Detonators for Civilian Uses

Lead diazide is used within a wide range of detonators, which typically have the responsibility of magnifying a tiny energy input in a chain reaction, which leads to the quick release of energy stored in a secondary explosive (US EPA, 1994). Lead diazide has high chemical stability, which enables the usage of detonators at higher temperatures during the application of modern emulsion explosives (emulsion explosives are replacing nitro-esters based explosives) (Federation of European Explosives Manufacturers, 2011b).

Detonators (also known as blasting caps in the USA) are small thin-walled cylindrical cases containing a sensitive explosive. Detonators serve as initiators of explosive charges. They consist of a cylindrical capsule (typically copper or aluminium) containing three or four main components. The first component is commonly referred to as the ignition charge (or priming mixture), typically a primary explosive. An electrical bridge wire or a black powder fuse may initiate this mixture, which then detonates a secondary or ‘booster’ charge, typically containing lead diazide (Ledgard, 2007). Lead diazide may be used as a booster charge as it is capable of transferring the necessary energy to the base charge. The base charge is the final component within a detonating device and usually consists of a secondary explosives such as PETN or RDX (Ledgard, 2007). In conclusion, lead diazide may be found in both the ignition charge (priming mixture) but also the secondary, ‘booster’ charge of blasting caps.

With regard to the presence of the substance in ignition charges (priming mixtures), consultation indicates that lead diazide is relatively insensitive to ignition by flame, say from safety fuse. To

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[9] In an earlier estimate, the Federation suggested that a total of 100 million detonators are manufactured in the EU each year. Of these, 52% are non-electric detonators (52 million units), 48% are electric detonators (48 million units) and 0.04% are electronic detonators (40,000 units). It can be assumed that lead azide is found in about 80% of civilian detonators (the remaining 20% refers to the products of a single manufacturer which are based on a different technology) with an average loading of 100 mg lead azide per detonator. This would mean that the EU consumption of lead azide in the manufacture of civilian detonators is 80 million x $1x10^{-7}$ tonne = 8 tonnes of lead azide (Federation of European Explosives Manufacturers, 2011).

overcome this problem, the effects of incorporating various ignition agents with lead diazide were examined. The only material which, when mixed with lead diazide, satisfied all the requirements as to good running and loading, fast binding (when subjected to pressure) and certain firing was lead styphnate. Thus it has become standard practice to use lead styphnate in conjunction with lead diazide in detonators. Accordingly, many detonators' priming mixture is a material called ASA compound. This compound is formed from lead diazide, lead styphnate and aluminium and is pressed into place above the base charge, usually TNT or PETN (http://explosives.org.au/ , 2009; Mayer *et al*, 2007). Aluminium is added to enhance the likelihood of lead diazide burning to detonation (Zukas *et al*, 2002).

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/booster 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).

Detonators containing lead diazide are commercially employed in a range of applications in mining, construction, tunnelling and oilfield use.

Military Detonators

Lead diazide detonators similar to those used in civilian applications may also be used in a military environment. An example military detonator containing lead diazide 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 aluminium/lead styphnate/lead diazide. This product is supplied to the UK Armed Forces in a full military pack.

Military Fuzes or Initiators

A type of detonator, which is much less common in the civilian world, is known as "fuze". These devices are usually mechanical in nature, but they can be electronic as well. They utilise the same explosive trains found in blasting caps/detonators, 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 diazide is mainly used to give a shock wave to initiate a secondary explosive in a Safety and Arming Unit, a device designed to initiate a munition.

The US army use a range of lead diazide based detonators, including the M55 stab detonator (which can be used in a large range of military items such as mortars and rockets) (Oyler et al, undated), and the M6 electric blasting cap and 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 diazide. A 1994 guidance document suggests that the substance was contained in several types of grenades of the US Army, typically in combination with lead styphnate and PETN or RDX (US Army, 1994b; US Navy, 2000).

Lead diazide is generally used in military detonators and munitions as it ensures a very long lifetime (it can properly function after decades) and due to its very high chemical and thermal stability (Federation of European Explosives Manufacturers, 2011b).

Space and Satellite Applications

Lead diazide has been used as the primary explosive for the initiation of high explosives in Apollo Space Program systems, and is used as an intermediate charge within the NASA Standard Detonator (NASA, 1973).

The NASA Standard Detonator (NSD) has been in use for a number of years. It consists of an output body attached to an electric initiator (NASA Standard Initiator or NSI). The output section has a diameter of approximately 0.25’’ and contains lead diazide and the relatively insensitive RDX (Tarbell *et al*, 1995). The detonator is designed to transfer shock waves and high-pressure energies for initiating detonating trains, Shielded Mild Detonating Cord (SMDC) Flexible Confined Detonating Cord (FCDC) and other linear explosive lines (Hi-Shear, undated).

Such powder detonators are used for (Hi-Shear, undated):

- explosive transfer lines actuation;
- range safety destruct;
- severance or separation of structures;
- Safe Arm Device/Flight Termination Actuation; and
- any application requiring detonating action.

The Federation of European Explosives Manufacturers has confirmed the use of the substance in satellites and space shuttles.

4.2.2 Locations and Quantities Used

Locations

The Federation of European Explosives Manufacturers indicates that lead diazide is used in civilian detonators by seven EU member-companies and in military detonators and munitions by two member-companies (Federation of European Explosives Manufacturers, 2011b).

Consultation with individual companies suggests that the numbers of companies involved in the production of articles for either civilian or military use may be somewhat higher than what the Federation has suggested. Generally, however, fewer than 10 sites currently use the substance in the production of detonators (some are involved in the production of articles for both civilian and military market segments). The companies are located in the Czech Republic, France, Germany, Poland, Spain, Sweden and the UK.

Quantity

The information provided by the Federation of European Explosives Manufacturers (see Section 4.1.3) is generally corroborated by information submitted by individual manufacturers-users of the substance, as described in the Confidential Annex (Section A2.2).

By way of comparison, the US army requires over 1000 lbs/year (0.45 t/y) of lead diazide for various uses (Fronabarger *et al*, undated). All of this comes from a diminishing stockpile produced in the 1950-1960s and which has age-related issues (there is no current manufacture of lead diazide in the USA) (Fronabarger *et al*, 2010).

Concentration in Articles

Some information on the presence of lead diazide in detonators has been provided by consultees and is reproduced in **Table 4.1**.

Table 4.1: Concentration of Lead Diazide in Detonators

Product	**Lead diazide content**	**Source**
Primer mixture	20-80%	**Company 27**
Civilian detonator	0.8%	**Company 2**
Seismic detonators	60 mg lead diazide <1% of the detonator	**Company 19**
Oilfield blasting caps	250 mg lead diazide <1% of the blasting cap	**Company 19**

Source: Consultation

The Federation of European Explosives Manufacturers (2011b) indicates that the minimum amount of lead diazide required per detonator in order to achieve proper initiation is 60 mg per unit. Different manufacturers may use different quantities with a maximum of 200 mg per unit. Overall, the average content of lead diazide in detonators is 100 mg. On the basis of this estimate, lead diazide may represent as low as 0.0001% of the final article. The Federation claims that there is no other known primary explosive used to initiate detonators that can be employed in per unit quantities lower than those of lead diazide.

Some additional detail can be found in the Confidential Annex (Section A3.1.2). It should be noted that in respect to munition fuzes, the concentration of lead diazide in the end-use article (e.g. artillery shell) is very low, well below 0.1%.

4.2.3 Recent and Future Trends

The trends in the use of lead diazide in the production of civilian and military detonators and fuzes are identical to the trends in production given that detonators/fuzes represent the vast majority of the EU consumption of the substance.

In recent years, a significant amount of research has been focused on alternatives for lead diazide in detonators[10], which indicates that the use of lead diazide in detonators could decline when an economically and chemically suitable alternative is developed (see Section 6). However, an important consideration is whether new lead diazide-free products would qualify and meet the specifications of the users (e.g. military and security forces).

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[10] This has particularly been the case in the USA where, in 1993, a series of executive orders were issued to reduce or eliminate the procurement of hazardous substances and chemicals by federal facilities.

4.2.4 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. The users are mining and construction/demolition companies as well as the defence departments of EU national governments. However, military detonators and munition fuzes may also be placed on the market and be used by downstream users in the production of specific munition articles (specific types of shells, etc.).

4.3 Use in Cartridge Actuated Devices

4.3.1 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) as well as commercial fire suppression systems.

Percussion primers provide the initiation stimulus for a large number of cartridges used in various CAD applications (Blachowski, undated). For example, a typical primer used by the US armed forces is the NOL-130 stab primer containing basic lead styphnate (40%), lead diazide (20%), barium nitrate (20%) and tetrazene (5%). Lead diazide has also been used in the CCU-61/A Impulse Cartridge, which provides pressure work for US Navy ejection seats (Hirlinger, 2009), the M252 delays cartridge, for a 5000 lb. capacity cargo parachute release and a number of aircraft/helicopter fire extinguishing actuating cartridges (US Army, 1994).

4.3.2 Locations and Quantities Used

No information on the current use of the substance in the EU is available. It is likely that military equipment produced in countries such as the USA which is operated by EU national armed forces may well contain CADs that depend on lead styphnate. The use of lead diazide in cartridge actuating appears to be significantly less prominent than the use of lead styphnate.

4.4 Use in Firearm (Small Calibre) Ammunition

4.4.1 Description of Use

With regard to lead diazide, information from the literature review would appear to suggest that lead diazide has been used as a priming compound in firearm ammunition (Dixon, 1998; Wheeler & Wilson, 2008) and Courtney (2010) also notes that rifle primers usually contain a combination of lead diazide and lead styphnate.

However, the relevance of such use is uncertain. No safety data sheets for relevant products containing lead diazide could be located. Furthermore, a range of recent literature sources fail to mention the use of lead diazide in modern primer cap compositions, indicating that its use may be out-dated or perhaps not relevant. Girard (2007) states that lead diazide may be used in primer compositions but notes that the most common primers today contain a mixture of lead styphnate, barium nitrate and antimony sulphide (Synoxyd primers).

There has also been (very limited) mention of the use of lead diazide within exploding ‘devastator’ bullets. These articles were produced by Bingham Limited, USA and were composed of a lacquer sealed aluminium tip with a lead diazide centre designed to explode on impact. However, the sale of these articles was restricted from 1981 onwards (Swift & Rutty, 2004).

4.4.2 Locations and Quantities Used

The use of lead diazide in this application in the EU has not been confirmed.

4.5 Extracorporeal Shock Wave Lithotripsy

4.5.1 Description of Use

Extracorporeal shock wave lithotripsy (ESWL) is the procedure by which shockwaves are generated at a point external to the body and are focused on a kidney stone in the body. The shockwaves themselves are relatively weak at their source and can thus traverse the body without any untoward effect. However, at the point they focus they are sufficiently powerful to fragment a kidney stone (Hashim *et al,* 2008).

Today there exist three primary types of shock wave generators (lithotripters) in ESWL. These are the electro-hydraulic shock-wave lithotripter, electromagnetic lithotripter and piezoelectric lithotripter. In addition to these methods, micro-explosive lithotripters have also been explored. These lithotripters utilised the explosion of tiny lead or silver diazide pellets within a parabolic reflector to generate a shock wave. Watanabe *et al* (1983) documented the successful use of micro-explosion lithotripsy in the defragmentation of bladder stones. Kuwahara *et al* (1987) demonstrated the safe use of this method for clinical treatment and Uchida *et al* (1988) considered micro-explosion lithotripsy to be the first choice for bladder calculi treatment, having used the technique to successfully treat 105 patients. 5-10 mg lead diazide pellets were used when micro-explosion ESWL was implemented (Miller 1985; Kuwahara *et al*, 1986; Takayama, 1993). However, despite this clinical success and the effectiveness of this type of generator in producing shock waves, the technology has not met with commercial success because of concerns regarding the storage and handling of the volatile lead diazide pellets (Uromed.gr, undated). Modern ESWL appears to have rendered micro-explosion ESWL obsolete.

4.5.2 Locations and Quantities Used

The use of lead diazide in this application in the EU has not been confirmed.

4.6 Imports and Exports of Articles from and into the EU

4.6.1 Information from Consultation

Imports

According to the Federation of European Explosives Manufacturers, imports of lead-based detonators into the EU account for 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 estimates that the amount of lead diazide imported into the EU in the form of articles does not exceed 0.001 t/y (Federation of European Explosives Manufacturers, 2011b).

Exports

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. 54 million detonators containing lead diazide remain in the EU and 24 million are exported with a lead diazide content of 2.4 tonnes (Federation of European Explosives Manufacturers, 2011). No specific information was provided on military detonators.

Some information on imports and exports was submitted by individual companies; this is presented in the Confidential Annex (Section A3).

4.6.2 Information from Trade Statistics

Information on the trade of key articles is available from the DG Trade Market Access Database[11]. Unfortunately, it is not possible to establish which elements of the statistical data may specifically relate to lead diazide-containing articles. The Federation of European Explosives Manufacturers has advised that these data provide useful insight to the EU explosives sector. The relevant information is not reproduced here.

4.7 Descriptions of Use Categories and Examples of Relevant Products

Table 4.2 presents the composition of some relevant products that contain lead diazide which have been identified in the open literature. The information is based on Safety Data Sheets. All products concerned are detonators.

The table is followed by **Table 4.3** which shows the applications, relevant process categories, environmental release categories, process categories and sector of end use for lead diazide in the EU. The table also gives the relevant NACE codes for the end uses identified[12].

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[11] Available here: http://madb.europa.eu/mkaccdb2/statistical_form.htm#. Potentially relevant product codes may include 3603.00.10 - Safety fuses; detonating fuses; 3603.00.90 - Other fuses and detonators; and 3604.90.00.00 - Other pyrotechnic devices.

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

Table 4.2: Examples of Lead Diazide based Articles – Safety Data Sheets

Manufacturer	**Description of product**	**Lead diazide content**	**Other ingredients**	**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 styphnate (CAS No. 15245-44-0) TNT, Trinitrotoluene (CAS No. 118-96-7)	2010	1
Austin Star (US)	Electric detonators Explosive components are RDX and lead compounds sealed in a metal shell	Not given	Lead styphnate (CAS No. 15245-44-0) RDX, Cyclotrimethylene Trinitramine (CAS No. 121-82-4) HNS, Hexanitrostilbene (CAS No. 20062-22-0)	2010	2
Maxam (ES)	Electric detonators Riodet®, Seismic Riodet®	Not given	Primary explosive: lead styphnate (and lead diazide) Secondary explosive: pentaerythritol tetranitrate (PETN) Pyrotechnic composition: lead peroxide, potassium permanganate, silicon, antimony	2009	3
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. Contains explosive charges and fusehead	<1%	Metal and plastic components - >60% Pentaerythritol tetranitrate (PETN) (CAS No. 78-11-5) - <1% Lead styphnate (CAS No. 15245-44-0) - <1% Aluminium (CAS No. 7429-90-5) - <1% Tetryl (N-Methyl- N,2,4,6-tetranitroaniline) (CAS No. 479-45-8) - <1%	2009	4

Table 4.2: Examples of Lead Diazide based Articles – Safety Data Sheets

Manufacturer	**Description of product**	**Lead diazide content**	**Other ingredients**	**Year**	**Source**
UEB-Maxam (ES)	Electric detonators for blasting	<1.5%	Lead styphnate (CAS No. 15245-44-0) - <0.5% 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	5
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 styphnate (CAS No. 15245-44-0)	2010	6
Davey Bickford (FR)	Non-electric detonators daveyquick®, Explosive components are PETN and lead compounds sealed in a metal shell	200mg	PETN, Pentaerythritol tetranitrate (CAS No. 78-11-5) – 800mg	2009	7
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 styphnate (CAS No. 15245-44-0)	2005	8
Hi-Shear (US)	PD12-5, 12-13 detonators	Not given	RDX, Cyclotrimethylene Trinitramine (CAS No. 121-82-4) Zirconium (CAS No. 7440-67-7) Potassium perchlorate (CAS No. 4778-74-7)	2008	9

Table 4.2: Examples of Lead Diazide based Articles – Safety Data Sheets

Manufacturer	**Description of product**	**Lead diazide content**	**Other ingredients**	**Year**	**Source**
Dynawell (DE)	Percussion Initiator DYNAWELL NB HNS (for oilfield use)	86mg	HNS, Hexanitrostilbene (CAS No. 20062-22-0) – 325mg	2009	10
Maxam (ES)	Riodet®, Seismic Riodet® RIODET IZ, RIODET IEP	10%	Lead styphnate (CAS No. 15245-44-0) – 6% 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	11
Kidde Aerospace (US)	Fire extinguisher actuator (sealed cartridge containing gas generating explosives)	65-75%	HNS, Hexanitrostilbene (CAS No. 20062-22-0) – 10-20% Zirconium (CAS No. 7440-67-7) – 5-15% Potassium perchlorate (CAS No. 4778-74-7) – 1-10% Fluoropolymer binder (CAS No. 9011-17-0) - 0.1-1% Graphite 0.1-1% (CAS No. 7782-42-5) - 0.1-1%	2007	12

Sources:

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

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

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

[4] http://www.oricaminingservices.com/download/file_id_5598/

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

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

[7] http://www.nitrobickford.fr/IMG/pdf/TDS_20-_20FT2_2077053Z_20_DQUICK_20A_202009_2004.pdf

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

[9] http://www.hstc.com/Products/OrdnanceProducts/PowerDetonators

[10] http://www.oiltools.ca/documents/TDZB-P-23BPIDWNBHNS1209.pdf

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

[12] http://www.kiddeaerospace.com/Files/KiddeAeroSpace/Global/US-en/KA002-1_1107.pdf

Table 4.3: Identified Uses and Process Categories for Lead Diazide

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**
Manufacture	**PROC 3**: Use in closed batch process (synthesis or formulation) **PROC 15**: Use as laboratory reagent	**ERC 1**: Manufacture of substances	As substance	**PC 11**: Explosives	**SU 9**: Manufacture of fine chemicals	Not relevant	C20.51 - Manufacture of explosives
			Formulation stage				
Formulation of primer mixtures (note: lead diazide can used in the fabrication of articles both as a substance and in mixtures)	**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) **PROC 8b**: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities	**ERC 2**: Formulation of preparations **ERC 4**: Industrial use of processing aids in processes and products, not becoming part of articles **ERC 6b**: Industrial use of reactive processing aids	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 4.3: Identified Uses and Process Categories for Lead Diazide

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**
Article fabrication stage – Applications confirmed as relevant to the EU							
Use of lead diazide/primer mixtures in fabrication of detonators for civil applications (quarries, mining, construction)	**PROC 5**: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact) **PROC 8b**: Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at 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 15**: Manufacture of fabricated metal products, except machinery and equipment	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.51 - Manufacture of explosives

Table 4.3: Identified Uses and Process Categories for Lead Diazide

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**
Use of lead diazide/primer mixtures in fabrication of detonators for military explosives and munitions	**As above**	**ERC 5**: Industrial use resulting in inclusion into or onto a matrix	In a mixture	**PC 11**: Explosives	**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
Use of lead diazide/primer mixtures in the initiation of high explosives in space shuttles	**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 **SU17**: General manufacturing	**AC 0**: Other (not intended to be released): pyrotechnic articles	C20.51 - Manufacture of explosives
End-use of articles							

Table 4.3: Identified Uses and Process Categories for Lead Diazide

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**
Detonation of detonators for civil applications	Use of articles containing lead diazide as a primary explosive	Outdoor use; substance consumed during use	Article	**PC 11**: Explosives	**SU 2a**: Mining (without offshore industries)	Not relevant	F43.1.1 - Demolition B5 - Mining of coal and lignite B7 - Mining of metal ores
Detonation of detonators for military explosives and munitions	Use of articles containing lead diazide as a primary explosive	Outdoor use; substance consumed during use	Article	**PC 11**: Explosives	**SU 22**: Professional uses: Public domain	Not relevant	O84.2.2 - Defence activities
Use of primer mixtures in the initiation of high explosives in space shuttles	Use of articles containing lead diazide as a primary explosive	Outdoor use; substance consumed during use	Article	**PC 11**: Explosives	**SU 0**: Other	Not relevant	C30.3.0 - Manufacture of air and spacecraft related machinery H51.2.2 - Space transport

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

Generally, lead diazide is either used on its own or first added to mixtures (primers) and then subsequently used to fabricate articles (e.g. detonators) on the same site where the substance is manufactured. Therefore, releases from the 'first use' of the substance in formulation and article fabrication are generally included in releases from manufacture, as submitted by individual companies and as shown in the SIC BREF Document.

Articles containing lead diazide-based mixtures may subsequently be used in the production of larger, more complex articles, e.g. a pyrotechnic device becomes a component of an artillery shell. Lead diazide is captive within the component (detonator), 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, as confirmed by **Company 20** and the Federation of European Explosives Manufacturers which suggests no releases to any environmental compartment (Federation of European Explosives Manufacturers, 2011b).

5.1.2 Releases from End Use of Lead Diazide Articles

Being a primary explosive, lead diazide essentially has to be consumed (burnt) during the active use of articles that contain it, i.e. during the detonation of detonators or the firing of munitions. 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, but rather formation of combustion products such as lead oxides, nitrogen oxides and nitrogen. Evidently, an issue arises with the release of lead to the environment.

If it assumed that <15 t/y of lead diazide used in the production of articles each year in the EU, then we can estimate the amount of lead present in these products. The average purity of lead diazide used is ca. 90% and the lead content of the molecule is 71%. Therefore, the use of <15 tonnes of lead diazide would mean use of <9.6 (15 x 0.90 x 0.71) tonnes of lead. It cannot be assumed that the entire amount of articles is consumed in a year – 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[13]. Huynh (2006) suggests that the long-term use of lead diazide and lead styphnate as primary explosives has resulted in lead contamination at artillery and firing ranges, becoming a major health hazard for civilian and military personnel.

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[13] 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).

On the other hand, the per unit (detonator, munition article, etc.) emission of lead will naturally be very small, at the milligram level. **Company 2** suggests that upon detonation of lead-based detonators, lead compounds are dispersed and are to be found in the final processed product (coal, metallic ores) or they end up being fixed in products (building aggregate).

5.2 Releases to the Working Environment

5.2.1 Introduction

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 diazide are given in bold, however, it should be noted that the table refers to lead, not specifically to lead diazide. It should not, therefore, be assumed that the substance is wholly (or indeed mainly) responsible for the perceived high levels of 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
Category 2: High exposure, moderate frequency	**Firing-range instructors** House renovators Lead miners Newspaper printers Plastics workers Rubber workers Steel welders and cutters

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

Exposure category	**Occupational exposure groups**
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 arguments made by consultees in their questionnaire responses that worker exposure to the substance is very limited. It should also be acknowledged that the nature of the substance is such that great precautions need to be taken to prevent worker exposure.

5.2.2 Releases and Exposure during the Production of Articles

Releases and Exposure from Manufacture of Mixtures and Articles

Limited 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 (who are also manufacturers of the substance itself) claim that there is very low if any worker exposure to lead diazide during the ‘first use’ of the substance in the fabrication of articles.

Three companies have provided information that can be reproduced in this part of the report. **Company 2** produces detonators for civilian and military applications, **Company 18** fabricates pyrotechnic devices and uses those in artillery shells, and **Company 20** purchases devices produced by other companies and uses them in the fabrication of the final article (military munitions). The information provided by these companies is summarised in **Table 5.2**.

Table 5.2: Worker Exposure to Lead (Diazide) during Production of Detonators

Worker exposure parameter	**Company 2**	**Company 18**	**Company 20**
	Production of civilian and military detonators	***Production of pyrotechnic devices for munitions***	***Production of military munitions using purchased detonators***
Type of product handled	Substance of purity ca. 93%	Substance of purity ca. 95%	Closed article containing lead diazide
Relevant process step where exposure occurs	Pressing	Pressing Crimping Transfer rate: 300 g in a conductive rubber vessel per day (8h)	None – Automatic or manual assembly into higher level article
Route of occupational exposure	Skin, inhalation	Skin	Not applicable
Exposure level (lead mg/m^3)	<0.05 mg lead/m^3	Dust, <1 mg/person/day of manufacture, without protection (est)	Nil
Ventilation conditions	Ventilation present	No ventilation	Not required for closed assemblies
Other exposure control measures	Textile gloves coated with PVC and ordinary respirators	Complete mask with cartridge against acid gas (ABE1 type); no gloves Conductive shoes against static electricity, glasses, fireproof overalls. Operations are automatic and the operators do not come into contact with lead diazide. Operators take detonators at the end of manufacture during and after crimping operation of detonators; at this step of manufacture the lead diazide is closed in an aluminium cap	None for exposure to lead diazide. Gloves; tooling and guarding to minimise physical injury from unintended detonation of an article
Frequency of exposure (days per year)	220	Unknown	Varies depending on contract need
Duration of exposure per day (minutes per day)	300	80	Varies depending on contract need
Number of employees exposed	6	4	Varies depending on contract need

Table 5.2: Worker Exposure to Lead (Diazide) during Production of Detonators

	Company 2	**Company 18**	**Company 20**

Source: Consultation

5.2.3 Releases and Exposure during End Use of Articles

No exposure during the handling of detonators is expected. **Companies 24** and **28** advised during fabrication of articles that primer mixture is loaded under pressure into metal cups or sleeves and sealed after filling. The subsequent user will not get in contact with the ingredients. The detonators also are not intended to be re-opened because of the risk of explosion. The Federation of European Explosives Manufacturers agrees that the downstream user never comes to direct contact with the substance due its airtight encasement inside a metal shell (Federation of European Explosives Manufacturers, 2011b).

Lead diazide is consumed during detonation and forms reaction products; no significant lead diazide emission is expected.

Blasting activities take place either in the open away from residential areas (open pit mines, quarries), in well-ventilated tunnels or underground mines. Some lead will be released upon detonation, for example inside mines. It is suggested that the relevant quantities are very small in comparison to the quantity of lead expelled by internal combustion engines of machines used by miners (input from **Company 2**). The Federation of European Explosives Manufacturers has provided an example: one detonator containing 60 mg of lead may be used in a salt mine to initiate 3 kg of explosive and produce approximately 10 tonnes of salt. Analytical tests of food-grade salt quality using the latest analytical equipment, no lead above detection level has been found (Federation of European Explosives Manufacturers, 2011b).

5.3 Worker Exposure Modelling Estimates

5.3.1 Exposure Estimates for Production of Articles

Overview

Lead diazide is both used in wet as in a dry phase to load articles. Exposure during production of articles is considered similar as the exposure during manufacturing of the compound lead diazide. Production of articles is commonly done on the same site as the manufacturing of lead diazide hence similar operational conditions and risk management measures. The reasonable worst-case situations during the production process of articles containing lead diazide is with the pure substance. The exposure estimates for manufacturing of lead diazide are therefore also relevant for production of articles containing lead diazide.

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 "*manual transfer*" have been assessed up to kilogram amounts in Section 3.5.3;
- manual transfer of dry material (maximum a few hundred grams) into or from the "closed vessels" have been assessed up to kilogram amounts in Section 3.5.3;
- manual transfer of the dry material of small quantities (milligrams) into devices;
- sampling has been assessed up to kilogram amounts in Section 3.5.3;
- cleaning (final cleaning of equipment and cleaning of the workplace) has been assessed up to kilogram amounts in Section 3.5.3.

Inhalation Exposure Estimates

Inhalation exposure was estimated using the Stoffenmanager 4.0 model[14]. The input parameters and resulting exposure estimates are presented in **Table 5.3**.

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; and
- 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. 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).

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

Task or process assessed	**Transfer of dry material - manual-filling devices**
Product and substance data	
Physical state of the substance	Solid-dry
Concentration	Up to 100%
Dustiness (category)	Granules/grains/flakes
Handling data	
Handling category	Handling of products in negligible amounts
Duration of task or process (hour)	1
Exposure control data	
Local controls used to limit emission from the source	No control measures at the source
Source in the near field:	Yes

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

Other sources of Lead Styphnate in the same room:		Yes
Room volume:		Volume 100-1000 m^3
General ventilation:		General ventilation (mechanical or natural)
Immission controls:		The employee does not work in a cabin
Work area regularly cleaned:		Yes
Equipment regularly inspected and well maintained:		Yes
Resulting exposure level estimate		
Estimation of exposure level (mg/m^3) per task	Without PPE	0.44
	With PPE	0.18
Estimation of exposure level (mg/m^3)-8 hours' time average	Without PPE	0.06
	With PPE	0.02
Estimation of exposure level (**mg Pb/m^3**) per task	Without PPE	**0.31**
	With PPE	**0.13**
Estimation of exposure level (**mg Pb/m^3**)-8 hours' time average	Without PPE	**0.04**
	With PPE	**0.014**
Source: TNO calculations		

We will use here the approach followed for the modelling estimates for inhalation exposure during manufacture of lead azide (see Section 3.5.3). Therefore, we compare the inhalation exposure estimates to the inorganic lead inhalation exposure limit of 0.05 mg/m^3 (8-h time weighted). It is clear that this 'benchmark' value is not exceeded. Thus, based on the assumptions and calculations made, the inhalation risks for workers are low. The measures taken by producers of articles containing lead azide (including PPE) are also noted.

Dermal Exposure Estimates

Dermal exposure has been estimated with RISKOFDERM version 2.1.

The input parameters for manual transfer of the dry material of small quantities (milligrams) into devices and resulting exposure estimates are presented in **Table 5.4**. The bottom of the table shows the results expressed in mg of lead per day and per kilogram of bodyweight per day (lead accounts for just over 71% of the molecular weight of lead diazide). In accordance with our approach outlined in Section 3.5.3, we initially assume 100% absorption through the skin when running the model.

The considerations regarding the input parameters are the same as during manufacturing with a one exception:

- 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 respectively 0.005 kg/min and 0.00333 kg/min.

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

Task or process assessed		**Transfer of dry material - manual-filling devices**
Product and substance data		
Type of product		Light or moderately dusty solid
Concentration		Up to 100%
Handling data		
Handling category		Filling, mixing or loading
Duration of task or process (hour)		1
Exposure control data		
Quality of the ventilation:		Normal or good
Frequency of skin contact:		Rare contact
Kind of skin contact:		Light contact
Significant amount of aerosols:		No
Level of automation		Manual
Application rate of product (kg/min)		3.33E-03
Resulting exposure level estimate		
Worst case (90%) estimation of exposure level (mg/day)	Without PPE	8.90E-02
	With PPE	8.90E-03
Worst case (90%) estimation of exposure level- (mg/kg bw/day)	Without PPE	1.27E-03
	With PPE	1.27E-04
Worst case (90%) estimation of exposure level (**mg Pb/day**)	Without PPE	**6.33E-02**
	With PPE	**6.33E-03**
Worst case (90%) estimation of exposure level- (**mg Pb/kg bw/day**)	Without PPE	**9.04E-04**
	With PPE	**9.04E-05**
Source: TNO calculations		

Following the approach taken in Section 3.5.3 for the manufacture of the substance, we adjust the exposure figures above to account for the low rate of absorption inorganic lead compounds of 0.01%. Thus, the estimate intake of lead under the scenario of dermal exposure is as shown in **Table 5.5**.

Table 5.5: Estimates of Lead Dermal Intake during the Production of Articles

Dermal intake estimates	**Transfer of dry material - manual-filling devices**
Dermal absorption rate: 0.01%	

Worst case (90%) estimation of exposure level hand loading (**mg Pb/day**)	Without PPE	6.33E-06
	With PPE	6.33E-07
Source: TNO & RPA calculations		

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 estimates in the table are far below the 'benchmark' value of 0.5 mg per day suggesting that risks to workers through dermal exposure are low, which is not surprising given the minimal intake through the skin. Again, we note the engineering and worker protection measures taken by the relevant companies, especially in light of the nature of the substance which requires that worker contact be minimised to the degree possible.

5.3.2 Exposure Estimates for End Use of Articles

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

6 CURRENT KNOWLEDGE OF ALTERNATIVES

6.1 Alternative Primary Explosives

6.1.1 Overview of Potential Substitutes

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
Metal salts of 5-nitrotetrazole, e.g. the mercuric or copper salt	-	60345-95-1 (Hg)
1,3,5-triazido-2,4,6-trinitrobenzene (TATNB)	-	29306-57-8
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

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

It is of note that efforts to find alternatives to lead styphnate and lead diazide 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 diazide in US Navy ordnance were imposed. In non-hermetic systems, lead diazide 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 diazide which may be considered alternative substance. These include silver azide and salts of picric acid such as lead picrate (2,4,6-trinitrophenol, lead salt) and ammonium picrate. These are discussed in Section 6.2.

6.1.2 Individual Alternatives to Lead Diazide

Diazodinitrophenol (DDNP)

DDNP is less sensitive to impact than mercury fulminate, lead diazide or lead styphnate. It is more stable and brisant than mercury fulminate and is used in blasting caps, loading fuse detonators and in priming compositions for military use. The initiating power of DDNP is slightly less than lead diazide. Some researchers 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 diazide. 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).

Tetrazene (Tetracene)

Despite the fact that lead diazide, 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 diazide, 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 density increases, its brisance falls off. 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, hence, it finds extensive use in cap compositions. It is used in cap compositions where as little as 2% in the composition results in an improved uniformity of percussion sensitivity (Agrawal, 2010). Overall, tetrazene cannot be considered 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. 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 diazide 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 diazide. 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 fuzes of grenade detonators.

An advantage of working with these high nitrogen compounds is that they can frequently be tailored, through the removal of acidic protons, into various metal or organic salts. Salt formation tends to lead to increased thermal stability, low volatility, greater density and the ability to tune important energetic properties like sensitivity. As a result, several metal salts of tetrazole-based systems have also been investigated, including copper 5-nitrotetrazole (also known as DBX-1) which can be used in M55 (US-made) stab detonators. Molecules capable of being converted into salts have also been studied, such as 5-nitriminotetrazole (NITz) and 2-methyl-5-nitraminotetrazole (MNATz) (Oyler *et al*, undated).

Fronabarger *et al* (2010) make particular mention to the suitability of DBX-1 as a replacement for lead diazide. They note that this material has better compatibility than lead diazide with a range of materials. DBX-1 has demonstrated compatibility with secondary explosives such as RDX, HMX, NOL-130, CL-20, HNS, PYX, ZPP and well as metals.

Researchers at the University of Munich have made efforts to make 5-nitrotetrazole salts that are safer to handle, explode more cleanly and produce fewer toxic by-products and smoke particles than today's popular explosives (such as TNT) or rocket propellants (such as perchlorate, a potential human health hazard). After making structural tweaks, such as adding nitro groups, the researchers say the compounds can be made to explode with comparable power to explosives like TNT and RDX. Tetrazoles are reportedly far less sensitive to shock or impact, allowing them to be handled more easily. Their explosions are much cleaner, producing mostly nitrogen gas instead of the smoky by-products of incomplete combustion of carbon-based compounds. The compounds are also non-toxic, so remains will not contaminate nearby land or water supplies. Switching to nitrogen-based detonators would reduce soldiers' exposure to toxic lead emissions and keep gun barrels clean, reducing the chance of weapon systems jamming. The cleaner explosives would also cut down on smoke emissions that might betray a soldier's position (Brindley, 2008).

A UK Ministry of Defence publication of 1974 found on the Internet (UK MoD, 1974) indicates that in the 1970s, silver and mercuric 5-nitrotetrazole were shown to be stable and would efficiently detonate RDX in large detonators. However, neither, in their then physical form, were technically suitable for the then UK design of small detonators. The silver salt dead pressed at loads too low for adequate consolidation; the mercuric salt detonated the RDX but not as efficiently as lead diazide. Subsequent research indicates that mercury nitrotetrazole may be an effective single component detonant with greater output than lead diazide. It is also claimed that, in contrast to lead diazide, mercury nitrotetrazole possesses the advantage of being highly inflammable. Further, its stability is not influenced by the presence of carbon dioxide and it may be stored without deterioration in tropical climates. Its sensitivity to electrostatic initiation is also relatively lower than that of other primary explosives in use (Agrawal, 2010). However, the presence of mercury in the molecule makes it less than an ideal replacement for lead diazide.

Finally, high-nitrogen new explosives such as 1,3,5-triazido-2,4,6-trinitrobenzene (TATNB) and 1,4-diformyl-2,3,5,6-tetranitratopiperazine have also been examined. These, however, also have their limitations. For example, TATNB undergoes decomposition reactions over a period of time which results in loss of its initiating power (Agrawal, 2010).

Explosive Complexes

Huynh *et al* (2006) report on green primary explosives based on 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). These have been tested and found to be safer to prepare, handle and transport than lead compounds, have comparable initiation efficiencies to lead diazide 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 $(\mathrm{cat})_2[\mathrm{M^{II}(NT)_4(H_2O)_2}]$ 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 (H_2O, NaCl, or NH_4Cl, and $NaNO_3$ or NH_4NO_3), (ii) have controllable explosive sensitivities allowing for mitigation of unexpected accidents, and (iii) deposit undisruptive decomposition products (iron or copper, N_2, CO_2, H_2O, 2% of NO_2, 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-N^2) cobalt(III) perchlorate ($[\mathrm{Co^{III}(NH_3)_4(NT)_2]ClO_4}$), pentaammine (5-cyanotetrazolate-N^2) cobalt(III) perchlorate ($[\mathrm{Co^{III}(NH_3)_5(CAT)](ClO_4)_2}$), and pentaammine (5-aminotetrazolate-N^2) cobalt(III) perchlorate ($[\mathrm{Co^{III}(NH_3)_5(DAT)](ClO_4)_3}$). 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).

6.1.3 Alternative Articles

One approach to eliminating the use of lead diazide in detonators has been the development of detonators free from primary explosives or 'non-primary explosive detonators' (NPEDs) (see

Figure 6.1). In these detonators, primary explosives are commonly replaced by a specially treated secondary explosive (Rustan, 1998). This system relies on the establishment of conditions in the detonator which cause a secondary explosive to undergo a deflagration to detonation (DDT) reaction (Sharma, 2006).

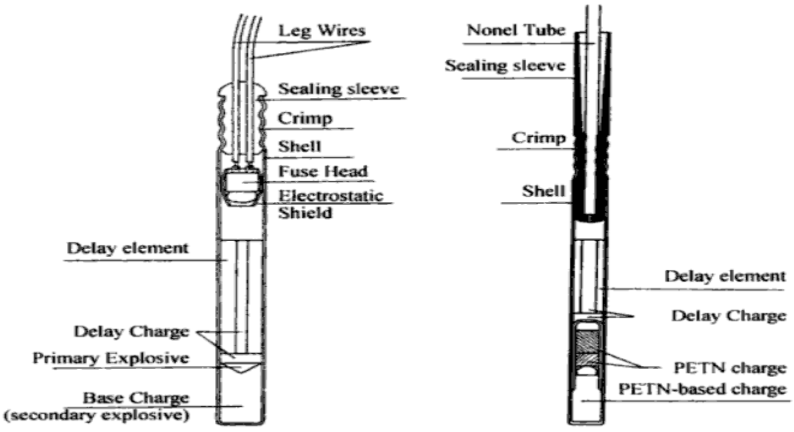

Figure 6.1: Comparison of a Conventional Electric Detonator with a NPED Detonator

Source: Hustrulid (1999)

Within DDT detonators, deflagration is initiated directly in a secondary explosive via a thermal reaction with an igniting device (e.g. a flame-front from a shock tube, or directly from a heated bridge wire). By incorporating suitable confinement to the secondary explosive, and/or control of the particle size, morphology, density and formulation of the secondary explosive, in addition to careful selection of the initiation means and detonator design a DDT reaction can be achieved. Subsequently, the detonation provides sufficient force to initiate an adjacent base charge of the detonator and in turn, the detonator directly initiates a shock tube of length of detonating cord attached to it (Sharma, 2006).

Nitro Nobel (now part of Dyno Nobel) was the first company to introduce a detonator for civil use which did not contain primary explosives; the Nonel (non-electric initiation system) NPED was the product of eight years of development and tests following the launch of their original Nonel in 1973 (Kennedy, 1994). More recently, Dyno Nobel has produced a NPED type detonator (US patent No.4.727.808), which they state gives increased safety in both manufacturing and handling (Dyno Nobel, 2007). The reasons for this increase in safety is due to NPEDs being considerably less sensitive than detonators containing primary explosives; furthermore NPEDs can often burn at atmospheric pressure without deflagration leading to detonation (Kennedy, 1994).

General problems with known NPED designs are to obtain a fast enough transition into detonation to give both reliable ignition and satisfactory time precision and to achieve this in combination with common pyrotechnical charges. In NPED type detonators speed is very important in the secondary explosive sequences. Detonation must be established rapidly to avoid having the detonator structures destroyed prematurely by the expansion forces from the reacting explosive (Dumenko, 1998). In addition, difficulties have arisen when trying to apply NPED principles to commercial detonators for rock blasting where special arrangements and transition mechanisms are needed (Dumenko, 1998).

In addition to DDT detonators, Sharma (2006) notes that other NPEDs have also been proposed, utilising flyer plates or lasers, however these have met with little commercial success due to operational and production difficulties.

6.2 Alternatives with Similar Structure

6.2.1 Identities of Potential Alternatives

We have examined whether there any substances similar to lead diazide (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 other azides, such as silver azide.

6.2.2 Hazard Profile of Potential Alternatives

Table 6.2 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 diazide. On the other hand, if classification of lead compounds is considered instead (also available in **Table 6.2**), this appears not to differ substantially from that of lead diazide, with the exception of the explosive properties that lead diazide is classified for.

A search in Annex VI of CLP Regulation has suggested that no harmonised classification and labelling is available for silver azide[15]. Neither has it been possible to identify relevant Safety Sheets that may give details of its hazard profile.

Table 6.2: 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	H201	
	Acute Tox. 3 *	H331	Exploding bomb
	Acute Tox. 3 *	H311	Skull and crossbones
	Acute Tox. 3 *	H301	
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*

6.2.3 Technical Suitability of Potential Alternatives

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. Ammonium picrate was used as a military explosive to fill armour-piercing shells because of its relative insensitivity to impact. It was also used in admixture with KNO_3 as a substitute for black powder or gunpowder. Ammonium picrate in conjunction with TNT has also been used in the past (Agrawal, 2010).

Picrates are known for decades and still have not been as widely used as lead diazide (or lead styphnate) in the applications discussed in this report. Moreover, the SIC BREF Document would suggest a very low manufacturing capacity for lead picrate compared to lead diazide (<0.3 t/y in 2004) which could make replacement difficult. Of note is the presence of lead

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[15] Notably, classification exists for sodium azide (here: http://ecb.jrc.ec.europa.eu/classification-labelling/clp/ghs/subDetail.php?indexNum=011-004-00-7&subLang=EN) and this suggests acute toxicity and chronic aquatic toxicity hazards.

picrate (as well as lead styphnate) in one of the detonator mixtures presented in **Table 4.2** (the final product, Reference 5). Lead picrate is present at very low levels, much lower than lead diazide or lead styphnate.

On the other hand, silver azide has the advantages of absence of more toxic metals its molecule. It has good initiation capability but its sensitivity and cost makes its commercial use very difficult (Agrawal, 2010).

Some technical characteristics of silver azide are available in Jung (2006). Silver azide has a density of 4.81 g/cm^3 which is slightly higher than lead diazide. The main barriers to widespread use of silver azide are its high cost and photosensitive nature. Silver azide rapidly decomposes when exposed to ambient light, especially of ultraviolet wavelengths. Even with this handling difficulty, the superior initiating qualities of silver azide over lead diazide have sustained interest in its use. Experimental results have shown that smaller quantities of silver azide than lead diazide were needed to successfully initiate charges of PETN under various conditions as well as the superiority of silver azide over lead diazide in initiating charges of RDX.

For completeness, **Table 6.3** is provided overleaf. This presents a summary of primary explosives with some structural similarities to lead diazide 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 than lead diazide. 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 substances containing lead of other heavy metals can be considered suitable alternatives for lead diazide.

6.2.4 Substitution of Lead Diazide by Lead Styphnate

There is no evidence that lead diazide can be interchanged with lead styphnate in its known applications. Both substances are frequently jointly present in mixtures but lead diazide is the main primary explosive of common detonators while lead styphnate is essentially used in primers for small calibre (military/sport/hunting) ammunition. Lead styphnate accompanies lead diazide in detonators in order to improve its sensitivity to ignition but it cannot replace lead diazide in its own right.

There has been no suggestion by any consultee that one can successfully act as a replacement for the other.

Table 6.3: Key Properties of Primary Explosives with Structural Similarities to Lead Diazide

Substance Name	CAS Number	Properties						
		Molecular Weight	**Detonating Velocity (m/s)**	**Sensitivity**	**Stability**	**Flammability**	**Toxicity**	**Overall value (as a primary explosive)**
Lead diazide	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
Ammonium azide	12164-94-2	60.06	4,300 (estimated)	Easily detonated	Low	Explodes when ignited	High	Low
Cupric azide (copper-II-azide)	14215-30-6	147.592 (minus hydration)	3,200 (estimated)	Very easily detonated	Very low	Explodes when ignited	Moderate	Low
Silver azide	13863-88-2	149.889 (minus hydration)	3,100 (estimated)	Easily detonated	Moderately low	Explodes when ignited	Moderate	High
Mercury azide (precipitated Mercury-II-azide)	14215-33-9	284.630	6,200 (estimated from non-stabilised dry form)	Easily detonated	Moderate	Explodes when ignited	High	Moderate
Tetrazide (Isocyanogen tetraazide)	-	220.12	Not calculated	Detonates rather easily	Moderate	Explodes when ignited	Moderate	Moderate
Lead-TNP – (Trinitrophloroglucinol lead salt)	51325-28-1	1065.69	Not calculated	High	Moderate	Explodes when ignited	Moderate	Moderate

Table 6.3: Key Properties of Primary Explosives with Structural Similarities to Lead Diazide

Substance Name	CAS Number	Properties						
		Molecular Weight	**Detonating Velocity (m/s)**	**Sensitivity**	**Stability**	**Flammability**	**Toxicity**	**Overall value (as a primary explosive)**
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)

6.3 Experiences of EU Industry with Alternatives

6.3.1 Overview of Consultation Responses

Three alternative substances and one alternative technology have been named by consultees as potential alternatives but without having the ability to fully replace lead diazide 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 reveals that:

- not all companies are currently working on alternatives and several of them could not name any substance/technique as a potential alternative;
- the alternatives identified as promising would only achieve partial rather than complete replacement of lead diazide (although one company has a somewhat different opinion on the suitability of a specific alternative for use in military munitions);
- there is significant concern among companies with regard to the qualification and certification of alternative primer mixtures. Articles intended to be used by military personnel (detonators, munitions) need to be especially reliable and meet specific requirements typically set by relevant authorities/defence agencies. The possibility of unilaterally changing an approved composition is non-existent;
- 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 10 years to more than 20 years without a clear indication (at present) that efforts might be fruitful for all applications of lead diazide.

The Federation of European Explosives Manufacturers has also argued that there is no other known primary explosive with the same or comparable physical and chemical stability to that of lead diazide. The Federation admits that new substances have been reported in literature, some of which have been experimentally prepared and tested (a few articles only). However, their multi-stage synthesis is complicated and dangerous (some of the intermediates are extremely unstable) and large amounts of wastewater and solvents arise during production (Federation of European Explosives Manufacturers, 2011b).

DDNP has been used as alternative primary explosive since end of the 19th Century. However, it has unpleasant aspects – dermatological issues and unclear toxic consequences; DDNP is also a much less known substance compared to lead diazide. In addition, DDNP is a part of nitro-aromatic substances, which do not have good toxicological profile as well. 200 mg of DDNP may be required per detonator – this is up to three and half times larger than the amount of lead diazide required. 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 diazide (Federation of European Explosives Manufacturers, 2011b).

The Federation believes that a suitable alternative may arise only through R&D in primary explosives and a result may be expected in less than 10-20 years (Federation of European Explosives Manufacturers, 2011b). However, it is expected that research and development of new primary explosives and their production on industrial scale would have negative results with regard to safety during production and usage in detonators. The function of millions of detonators needs to be tested to prove the safety and reliability level of alternatives at a scale comparable to that of lead diazide.

6.3.2 Views of Industry Stakeholders on the Suitability of Picrates and Silver Azide

Views of consultees on the suitability of picrates or silver azide as a replacement of lead diazide and on the potential for replacement of lead diazide by lead styphnate are provided in the Confidential Annex (Section A6.4).

6.3.3 Potential Cost of Alternatives

In respect of the cost of replacing lead diazide (and lead styphnate), 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 detonator/igniter 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, 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 detonator/munition designs in production within the EU and every one in which a new detonator is used would have to be tested.

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ANNEX 1. GLOSSARY

Term	**Description**
ANFO	Ammonium Nitrate/Fuel Oil. ANFO is a widely used explosive mixture
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road. It governs transnational transport of hazardous materials
ASA	Lead Diazide, Lead Styphnate and Aluminium. ASA compound is a primary explosive used in many detonators
Blasting cap	A small, sensitive primary explosive device generally used to detonate a larger, more powerful and less sensitive secondary explosive such as TNT. A component of detonators
Brisance	Brisance refers to 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
CL-20	CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) is a secondary explosive related to the explosives RDX and HMX
CTA	Cyanuric Triazide. It is also known as Triazine Triazide (TTA). See TTA below
DBX-1	Copper 5-nitrotetrazole is a tetrazole-based metal salt
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
Dead pressed	Dead pressed refers to a highly compressed condition which tends to prevent the transition from deflagration to detonation that would otherwise take place
Deflagration	Deflagration refers to subsonic combustion that usually propagates through thermal conductivity. Deflagration is different from detonation (which is supersonic and propagates through shock compression)
Detonator	A device used to trigger an explosive device
ESWL	Extracorporeal Shock Wave Lithotripsy. ESWL is the procedure by which shockwaves are generated at a point external to the body and are focussed on a kidney stone in the body
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

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HMX	HMX (also called octogen) is a powerful and relatively insensitive nitroamine high explosive, chemically related to RDX
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 oxidising trinitrotoluene (TNT) with a solution of sodium hypochlorite. HNS has a higher insensitivity to heat than TNT, and like TNT it is very insensitive to impact
Initiating value	Also known as initiation efficiency or strength of initiation explosives blasting caps and detonators is expressed in terms of min weight of primary (or initiating) explosive or as the smallest number of blasting cap(s) or detonator(s) required to cause maximum detonation of a high explosive
Intermediate charge	In general, detonators consist of an ignition charge, intermediate charge, and a base charge. Each charge in the train is used to transition from heat to shock
MIC	Metastable Interstitial Composite 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
MNATz	2- methyl-5-nitraminotetrazole
NACE codes	NACE Code is 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
NITz	5-nitriminotetrazole
NOL-130	NOL-130 is a primer mix. It is comprised of lead styphnate (basic) 40%, lead diazide (dextrinated) 20%, barium nitrate 20%, antimony sulphide 15%, and tetrazene 5%
NPED	Non-Primary Explosive Detonators. These detonators are free of primary explosive. NPED rely on conditions in the detonator which cause a secondary explosive to undergo a DDT reaction
NSD	NASA Standard Detonator. The NASA Standard Detonator is a device used by NASA for applications where a charge must be detonated
NSI	NASA Standard Initiator. NSI (also known as ZPP, or zirconium – potassium perchlorate) is one of the most common initiators. It is a mixture of metallic zirconium and potassium perchlorate
Percussion cap	Found in firearms. The percussion cap is a small cylinder of copper or brass with one closed end. Inside the closed end is a small amount of a shock-sensitive explosive material such as mercury fulminate. The percussion cap is placed over a hollow metal "nipple" at the rear end of the gun barrel. Pulling the trigger releases a hammer, which strikes the percussion cap and ignites the explosive primer. The flame travels through the hollow nipple to ignite the main powder charge
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

Term	**Description**
Primary explosive	Primary explosive is a sensitive explosive initiated by burning. They have a low deflagration to detonation transition and go from burning to detonation very quickly. Primary explosives are often referred to as initiating explosives because they can be used to ignite secondary explosives
Primer (cap)	A relatively small and sensitive device used to initiate the functioning of an explosive, igniter train, or pyrotechnic charge; it may be actuated by friction, percussion, heat, pressure, or electricity
PYX	PYX, a code name for 3,5-dinitro-N,N’-bis(2,4,6-trinitrophenyl)- 2,6-pyridinediamine, is a powerful insensitive high explosive with similar properties and uses as RDX and HMX
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
Secondary explosive	A secondary explosive is less sensitive than a primary explosive and requires substantially more energy to be initiated. Detonation in a secondary explosive is initiated by shock waves
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
SMDC	Shielded Mild Detonating Cord
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)
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
TNT	2,4,6-trinitrotoluene. TNT is one of the most commonly used explosives for military and industrial applications
TTA	Triazine Triazide. TTA is 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 diazide. It is a heavy metal-free polyazide compound containing only carbon and nitrogen
ZPP	Zirconium-Potassium Perchlorate. It is also known as NASA Standard Initiator (see NSI above)