ANNEX XV REPORT

PROPOSAL FOR A RESTRICTION ON THE USE OF 2,4-DINITROTOLUENE IN ARTICLES

SUBSTANCE NAME: 2,4-Dinitrotoluene

IUPAC Name: 1-methyl-2,4-dinitrobenzene

EC NUMBER: 204-450-0

CAS NUMBER: 121-14-2

CONTACT DETAILS:

EUROPEAN CHEMICALS AGENCY

VERSION NUMBER: 1
DATE: 24 June 2021

P.O. Box 400, FI-00121 Helsinki, Finland | Tel. +358 9 686180 | echa.europa.eu

Contents

TABLES

Summary

2,4-dinitrotoluene (2,4-DNT) is classified under Regulation (EC) No 1272/2008 (CLP) as a carcinogen category 1B, H350 (may cause cancer)[1] and was therefore included in the candidate list for authorisation (13/01/2010; ED/68/2009[2]) and into Annex XIV of REACH (Commission Regulation (EU) No 143/2011) on the basis of Art 57(a) of REACH with a sunset date of 21/08/2015. Following an assessment of the available evidence in accordance with Article 69(2) of the REACH Regulation, ECHA considers that there are uses of the substance which may lead to a non-adequately controlled risk from 2,4-DNT presence in articles. This Annex XV restriction proposal addresses those risks in articles not already regulated. There is no information available on current manufacture, import or export of 2,4-DNT in the EU and ECHA has received no registrations for the substance.

2,4-DNT is an isomer of the multi-constituent substance DNT (EC: 246-836-1). Two of the isomers of DNT, 2,4-DNT and 2,6-DNT, make up 95 % of DNT. Four other isomers (2,3-, 2,5-, 3,4-, and 3,5-DNT) make up the remaining 5 %. Currently, there are 2 registrations for DNT (1 – 10 tonnes/year and as an intermediate). Before 2010, technical grade DNT (assuming common concentrations of 75-80 % of 2,4-DNT in technical DNT) was produced in 5-6 places in EU for the production of toluene diisocyanate. DNT containing a 50-55 % concentration of 2,4-DNT has been imported for use as a binding agent in the non-ferrous metal industry and import of propellants in the range 1-10 t/year with technical grade DNT has also been reported before 2010. Other DNT isomers are not specifically targeted by this screening report but they may be also in scope of if included in articles, when 2,4-DNT is present in mixtures above the concentration limit of 0.1% and the presence of 2,4-DNT is a result of using DNT-mixtures with varying isomer content ratios.

Articles, where the current or previous use of 2,4-DNT has been identified, include: refractories, in automotive airbags, in seat belt pre-tensioners, in plastic bottles used in industrial settings for sample taking purposes, as propellants for military and civil small-arms ammunitions, as gelatinising-plasticising agent in explosive compositions, and as a plasticising and waterproofing agent for propellants in gun powders. The latter two in the list are considered as mixtures if not produced as an integral part of an article[3]. Two notifications of a substance in articles (SiA) have been made under Article 7(2) of REACH for 2,4-DNT; for the use as plasticiser in plastic sample bottles used at industrial settings, for which the notifying entity has now ceased, and for the use in propellants for military ammunition articles. Furthermore, the US Environmental Protection Agency lists possible uses of 2,4-DNT in sports equipment and in outdoor toys such as sandboxes. No details of the use or manufacture of these articles are available.

A search of the SCIP database[4] for 2,4-DNT indicate there are articles in the EU containing the substance used in vehicles, ceramic articles and electronic devices. This information confirms there are additional articles (probably imported articles) that contain the substance.

[1] https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/6510

[2] Inclusion of substances of very high concern in the candidate list, Decision by the Executive Director

[3] See *Guidance on requirements for substances in articles* (ECHA 2017) in https://tinyurl.com/y5tao8yb

[4] In accordance with the Waste Framework Directive (WFD), companies supplying articles containing substances on the Candidate List in a concentration above 0.1% w/w on the EU market have to submit information on these articles to ECHA, from 5 January 2021. The information provided is included in the SCIP database, i.e., Substances of Concern In articles as such or in complex objects (Products): https://echa.europa.eu/scip

2,4-DNT can be released from articles into the water, air, and soil at places where they are produced or used. This restriction proposal targets consumer and certain worker uses in articles where release and exposure of 2,4-DNT cannot be excluded and risk management measures are difficult to implement.

2,4-DNT is applied in plastic sampling bottles used in industrial settings for sample taking where the substance acts as a softener. Possibility of migration and worker exposure of 2,4-DNT from the bottle cannot be excluded from use of the articles. Traces of 2,4-DNT may also be found in refractory products.

Consumer exposure may occur from civilian small arms ammunition use such as hunting and sports shooting, if the ammunition propellant contains 2,4-DNT. Shooting of the firearm does not consume all 2,4-DNT in the ammunition and exposure via inhalation or dermally may occur. Two other consumer uses found are in seat belt pre-tensioners, where an explosive charge causes the gas generator to produce a volume of gas and thus pressure which then acts on a mechanical linkage to pull the seat belt, and in air bags, where deployment releases gas in a similar manner as in pre-tensioners. For the vehicle safety systems, some other groups at risk of exposure in addition to the driver include e.g. car repair technicians. In these uses, inhalation and dermal exposure may occur.

Studies of DNT carcinogenicity have been conducted in ammunition production facilities, copper mining industry and at ammunitions production facilities where an association between cumulative DNT exposure and renal cell cancer has been found. Particularly dermal, but also inhalation DNT exposure association with renal cancer has been found among miners in different roles in relation to DNT containing explosive stick handling and possible inhalation exposure.

2,4-DNT is considered as a non-threshold substance for which no DNEL can be derived and therefore the ECHA as the Dossier Submitter is of the view that 2,4-DNT poses a risk to human health if incorporated in articles that is not adequately controlled. The use of 2,4-DNT in production of articles in the EU is subject to authorisation requirements under Title VII of REACH. Authorisation requirements do not apply to imported articles and it is thus possible that articles containing 2,4-DNT are produced outside the Union and subsequently imported in the EU, causing a risk to human health that needs to be addressed.

An analysis of risk management options (RMOs) was conducted to identify the most appropriate measure to address these risks. The Dossier Submitter has further concluded that action is required to reduce risks for consumers and professional and industrial workers on a Union-wide level and that the proposed restriction is the most appropriate measure. The restriction is assumed to impose very low costs to reduce a potential risk; given the information at hand, it is assumed that the measure is proportionate to the risk. Alternatives to 2,4-DNT exists for the identified uses. As there is no EU production of articles, there is no need to transition to alternatives or stocks. If there are any imported articles, time is needed for importers to transition to the articles not containing 2,4-DNT. Therefore, it is assumed 12 months would be sufficient transition time. For the restriction it is proposed to use the same concentration limit as in the toys legislation[5]. The scope of the proposed restriction covers articles placed on the EU market that contain 2,4-DNT (seat belt tensioners, plastic sample bottles, ammunition, refractory materials, and others). Specific derogations are proposed.

[5] Directive 2009/48/EC on the safety of toys

Standardised laboratory methods for measuring 2,4-DNT in articles (and environmental samples) do exist, suggesting that the restriction is practical and monitorable. The presence of articles on the market containing 2,4-DNT could be monitored using databases or applications such as the ones that were used as sources for this Annex XV report preparation. The restriction is targeted to the effects or exposures that are of most concern, e.g. consumer and certain worker uses. The restriction is assumed to impose very low costs to reduce a potential risk; given the information at hand, it is assumed that the measure is proportionate to the risk.

A call for evidence was held 27/1/21 to 10/3/21 (https://echa.europa.eu/previous-calls-for-comments-and-evidence/-/substance-rev/27201/term); 2 comments were received, one giving further information on the occupational exposure, to 2,4-DNT (from production and handling of explosives) between 1990 and 2021. No additional information on uses or challenging the assumptions made was received.

Proposed restriction

Brief title: Restriction in articles for consumer and certain professional uses.

Table 1: proposed restriction

Column 1	**Column 2**
2,4-Dinitrotoluene EC Number: 204-450-0 CAS Number: 121-14-2	1. Shall not be placed on the market, or used, as a substance in articles for supply to the general public or to professional workers in concentrations $\geq$ 0.1 % weight by weight. 2. Paragraph 1 shall not apply to a substance in articles placed on the market or used in: a. Explosives, b. Ammunition used for military use. 3. Paragraph 1 shall not apply to a substance in articles regulated by: a. Directive 2009/48/EC on the safety of toys, b. Regulation (EU) 2017/745 on medical devices, 4. For the purposes of this entry, professional uses mean uses by workers that take place outside of industrial premises and where fixed risk management measures cannot be used or where consumers are exposed. 5. The restriction should enter into force after 12 months.

1

1. The problem identified

1.1 Background

2,4-dinitrotoluene (2,4-DNT) is classified under Regulation (EC) No 1272/2008 (CLP) as a carcinogen category 1B, H350 (may cause cancer) and was therefore included in the candidate list for authorisation (13/01/2010; ED/68/2009[6]). It was included into Annex XIV of REACH (Commission Regulation (EU) No 143/2011) on the basis of Art 57(a) of REACH with a sunset date of 21/08/2015. No applications were received for the use of 2,4-DNT as a substance, substance in a mixture or incorporation of the substance into articles. The supply of 2,4-DNT to the general public is currently restricted as a substance and in a mixture containing $\geq$ 0.1 % DNT (Annex XVII of REACH, entry 28 and appendix 2).

2,4-DNT is available commercially as a purified isomer or as a component of technical grade dinitrotoluene (DNT)[7]. Technical grade DNT is a mixture of isomers (approximately 80 % of 2,4-DNT and 20 % of 2,6-DNT) which is primarily used as a non-isolated chemical intermediate in the production of toluene diisocyanate (TDI). This in turn is used to make flexible polyurethane (PU) foams. The use of 2,4-DNT as a non-isolated intermediate is exempted from REACH.

Articles, where the use of 2,4-DNT (current or previous) has been identified, include: as a temperature specific cross-linking agent for refractories, in automotive airbags, in seat belt pre-tensioners, in plastic bottles used in industrial settings for sample taking purposes, as propellants for military ammunitions, as gelatinising-plasticising agent in explosive compositions, and as a plasticising and waterproofing agent for propellants in gun powders. However, only two notifications of a substance in articles (SiA) have been made under Article 7(2) for 2,4-DNT; for the use as plasticiser in plastic sample bottles used at industrial settings, for which the notifying entity has now ceased, and for the use in propellants for military ammunition articles.

2,4-DNT is a non-threshold carcinogen. Annex I Section 6.5 of REACH requires for human effects for which it was not possible to determine a DNEL, a qualitative assessment of the likelihood that effects are avoided when implementing the exposure scenario shall be carried out. In addition, RAC (2012) has taken a position in relation to applications for authorisations that for such substances adequate control is not achievable, neither for the use of that substance on its own nor in a mixture or the incorporation of the substance into an article.[8] Therefore, only a qualitative assessment is carried out for the substance.

According to ECHA guidance Part E (ECHA, 2016) and R.8 (ECHA, 2012), a qualitative approach has to be chosen when no reliable dose descriptor (without identified thresholds) can be set for a given endpoint. The purpose of the qualitative risk assessment is to assess 'the likelihood that effects are avoided when implementing the exposure scenario…' as expressed in REACH Annex 1, Section 6.5. As these are non-threshold substances it cannot be excluded that risks to consumers can occur. In addition, traditional operational conditions (OC) and risk managements measures (RMM), such as level of containment and

[6] Inclusion of substances of very high concern in the candidate list, Decision by the Executive Director

[7] EC: 246-836-1, CAS: 25321-14-6.

[8] https://echa.europa.eu/documents/10162/13555/common_approach_rac_seac_en.pdf

use of personal protective equipment, are not implementable by consumers and are also often difficult to implement by professional users. The only way to manage the risk in the case of articles where there is exposure to consumers and professional users is to limit the presence of unwanted substances.

The Dossier Submitter takes note of the EU General Court judgment of 7 March 2019 in Case T-837/16, Sweden v. Commission and the Commission's document from 27 May 2020 on the assessment of alternatives: Suitable alternative available in general & requirement for a substitution plan[9] in relation to applications for authorisation. The Commission document states that "In other words, the substitution plan creates an obligation to set out and implement the actions and the timetable towards substitution of the hazardous substance". The Dossier Submitter recognises the aim of REACH to substitute the SVHC substance on the EU market, including the SVHCs in articles, where this is technically and economically viable.

1.2 Manufacture and uses

1.2.1 Manufacture and import (brief overview)

Before 2010, DNT was manufactured at 5 or 6 sites in the EU (Technical report, 2010) where the substance was exclusively used in the manufacture of toluene diisocyanate (TDI). Most of the sites manufactured 'technical grade' DNT in quantities between 540 000 and 810 000 tonnes per year, which is equivalent to 405 000 and 648 000 tonnes of 2,4-DNT per year (assuming common concentrations of 75-80 % of 2,4-DNT in technical DNT).

One EU company has been reported as importing 50-55 % 2,4-DNT in the range 100-1 000 tonnes per year for use as a binding agent in the non-ferrous metal industry. Import of propellants that contain technical grade DNT of an unknown 2,4-DNT content had also been reported in the range 1-10 t/year (ECHA, 2010). Currently, there are 2 registrations for DNT (1 – 10 tonnes/year and as an intermediate) with a life cycle description of formulation into mixture used in explosives.

There is no current manufacture or import of 2,4-DNT in the EU as ECHA has not received any authorisation for applications for this substance and has no information if there is manufacture for the uses exempted from authorisation or for export.

1.2.2 Uses

Use of the substance or mixture (brief overview)

2,4-DNT is mostly used as chemical intermediate in the production of toluene diisocyanate (4-methyl-m-phenylenediisocyanate). It is hydrogenated to yield toluenediamine (TDA) and this diamine is reacted with phosgene to yield toluenediisocyanate (TDI), which is used to make flexible polyurethane foams. Other, minor uses as an intermediate include the use in the production of dyes and dyestuffs and rubber chemicals.

Legacy uses as an intermediate in the synthesis of dyes have been described in the literature. 95 % 2,4-DNT ('pure' DNT) was used in the past in the manufacture of other

[9] https://echa.europa.eu/documents/10162/13637/ec_note_suitable_alternative_in_general.pdf

dyes (Technical report, 2010). The available information suggests that there is at present no use of 2,4-DNT in dye manufacturing (ECHA, 2010).

2,4-DNT can also be used in smokeless propellants for explosives and ammunitions where it acts as a stabiliser, flash and temperature suppressor (ECHA, 2010). The role of DNT has also been described as a plasticiser [10] and as a waterproofing agent (Technical report, 2010). 2,4-DNT can also be the main energetic compound together with nitroglycerine in some propellants and the propellants may then contain 2,4-DNT in concentrations of +/- 10 % (US Department of Defense, 1973).

According to the Technical report (2010), DNT was still used as an additive in the manufacture of explosives (dynamite) in 2010 as there was one EU based company which still supplied 'pure' DNT and DNT 65/50 to EU and non-EU customers for the manufacture of explosives. The amounts of DNT used in or supplied to the explosives sector were however unclear. DNT (50/55) has been used also in the non-ferrous metals industry as a temperature-specific cross-linking agent for refractories in amounts of less than 1 000 t/year (Technical report, 2010).

The 'pure DNT' is also used in applications for which limited information is available, such as a fuel additive (Technical report, 2010). DNT 65/50 may also be used as a component of explosive materials (Technical report, 2010).

Recycling of trinitrotoluene (TNT) ammunition may also lead to DNT isomers present in the product as an impurity (Technical report, 2010).

Uses of substances in articles

There are two SiA notifications made under Article 7(2) for 2,4-DNT; for the presence as plasticiser in plastic sample bottles used at industrial settings and for the presence in propellants for military ammunition articles. Notification is not required if a substance is present in the specific articles in quantities less than one tonne per producer or importer per year.

The sections below cover also other uses of 2,4-DNT in articles, however as they have not been notified to ECHA according to Article 7(2), ECHA assumes that these articles are not currently used in EU, have not been notified by importers, or the amount is less than one tonne per year in articles. There have been no Safety Gate notifications for 2,4-DNT.[11]

Occupational uses

Ammunition

Propellants are usually regarded as substances/mixtures within the context of the REACH Regulation and thus as such are not within the scope of this report. However, when they are as an integral part of an article (e.g. within an ammunition or artillery shell), they are regarded as part of the article. The ammunition cartridge containing the propellant is designed to launch a projectile and the shape, surface and design of such ammunition

[10] Energetic material pyrotechnic compositions often employ plasticisers to improve physical properties of the propellant binder or of the overall propellant, to provide a secondary fuel, and ideally, to improve specific energy yield (e.g. specific impulse, energy yield per gram of propellant, or similar indices) of the propellant. An energetic plasticiser improves the physical properties of an energetic material while also increasing its specific energy yield.

[11] Reviewed 15 December 2019 for 2,4 DNT, DNT and technical DNT.

cartridges therefore determine their function to a greater degree than does its chemical composition.[12]

2,4-DNT is used mostly in single-based or double-based solid propellants. Single-based powders contain nitrocellulose as the sole energetic material. Jenkins and Vogel (2014) did not list 2,4-DNT as an ingredient for double base propellants, and it seems that even if it can be found from this propellant type, it is not as often included in the principal ingredients as in single base propellants. The review by Pichtel (2012) lists 2,4-DNT in the composition of single and double based propellants.

2,4-DNT can also be found in variety of concentrations in small arms ammunitions such as rifle and pistol projectiles. For some uses 2,4-DNT can still be found in the final product. One identified use of 2,4-DNT is in propellants for ammunition and explosives. Propellants may be found as an integral part of an article in a wide range of explosive articles including (but not limited to):

- *Articles from recycled trinitrotoluene (TNT) ammunition*
- *As an impurity in TNT containing explosive articles and ammunition*
- *Other explosive articles*
- *Small arms ammunition cartridges*
- *Artillery ammunition*

In addition, manufacturing or recycling of TNT ammunition may lead to DNT isomers being present in the product as an impurity. It is unknown if such recycled material is incorporated into explosive articles[13].

<u>Refractory products</u>

2,4-DNT has had applications in refractory products where it is used as a temperature specific cross-linking agent for refractories. It is possible that some of these applications fall within the definition of an article under the REACH regulation. Such products where DNT is transformed to another substance with possibility of traces of DNT in the final product[14]:

- *fired carbon cathodes - primary aluminium smelting*
- *fired carbon blocks - primary aluminium smelting*
- *ferro-alloy manufacture as furnace linings, inorganic chemical vessel linings e.g. phosphoric acid*
- *carbon ramming pastes - primary aluminium smelting, blast furnace linings, ferro-alloy furnace linings*
- *grouts - blast furnace linings, ferro-alloy furnace linings*
- *tap hole clays – ferro-alloy furnace linings*

[12] ECHA QA ID No 1059: https://echa.europa.eu/support/qas-support/qas

[13] As defined by Article 3(3) of REACH, an article "means an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition".

[14] Possibility for the products to have traces of 2,4-DNT was indicated in consultation for EU RAR 2008. European Union Risk Assessment Report on 2,4 – Dinitrotoluene

- *bricks*

The production of these refractory products is within the scope of the authorisation, if 2,4-DNT is used in treating of these articles, as this is not regarded as an intermediate use according to the Commission and ECHA. The interpretation has earlier been challenged by the industry in relation to other substance and the industry is therefore not applied authorisation for this specific use. ECHA is not assessing this use in this article 69(2) report as this should be covered by the authorisation.

Plastic containers

The notifying entity for plastic containers has ceased the use but it cannot be excluded that other companies are importing and using these containers, even though a notification is required if the tonnage per importer per year is above 1 t.

Consumer uses

Ammunition

In addition to occupational uses of ammunition, civilian small arms uses such as hunting and sport shooting may apply 2,4-DNT containing cartridges.

Automotive airbags and seat belt pre-tensioners

Use of 2,4-DNT in automotive airbags has been cited and some current uses in seat belt pre-tensioners have been indicated by vehicle manufacturers. In these automotive safety applications, 2,4-DNT is used in the pyrotechnic charge component that fires to pull the seat belt in to pull the passenger away from the airbag while it is deployed with a similar pyrotechnic application.

Some vehicle safety systems such as air bags have been indicated to use 2,4-DNT (EU RAR, 2008). Also, seat belt pre-tensioners have been suggested as a possible use. According to the Technical report (2010), vehicles with 2,4-DNT containing parts are not placed on the EU market. However, some vehicle manufacturers do indicate to have 2,4-DNT in some of their models' seat belts, likely referring to the pre-tensioners.[15,16]

Other

The presence of 2,4-DNT in refractory products is considered an uncertainty. Some products can be considered as articles (such as bricks), but no new information on the use of 2,4-DNT in these articles was discovered during the work on this restriction proposal report.

In addition, the US EPA Chemical and Products Database (CPDat) indicates there are a number of other uses of 2,4-DNT that have not been previously identified in EU articles.

---

[15] Pursuant to REACH article 33(2) a supplier of a product which include any article which contains more than 0.1 % by weight of Candidate List Substance to provide their customers with sufficient information, available to the supplier, to allow safe use of the article including, as a minimum, the name of that substance. See e.g. Toyota Aygo:

https://www.toyota-europe.com/world-of-toyota/feel/environment/just-better/chemical-management

[16] https://www.ford.co.uk/content/dam/guxeu/uk/useful-information/reach/Art-33-1-Information-Example-U502-Explorer.pdf

It is not clear if relevant articles in Table 2 are imported into the EU (potential consumer articles are highlighted in red).

Table 2: List of 2,4-DNT uses in substances, products and articles according to US EPA Chemical and Products Database

Category	Category Description	Categorization Type
Appliance, heating, lawn garden	Products used outside the home (includes outdoor toys such as sandboxes, canopies and shelters, garden statues, outdoor lighting and seating, outdoor power equipment, etc.)	CPCat Cassette
Consumer use, detected	Chemicals detected in substances or products (note that these chemicals may be absent from an 'ingredient list' for the product and thus unexpected, but have been detected in product testing studies)	CPCat Cassette
Explosives	Explosives and pyrotechnics	CPCat Cassette
Heating, fire, lawn garden	Products used outside the home (includes outdoor toys such as sandboxes, canopies and shelters, garden statues, outdoor lighting and seating, outdoor power equipment, etc.)	CPCat Cassette
Industrial manufacturing		CPCat Cassette
Manufacturing, chemical	General term used only when the only information known from the source is 'chemical,' typically related to manufacturing of chemicals, or laboratory chemicals	CPCat Cassette
Personal care, cosmetics, prohibited ASEAN	Chemicals prohibited from use (i.e. completely banned) in the ASEAN countries (Association of Southeast Asian Nations)	CPCat Cassette
Sports equipment	Sporting equipment (e.g. soccer balls, basketball rims, fishing rods, tents, boating accessories, fitness equipment, boats/boating equipment, etc)	CPCat Cassette

Source: EPA Chemical and Products Database (CPDat)

URL: https://comptox.epa.gov/dashboard/DTXSID0020529#exposure

1.3 Uses advised against by the registrants

No registrations have been submitted to ECHA.

2. Hazard, exposure and risk

2.1 Identity of the substance and physical and chemical properties

Identity of the substance(s) and physical and chemical properties

Name and other identifiers of the substance(s)

Chemical name: 2,4-Dinitrotoluene

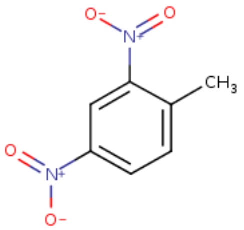
EC Number: 204-450-0

CAS Number: 121-14-2

IUPAC Name: 1-methyl-2, 4-dinitrobenzene

Molecular Formula: C7H6N2O4

Structural Formula:



Molecular Weight: 182.14

Typical proportion %: ≥99 %

Real proportion (range) in %: No data available

Physicochemical properties of 2,4-Dinitrotoluene

Table 3: Physicochemical properties of 2,4-Dinitrotoluene

Property	Value	Reference
Physical state at 20 ºC and 101.3 KPa	Solid	EU RAR (2008)
Melting / freezing point	69.9 ºC	EU RAR (2008)
Boiling point	319.5 ºC	EU RAR (2008)
Vapour pressure	7.9·10-3 Pa at 20 ºC	EU RAR (2008)
Water solubility	166 mg/l at room temperature	EU RAR (2008)
Partition coefficient octanol/water (log value)	1.98	EU RAR (2008)
Dissociation constant	Not available	

2.2 Justification for grouping

2,4-DNT is an isomer of the multi-constituent substance DNT (EC: 246-836-1)[17] that has altogether six isomers: 2,4- and 2,6-DNT are the two major forms and 2,3-DNT, 2,5-DNT, 3,4-DNT and 3,5-DNT are minor isomers (ATSDR, 2016). 2,6-DNT (EC: 210-106-0) is classified as Carc. 1B (may cause cancer), Acute Tox. 3, Muta. 2, STOT RE 2, Aquatic Chronic 3 and Repr. 2. 2,6-DNT is often found in smaller amounts and as impurity in 2,4-DNT containing articles as even "pure" 2,4-DNT has five percent of other DNT isomers, mostly 2,6-DNT. However, if the articles containing 2,6-DNT contain > 0.1 % of 2,4-DNT then they would also be included in the restriction. This restriction proposal however only covers the use of 2,4-DNT in articles.

[17] See DNT registrations: https://echa.europa.eu/information-on-chemicals/registered-substances/-/disreg/substance/100.042.564

2.3 Classification and labelling

Regulation (EC) No 1272/2008 (CLP Regulation)

The classification and labelling of 2,4 DNT is given in Table 3.

Table 4: Entries in Annex VI of CLP for relevant substances

Index #	International Chemical Identification	EC #	Classification	Specific Conc. Limits, M-factors	Notes	ATP inserted / updated
609-007-00-9	2,4-dinitrotoluene;	204-450-0	Acute Tox. 3 H301, H311, H331; Muta. 2 H341; Carc. 1B H350; STOT RE 2 H373; Aquatic Acute 1 H400; Aquatic Chronic 1 H410; Repr. 2 H361f.	-	-	CLP00/ATP 01

Self-classification

There have been 137 notifications to the C&L inventory, some of them indicating the following additional endpoints: Carc. 2 H351, STOT SE 1 H370, STOT RE 1 H372.

2.4 Human health assessment

2,4-DNT is classified as carcinogenic category 1B substance, which was the basis for the identification as Substance of Very High Concern (SVHC). The EU RAR (2008) identified carcinogenicity and mutagenicity as the key areas of concern because it is not possible to identify a clear threshold below which there would be no risk of cancer for the development of these effects in humans. As the substance is mutagenic it is assumed the Mode of Action for carcinogenesis is non-threshold.

Epidemiological studies of DNT carcinogenicity have been conducted in relatively small groups of workers in ammunition production facilities, copper mining industry and at ammunitions production facilities (Stayner et al., 1993, Brüning et al., 1999, Brüning, 2001, Brüning et al., 2002). As summarised in Seidler et al. (2014), the epidemiological and animal studies point to possible aetiological role of DNT exposure on renal and urothelial cancer. Seidler et al. (2014) review the aforementioned studies of Brüning, reporting increased renal cell carcinoma risk and toxic nephropathy with proximal tubular damage in small number of DNT-exposed underground miners. Seidler et al. (2014) found an association between cumulative DNT exposure and renal cell cancer in cohort of 16 441 male workers in the Mansfield copper mining industry, in the former German Democratic Republic, was published. The study found particularly dermal but also inhalation DNT exposure association with renal cancer among miners in different roles in relation to DNT containing explosive stick handling and possible inhalation exposure. They argue that also the findings of Brüning et al. (1999) of dose-dependent increase in tubular damage due DNT exposure indicate a plausible pathological pathway from exposure to carcinogenesis.

2.5 Humans via the environment

It has been reported that, as a result of its moderate solubility, DNT can be transferred to plants via root uptake from soil and is expected to accumulate readily in plant materials (EPA, 2008). 2,4-DNT and its metabolites have been extracted from plant material in studies where different plant species have been exposed to 2,4-DNT . DNT's bioavailability and toxicity to plants are greatly altered by soil properties. Studies have found that the toxicity of 2,4- and 2,6-DNT for various plant species is significantly and inversely correlated with soil organic matter content (Rocheleau et al., 2010).

2.6 Exposure Assessment

For this restriction report only the uses of 2,4-DNT in articles are considered. 2,4-DNT in articles can be present in propellants used in artillery and small arms ammunition, plastic containers, in vehicle safety systems and possibly in TNT ammunition due to impurity or recycling of 2,4-DNT containing ammunition. Furthermore, traces of 2,4-DNT can possibly be found in refractory products. Other potential uses in articles have been indicated. An interrogation of the SCIP database for 2,4-DNT indicate that the substance is found in several article types: vehicles, ceramic articles and electronic devices. This information confirms there are additional articles (probably imported articles) that contain the substance. The results are included as a confidential annex to this report.

Worker exposure assessment

Plastic containers

In 2010, ECHA received a SiA notification reporting a use of 2,4-DNT in plastic sampling bottles as a softener. The bottles were used in industrial workplaces only. The use is no longer active for the notifying entity[18] but it is not clear if such containers or other plastic articles possibly containing 2,4-DNT are used elsewhere in the EU. No information was received that would indicate whether, and to which extent, 2,4-DNT is released from plastic containers. Neither is there information on exposure to 2,4-DNT from plastics available.

Although exposure measurements or estimation are not available for 2,4-DNT in plastics articles, it is possible to elaborate qualitative argumentation to estimate the exposure potential for this particular use. First, plasticisers/softener are used in relatively high concentration in plastic matrix to deliver their function; up to 35 % of plasticisers in soft PVC have been reported and measured[19].

Second, plasticisers show a relatively high diffusivity in (soft) plastic material like PVC. In fact, the equation proposed under Food Contact Material (JRC, 2015) to get a first estimation of the diffusion coefficient of plasticisers in soft PVC gives rise to the highest

[18] Communication via email in 2020.

[19] Specific default (maximum) concentrations of additives (per technical function) in plastic articles are proposed by European Plastics Converters Association (EuPC) in their Plastic Industries Supply Chain Exposure Scenario Tool: https://www.polymercomplyeurope.eu/pce-services/pestool-service and www.pestool.eu.

values of the diffusion for a given value of temperature and molecular weight if compared to other combination of additives and plastic materials. Moreover, diffusion is inversely proportional to the molecular weight (smaller molecules diffuse easier in the plastic matrix3). 2,4-DNT has a relatively low molecular weight (182 g/mol), lower than e.g. phthalates used as plasticisers (DEHP, BBP, DBP, DIBP) that have been reported to have high exposure potential for dermal and oral route.

Third, there is also an indication from the ECHA PLASI Project that the partitioning from plastic material surface and contact media (water, saliva, skin) is regulated mainly by solubility (S) and/or octanol water partition coefficient (Kow)[20]. In particular, chemicals with low Kow have higher potential to be transferred from the plastic surface to the contact medium, as shown in different studies[21,22]. 2,4-DNT has a relatively low Kow (Log Kow = 1.98) suggesting a tendency for the substance to migrate to water, saliva or skin once it has reached the plastic surface. Other plasticisers like DEHP, BBP, DBP, DIBP with much higher log Kow, ranging from 4 to 6, have been reported to have high potential for exposure

Therefore, the exposure potential of 2,4-DNT as softener / plasticiser in plastic articles and more in general as additive in any plastic material can be predicted to be high, since, based on its physico-chemical properties, it is assumed to diffuse easily in the plastic matrix and partition from surface to contact medium (water, saliva or skin).

2,4-DNT in TNT and other explosives

ECHA has not received any applications for authorisation on 2,4-DNT, thus it is assumed that all uses of 2,4-DNT in explosive articles, if any, are related to imports.

2,4-DNT can be found in TNT as an impurity or as intentionally added, however the concentrations are considered to be low in comparison to applications in propellants (Table 5.) 2,4-DNT may also be present in TNT which is recovered from old explosives and ammunition (Technical report, 2010).

During the consultation for the Technical report (2010) one company was reported to have used DNT in small concentrations in Octol but discontinued the use already in 1990s. Octol is a melt-castable high explosive mixture consisting of HMX[23] and TNT in different weight proportions where DNT functioned as melting/solidification moderator (Technical report, 2010). During the consultation it was further confirmed that DNT may be found in use as an intentional component in explosives and past use in dynamite was also reported (Technical report, 2010).

[20] See ECHA PLASI (Plastic additives initiative) Project https://echa.europa.eu/comparing-relative-release-potential and https://echa.europa.eu/documents/10162/13630/plastic_additives_supplementary_en.pdf/79bea2d6-8e45-f38c-a318-7d7e812890a1

[21] Correlation of partition coefficients $K_{Polymer/Food}$ and $K_{Octanol/Water}$ for potential migrants in food contact polymers, Asako Ozaki, Anita Gruner, Angela Störmer, Rainer Brandsch, Roland Franz, Poster presentation at the 4th international Symposium on Food Packaging, 19-21 November 2008, Prague

[22] Screening-level models to estimate partition ratios of organic chemicals between polymeric materials, air and water; Efstathios Reppas-Chrysovitsinos, Anna Sobek and Matthew MacLeod, Environ. Sci.: Processes Impacts, 2016, 18, 667. Available at: https://pubs.rsc.org/en/content/articlepdf/2016/em/c5em00664c

[23] Also known as Octogen.

In 2010, one company still supplied DNT 95 and DNT 65/50 to EU and non-EU customers for the manufacture of explosives. In 2010 the general amounts of DNT 95 sold in the EU for explosives/ammunition was in the 100-1,000 t/y range and for DNT 65/50, EU sales for the manufacture of explosives were in the 10-100 t/y range (Technical report, 2010).

The information gathered for the Technical report (2010) concludes that DNT can be present as an impurity in TNT but is often the form of the DNT isomer mixture, rather than 2,4-DNT only.

TNT and other explosives are only relevant for this screening report if they are incorporated in articles as per definition of REACH.

Table 5: Uses of DNT resolving in possible presence of 2,4-DNT in articles. "Form of DNT" specifies the percentage of 2,4-DNT when a mix of isomers is used in the manufacture process. Table adjusted from Technical report (2010).

Use	Description	Transformation during use	Form of DNT	Presence of DNT in the final product
Manufacture of TNT explosives (2,4-DNT impurity)	Mining & Demolition	No	Technical grade	<1 % as impurity
Manufacture of explosives	Mining & Demolition	No	'Pure' 2,4 DNT (DNT 95+) & technical grade DNT (65/50))	<1 % as a melting/ solidification moderator; a few % in dynamite (old use)
Manufacture of propellants	Manufacture of weapons and ammunition	No	DNT 95 (or higher) technical grade (DNT 80)	2.5-17 %
Recycling of explosives and ammunition	Manufacture of weapons, explosives and ammunition	No	Technical grade	<1 % as impurity
Manufacture of propellants for automotive airbags & seat belt pre-tensioners	Manufacture of explosives and accessories for motor vehicles	No	Unknown	See "Manufacture of propellants"

Consumer exposure assessment

Propellants in small arm and artillery ammunition

According to ECHA (2010) there are some literature referring to DNT in gunshot / post-blast residues (studies cited in Joshi et al. (2009)). Technical report (2010) refers to a study of Walsh et al. (2009) where it was shown how military training with artillery produces excess propellant that is burned on the training range can result in point sources containing high concentrations of unreacted propellant constituents such as nitroglycerine and 2,4-DNT. Both are found at firing positions and propellant disposal areas.

Exposure of military personnel and therefore the use of artillery or other large weapon system applying 2,4-DNT containing propellants is outside the scope of this restriction proposal and only discussed to extent it benefits the overall assessment of propellant use in small arms. Background of military use and discussion of exposure potential is discussed in Annex 1.

Firing point or firing position residues are a function of the efficiency of the weapon system and the composition of the propellant. Especially larger weapon systems with longer barrels, rifled barrels or larger propellant loads consume propellants more efficiently, whereas shorter barrels and smaller propellant loads leave relatively more residues (Walsh et al., 2011, EPHW, 2019) Evidence of post-blast residues in the vicinity of the barrel (within meters) have been reported in the literature. 2,4-DNT is found embedded in fibrous propellant post-blast residues (Figure 2). The weapon systems mentioned to produce 2,4-DNT residues are listed in Table 6. From a life-cycle point of view, the use of 2,4-DNT containing propellants may also eventually lead to occupational exposure in military waste disposal and recycling facilities (Letzel et al., 2003).

Table 6: Weapon systems producing releases of 2,4-DNT

Weapon system		Propellant	Rounds	Residues /round (mg)	Source	Consumption efficiency	Compound remaining
Howitzers	105-mm	M1-I & II	71	34	Walsh et al. 2009	N.A.	N.A.
	105-mm	M1	22	6.4	Walsh et al. in Ch 4 Jenkins et al. 2007	N.A.	N.A.
	155-mm	M1	60	1.2	Walsh et al. 2005	N.A.	N.A.
Tank (leopard)	105-mm	M1	90	6.7	Ampleman, 2009	99.998 %	0.0022 %
Machine gun	7.62-mm	WC846	100	0.0018	Walsh et al. 2012	99.95 %	0.05 %

Propellant use

2,4-DNT is used as an energetic compound in nitrocellulose (NC) which is the most common propellant. Propellants are classified by the major energetic constituents. For the NC based propellants, NC alloyed with or without DNT is known as single base propellant. These are typically used with howitzer and tank munitions. Double-base propellants contain nitroglycerine and may contain DNT. These are used with mortar, small arms, and rocket munitions. They burn faster than single-based propellants. Triple-base propellants contain nitroguanadine, which burns cooler than other propellant compounds while delivering comparable barrel pressures. Other energetic components in triple-base propellants include nitroglycerine and in some cases DNT. These propellants tend to be used with long-barrelled, large-calibre weapons systems (Walsh et al., 2011)

When a gun or rocket is fired, the combustion of the propellant is never complete. Energetic residues will be deposited on the ground from the end of a gun barrel or behind a rocket launcher. These residues will contain the constituents of the original propellant formulation, typically (but not always) in the ratios of the unburned propellants. Combustion efficiency is influenced by barrel length, combustion temperature and pressure, the propellant formulation, and propellant age. Small arms thus cover such common weapon systems as pistols, rifles, and machine guns. As small arms projectiles are generally non-detonating, we looked only at firing points. Combustion efficiencies according literature are from 0.002 to 0.5 % depending on the used weapon type and amount of DNT in the propellant (Table 7).

The tasks/activities assessed for possible exposure were inhalation and/or dermal exposure to 2,4-DNT when loading and unloading the weapon, firing and deposition to the ground and exposure via environment.

Scenarios:

ES 1 Military use (used to define some parameters for ES2 and ES3)
CS 1: Loading and unloading – dermal exposure
CS 2: Firing – inhalation and dermal exposure
CS 3: Via environment/contaminated soil – dermal exposure

ES 2 Small arms – hunting or shooting indoors
CS 1: Loading and unloading – dermal exposure (contamination inside the gun)
CS 2: Firing – inhalation and dermal exposure
(CS 3: Via environment/contaminated soil – dermal exposure)

ES 1. Military use, information from the scientific studies

Table 7: Propellant mass, DNT-concentration and unburnt propellant and DNT in various military and small-arms weapons. MG = machine gun.

Weapon	Amount	DNT conc.	Unburnt and deposit	Unburnt DNT	Deposit area	Rounds	Conc.	Conc	Source
	g	g	mg	%	m2		mg/m2	mg/kg	
Tank firing 105-mm	3000	300	7.89	0.0026	929	90	0.76		Ampleman et al 2009
Tank firing 105-mm	6000	600	15.78	0.0026	929	90	1.55		Ampleman et al 2009
Artillery firing 105-mm		42	34	0.08					Ampleman et al 2009
Artillery/howitzer firing 105-mm		varied	varied	0.3-0.05				0.4-43	Diaz et al 2008
Artillery firing 155-mm		275	1.2	0.001					Ampleman et al 2009
Artillery firing (Nicolet study)	840	0.8	1.84	0.23					Ampleman et al 2008
Artillery firing (Nicolet study)	467	0.47	1.83	0.39					Ampleman et al 2008
Small arms (7.62-mm MG)		0.27	1.50	0.56					ERDC/CRREL TR-11-13 Walsh et al 2011
Small arms (7.62-mm MG)		4	0.0018	0.05					Walsh et al 2007a
Small arms (pistol, rifle, machine gun, mounted arms)								0.4-17	ERDC/CRREL TR-11-13 Walsh et al 2011

The difference in deposition rate means that higher temperature and pressure are resulting in the tank gun barrel, leading to a cleaner combustion with smaller amounts of residues. This could be explained by the fact that the barrel is longer for a tank than for the howitzer leading to more time at elevated pressure and temperature leading to a cleaner combustion.

However, for this report no specific exposure assessment was conducted for the military uses. Further details of 2,4-DNT used in military, especially in artillery ammunition, is provided in Annex 1.

ES 2 Exposure scenario for civilian small arms use in hunting/shooting

Small arms cartridges may contain 2,4-DNT. Based on the studies from Walsh et al. (2007a) and Walsh et al. (2011), the amount of 2,4-DNT in propellant of rifles and shot gun cartridges is between 0.27 - 4 g. According to some webpages of companies selling ammunition cartridges, the weight of rifle and shot gun cartridges are 3.6 - 28 g and 28 - 60 g respectively. In some publicly available Safety Data Sheets (SDS), the amount of 2,4-DNT is in maximum 2 % (w/w) in small arms cartridges. It is unsure whether these articles that contain 2,4-DNT are sold in the EU market. In the exposure assessment the weights of the cartridges for rifles and the concentration of 2 % for 2,4-DNT is used, even though considered to be as a worst case.

The rate for deposition in hunting (rifles) is probably much worse than in artillery firing since it depends on how well the combustion occurs. Longer barrel gives better combustion. Based on the studies performed by Walsh et al. (2007a, 2011), the estimated deposition rate is between 0.05-0.5 % for small arms.

Hunting and sport shooting may occur outside and training for hunting and sport shooting in indoor shooting range. In the simplified calculations it is assumed that for hunting that occurs outside, the duration of the exposure/activity is 2.5 hours (10 shots). For indoor shooting it is estimated that 50 shots are fired in 1 hour. Frequency of the hobby activity is assumed to be frequent (>15 times per year) and no correction factors are utilised in estimations. For both activities it is assumed that 80 or 100 % of the unburnt deposition is released to the surrounding air. The estimated airborne concentration of 2,4-DNT in outdoor and indoor is compared to the current lowest national OEL for 2,4-DNT in Europe and also to the long-term DNEL for general population that the registrant of DNT has derived in his dossier[24]. For general population, long-term DNEL is more suitable than acute DNEL since the substance is a carcinogen. The calculations are presented in the Table 8.

High exposure to lead has been measured for workers and shooters in shooting galleries during 2000-2014 in Finland (Kiilunen, 2017). In case the bullets include 2,4-DNT,

---

[24] OELs and DNEL according to GESTIS International Limit Values database and registration dossier for DNT (https://limitvalue.ifa.dguv.de/WebForm_ueliste2.aspx and https://echa.europa.eu/fi/registration-dossier/-/registered-dossier/30782/7/6/2 , respectively). ECHA notes that 2,4-DNT is a non-threshold carcinogen for which it was not possible to determine a DNEL, however the DNEL used by the registrant of DNT has been used as a comparison with the use of the national OEL value.

exposure to 2,4-DNT in shooting galleries is possible. However, the exposure is dependent on weapon and bullet type, exposure duration, frequency of shooting, room ventilation and other activities/shooters in the room at the same time. The exposure to 2,4-DNT in outdoor hunting is possible, but not very likely. Dermal exposure to organic gunshot residues, which includes 2,4-DNT, was studied qualitatively by Hofstetter et al. (2017) and the study indicated that residues can be found from hands and other part of the upper body of the shooter including clothing.

Conclusions:

On the basis of the calculations provided in Table 7 and Table 8 the exposure via inhalation is possible for people engaging in hunting or shooting activities. When the estimations of exposure during shooting outdoor (hunting) is compared to the OEL (8 hour) or long-term DNEL of 2,4-DNT, the calculated risk characterisation ratios (RCR) are from 0.002-0.3 and 0.05-6 respectively. The estimated RCRs for indoor shooting are higher than in outdoor being from 0.1-11 and 2->200 respectively. The Dossier Submitter is of the view that the calculations provides evidence of the exposure and risk and the worst-case scenario should be considered as the substance is a non-threshold carcinogen. Exposure via skin is possible for hands, fore arms and face, however, no estimations for this exposure route has been made. Finally, exposure for humans via environment can also be considered possible, but unlikely.

Table 8: Estimations for inhalation exposure to 2,4-DNT shooting indoors and outdoors (i.e. sport shooting and hunting). Table a) exposure estimations compared to the OEL (8 hour), b) to the long-term DNEL derived by the registrant for DNT.

a)

Activity	N	bullet	DNT (2%)	Unburnt DNT	Unburnt and deposit	Release to the air	Duration/Exposure time	Volume outdoor/ room *	Dilution factor**	Conc in breathing zone	Conc (8 h)	OEL (8 h)	RCR
		g	g	%	mg	%	h	m^3		mg/m^3		mg/m^3	8 h
Least exposure: shooting (outdoor)	10	3.6	0.72	0.05	0.36	80	2.5	100	2.5	0.003	0.0004	0.15	0.002
Worst case: shooting (outdoor)	10	28	5.6	0.56	31.36	100	2.5	100	2.5	0.31	0.039	0.15	0.26
Least exposure: shooting (indoor)	50	3.6	3.6	0.05	1.8	80	1	20	0.6	0.120	0.015	0.15	0.10
Worst case: shooting (indoor)	50	28	28	0.56	156.8	100	1	20	0.6	13.1	1.63	0.15	10.9

b)

Activity	N	bullet	DNT (2%)	Unburnt DNT	Unburnt and deposit	Release to the air	Duration/Exposure time	Volume outdoor / room *	Dilution factor**	Conc in breathing zone	Conc (6 h)	DNEL long-term	RCR
		g	g	%	mg	%	h	m3		mg/m3		**mg/m3**	6 h
Least exposure shooting (outdoor)	10	3.6	0.72	0.05	0.36	80	2.5	100	2.5	0.003	0.0005	**0.009**	**0.053**
Worst case shooting (outdoor)	10	28	5.6	0.56	31.36	100	2.5	100	2.5	0.31	0.052	**0.009**	**5.81**
Least exposure shooting (indoor)	50	3.6	3.6	0.05	1.8	80	1	20	0.6	0.120	0.020	**0.009**	**2.22**
Worst case shooting (indoor)	50	28	28	0.56	156.8	100	1	20	0.6	13.1	2.18	**0.009**	**242.0**

* Outdoor is considered as 100 m3 and shooting gallery as 20 m3

** Dilution factor is a factor for air volume changes outdoor/indoor, the value is from ECETOC TRA Consumers V.3.1

Five countries in Europe have an OEL for 2,4-DNT. The range for the national OELs is 0.15-1.0 mg/m3 (8 h), for 15 minutes there is only 0.3 mg/m3. The long-term DNEL is derived by the registrant.

Seat belt pre-tensioners and airbags

Technical report for 2,4-DNT (2010) indicated the possibility that the substance could be used in both air bags and seat belt pre-tensioners. Suppliers and manufacturers at the time confirmed that they do not use 2,4-DNT in the articles for the European market. However, some manufactures have provided information of the use according to Article 33 of REACH, e.g. Toyota and Ford[25].

Seat belt pre-tensioners include electronic, mechanical and pyrotechnic solutions to hold a passenger firmly on their seat at a start of a collision, allowing a controlled contact with the inflated airbag. 2,4-DNT is used in the pyrotechnic version of pre-tensioner. An explosive charge causes the gas generator to produce a volume of gas and thus pressure which acts on a mechanical linkage to pull the seat belt. The pre-tensioner needs replacing after deployment. The deployment consumes the explosive in the seat belt assembly. Ford advices that potential exposure to customers is minimised if the car and its parts are used, repaired, maintained and disposed as intended[26]. Disposing an end of life vehicle legally in the European Union takes place in Authorized Treatment Facilities (ATF). Other information on the exposure than the remark above is not available to ECHA.

These uses have not been notified to ECHA according to Article 7(2). A search of the SCIP database has indicated motor vehicle waste includes 2,4-DNT, which supports the discussion above.

Specific exposure scenario was created for this use: **ES 3 Use in safety equipment in car** (airbags and pre-tensioners in seat belts). This scenario is relevant only during a sudden crush or stop when the system reacts.

ES 3. Use in airbags and seat belt pre-tensioners

The amount of 2,4-DNT in this use is unknown. If we consider this through the sodium azide (NaN_3) a commonly used inflator in this application, a typical driver-side **airbag** contains approximately 50–80 g of NaN_3, with the larger passenger-side **airbag** containing about 250 g. Within about 40 milliseconds of impact, all these components react in three separate reactions that produce nitrogen gas. On average, there can be **seven airbags and five seat belts** in the car. The inflator is located in a closed system. The car manufacturer advices that potential exposure to consumers is minimal if the car has been maintained well. The inflator substance will be released only when there is a triggering factor i.e. crash event. The used amount of 2,4-DNT as an inflator in car-safety applications is unknown.

However, if the substance is used in these applications there will be releases to the interior air in case of a crash. For calculations, see Table 9: Estimations for inhalation exposure from the use of 2,4-DNT in airbags and seat belt pre-tensioner. OEL-values for 8h and long term DNELs in tables a and b, respectively.

Assumed that the amount of 2,4-DNT is comparable to sodium azide, another substance used for this purpose, then one pre-tensioner would contain 50 grams of 2,4-DNT. There could be 5

[25] https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=2ahUKEwi3ytek6tHsAhVJsaQKHZ2BC8wQFjAAegQIAhAC&url=https%3A%2F%2Fwww.toyota.hu%2Fdownload%2Fcms%2Fhuhu%2FToyota%2520Aygo_SVHC%2520Information_032019_tcm-3033-1572338.pdf&usg=AOvVaw15sytWN_78pxTfiJITxILL

[26] https://www.ford.co.uk/content/dam/guxeu/uk/useful-information/reach/Art-33-1-Information-Example-U502-Explorer.pdf

pre-tensioner capsules in a car. The total amount of 2,4-DNT would be in that case be 250 g in one car (only pre-tensioners). Residual amount of 2,4-DNT after incomplete burning is assumed to be 1250 mg (worst case scenario - 0.5 %). The air volume inside car is estimated to be 5 m^3. The systems are closed and there are no releases of 2,4-DNT in normal situation. However, in case of collapse, it is assumed that 10 and 30 % of the unburnt amount is released to the indoor air in car. Dilution factor of 2.5 is also considered since there would be some air changes due to the possibility of broken windows or other damage. The estimated concentration of 2,4-DNT inside the car is compared to the lowest national OEL (8 hour) in EU for 2,4-DNT and also to the long-term DNEL for general population that the registrant has derived in his dossier for DNT. For general population, long-term DNEL is more suitable than acute DNEL since the substance is a carcinogen, even though the duration of the exposure situation is probably short. When the exposure estimates are compared to the long-term DNEL correction factors for very infrequent use (taken from ECETOC TRA Consumers modelling tool) can be used since the exposure situation will happen very rarely[27].

Conclusions:

The estimated inhalation exposure to 2,4-DNT will be high compared to the lowest national OEL (8 hour) in EU for 2,4-DNT and also to the long-term DNEL for general population if the car safety system (air bags or seat belt pretensioners) reacts and 2,4-DNT is released to the interior of the car and there are people in the car. The comparison with the OEL and using the DNEL already indicated risks to consumers, thus the Dossier Submitter is of the view that the risks are not adequately controlled as the substance in a non-threshold carcinogen.

The possibly exposed groups may contain, apart from the driver, also people and occupational groups attending accident sites often e.g. the police or fire personnel. Also, car repair technicians handling and replacing pre-tensioners and air bags may be at risk of exposure.

[27] For the calculations, a CSR provided for DNT registration dossier was utilised. Both limit values, OEL and DNEL, has been used since the DNEL derivation is not transparent in the dossier. The registrant has derived DNELs in their dossier, however the derivation process is not described comprehensively. It is described that the study is repeated dose study and the assessment factor is 50 and 25 for long-term and acute DNELs, respectively. However, the starting point value is not transparent. OELs are prepared by national experts and the values are very similar between countries.

Table 9: Inhalation exposure from the use of 2,4-DNT in airbags and seat belt pre-tensioner. OEL-values for 8h and long term DNELs for DNT in tables a and b, respectively.

Table a)	N	DNT	Unburnt DNT	Unburnt and deposit	Release to the air	Volume in car interior *	Dilution factor**	Additional adjustment factor for very infrequent exposure***	Conc in car interior	OEL (8 h)	RCR
		g	%	mg	%	m3			mg/m^3	**mg/m^3**	
One air bag/seat belt pretensioner	1	50	0.50	250	10	5	2.5	0.01	0.02	**0.15**	**0.1**
One air bag/seat belt pretensioner	1	50	0.50	250	30	5	2.5	0.01	0.06	**0.15**	**0.4**
Five air bags/seat belt pretensioners	5	250	0.50	1250	10	5	2.5	0.01	0.10	**0.15**	**0.7**
Five air bags/seat belt pretensioners	5	250	0.50	1250	30	5	2.5	0.01	0.30	**0.15**	**2.0**

Table b)	N	DNT	Unburnt DNT	Unburnt and deposit	Release to the air	Volume in car interior*	Dilution factor**	Additional adjustment factor for very infrequent exposure***	Conc in car interior	DNEL long-term	RCR
		g	%	mg	%	m^3			mg/m^3	**mg/m^3**	
One air bag/seat belt pretensioner	1	50	0.50	250	10	5	2.5	0.01	0.02	**0.009**	**2.2**
One air bag/seat belt pretensioner	1	50	0.50	250	30	5	2.5	0.01	0.06	**0.009**	**6.7**
Five air bags/seat belt pretensioners	5	250	0.50	1250	10	5	2.5	0.01	0.10	**0.009**	**11.1**
Five air bags/seat belt pretensioners	5	250	0.50	1250	30	5	2.5	0.01	0.30	**0.009**	**33.3**

* It is assumed that the air volume inside the car is $5m^3$; **In case of windows breaking/other damage allowing air in; **Dilution factor is a factor for air volume changes outdoor/indoor, the value is from ECETOC TRA Consumers V.3.1; Five countries in Europe have an OEL for 2,4-DNT. The range for the national OELs 0.15-1.0 mg/m3 (8 h), for 15 minutes there is only 0.3 mg/m3. Long-term DNEL is derived by the registrant.

Other consumer uses

There are a number of potential uses in articles (not notified according to Article 7(2)), but there is very limited information on any potential exposures.

Environmental exposure assessment

In relation to the uses discussed, 2,4-DNT is mainly found on the topsoil layer where it accumulates when using propellants in small arms ammunition and heavy weapons such as artillery (Walsh et al., 2011). Further information on environmental exposure assessment especially in military use is available in Annex 1.

Summary of the existing legal requirements

Under REACH, 2,4-DNT was included in the candidate list for authorisation (13/01/2010; ED/68/2009) and included into Annex XIV of REACH (Commission Regulation (EU) No 143/2011) on the basis of art 57(a) Carc 1B. with a sunset date of 21/08/2015. By this sunset date ECHA has not received any application for authorisation. It should be noted placing on the market or the use of an article which contains an Annex XIV substance is not subject to the authorisation requirement (See AfA Q&A nr: 0564[28]). Therefore, imported articles are not covered by authorisation.

REACH has several requirements for substances on the candidate list including notification of its presence in articles if the concentration of the substance is > 0.1 % and 1 tonne per year (Article 7(2)) and that suppliers must inform their customers on request if an article contains more than 0.1 % by weight of the substance in question (Article 33(b)).

2,4–DNT as a substance or a constituent of other substances, or mixtures containing it ≥ 0.1 % are restricted for supply to the general public (Annex XVII entry 28, appendix 2)[29]. This does not apply to medicinal products for human or veterinary use, as defined by Directive 2001/83/EC and Directive 2001/82/EC, respectively; cosmetic products as defined by Directive 76/768/EEC; the following fuels and oil products: motor fuels which are covered by Directive 98/70/EC, mineral oil products intended for use as fuel in mobile or fixed combustion plants, fuels sold in closed systems (e.g. liquid gas bottles); artists' paints covered by Regulation (EC) No 1272/2008.

Information on existing EU legislations relevant for 2,4-DNT is available on ECHA's website under EU Chemicals Legislation Finder (EUCLEF)[30].

2.7 Risk Characterisation

According to the EU RAR (2008) the most probable route of human exposure to 2,4-DNT is inhalation and dermal contact of workers involved in the production and use of 2,4-DNT containing explosives. Due to evidence that 2,4-DNT containing fibres are deposited on clothes of the operators of artillery guns, an inadvertent ingestion is also a possible source of exposure

---

[28] https://echa.europa.eu/support/qassupport/browse//qa/70Qx/view/scope/reach/authorisation.

[29] Commission Regulation (EU) No 109/2012 of 9 February 2012 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XVII (CMR substances)

[30] https://echa.europa.eu/fi/legislation-obligation/-/obligations/100.001.062

in addition to dermal and inhalation exposure. Inhalation exposure is also concern in civilian small arms use, such as hunting and sport shooting, if the ammunitions used contain 2,4-DNT. The use of 2,4-DNT in explosive articles in mining and demolition purposes is also known. However, no indication for current use of such articles in EU was found during the screening done for this report.

The ammunition use on fixed ranges during training leads to the accumulation of 2,4-DNT in the top-soil layer, thus dermal exposure from handling soil may be possible. In addition, 2,4-DNT may be taken up by plants and expose humans through the environment. Furthermore, the use of 2,4-DNT in vehicle safety systems may lead to exposure of the driver, safety personnel attending accident sites and vehicle repairing technicians replacing these safety systems. Also, roadside accumulation of 2,4-DNT may be leading to uptake of plants and exposure to humans through the environment, however, information of 2,4-DNT roadside accumulation is not available.

As the exposure potential of 2,4-DNT as softener / plasticiser in plastic articles and more in general as additive in any plastic material can be considered high and it seems to diffuse easily in the plastic matrix and partition from surface to contact medium (water, saliva or skin), the risk of exposure from using plastic sample bottles cannot be excluded.

In the (EU RAR, 2008) the conclusion was that there is a need for limiting the risks because of concerns for carcinogenicity and mutagenicity as a consequence of inhalation and dermal exposure arising from all worker scenarios. There was no conclusion for risk reduction measures beyond those which are being applied already for the general public because exposure of consumers is not assumed to exist. In humans exposed via the environment there is a need for limiting the risks because of concerns for carcinogenicity and mutagenicity as a consequence of oral exposure arising from one manufacturing site.

According the Annex I paragraph 6.5, ECHA guidance Part E (ECHA, 2016) and R.8 (ECHA, 2012) and the 'Common approach of RAC and SEAC in opinion development on applications for authorisation'[31], the adequate control route is not possible for a non-threshold substance (such as 2,4-DNT)[32]. Based on this position, the Dossier Submitter is of the view that 2,4-DNT poses a risk to human health if incorporated in articles that is not adequately controlled.

Therefore, it is the Dossier Submitter's view that a risk of carcinogenicity from exposure to 2,4-DNT for military personnel and other users of artillery ammunition cannot be excluded. Furthermore, aggregated exposure to 2,4-DNT from firing artillery ammunitions and other explosive articles such as small arms ammunition cannot be excluded through environmental accumulation and subsequent human exposure. Finally, a risk to humans from imported articles cannot be excluded.

3. Justification for an EU-wide restriction measure

Based on the following reasons a Union-wide action to address the risks associated with EU manufactured or imported articles containing 2,4-DNT seems warranted:

---

[31] https://echa.europa.eu/documents/10162/13555/common_approach_rac_seac_en.pdf

[32] In practice, this means that applicants for authorisation have to demonstrate the rationale for an authorisation via the so-called socio-economic route. RAC will analyse if operational conditions and risk management measures ensure that the exposure levels are as low as technically and practically possible, however.

- To ensure a harmonised high level of protection of human health across the Union;
- To ensure the free movement of goods within the Union, where relevant.

4. Baseline

4.1 Problem definition

Technical DNT is currently manufactured in the EU as a non-isolated intermediate in quantities of 540 000 to 810 000 tonnes per year. The majority of this use is in the manufacture of TDI.

In US, total production of 2,4-DNT in 2016 was in range of 11-45 tonnes (EPA CDR 2016). Data from 2013 lists 14 plants producing, processing or using 2,4-DNT at minimum of approximately 150 tonnes to maximum of 1400 tonnes per year in US.

The use of 2,4-DNT in production of articles in the EU is subject to authorisation requirements under Title VII of REACH. At the time of the writing of this report, no applications for authorisation were received. Authorisation requirements do not apply to imported articles and it is thus possible that articles containing 2,4-DNT are produced outside the Union and subsequently imported in the EU, causing a risk to human health.

4.2 How the situation would evolve without any regulatory measures

Without a restriction there would continue to be articles imported for occupational and professional uses and potentially consumer articles imported. This could leave consumers and workers exposed to a carcinogen for which a safe threshold cannot be established. Furthermore, this would lead to a situation, in which the premise of REACH to substitute SVHC by suitable alternatives or technologies where these are economically and technically viable, would not apply to imported articles.

5. Impact assessment

5.1 Scope of the impact assessment

The Impact Assessment is based on the premise that there are possibly articles placed on the EU market that contain 2,4-DNT (seat belt pre-tensioners, plastic sample bottles, ammunition, refractory materials, and others).

5.2 Potential restriction options

A number of potential restriction options by the Dossier Submitter have been considered for a potential restriction. Limit value of higher than 0.1 % of 2,4-DNT weight by weight is proposed for all options being a practical value used for the notification of substances in articles according to article 7(2) of the REACH Regulation. The restriction options are listed in Table 10.

Table 10: Considerations related to potential restriction options

Potential restriction option		**Risk considerations**	**Impact considerations**	**Efficiency considerations**	**Risk reduction considerations**
1	Restriction on placing on the market of all articles containing 2,4-DNT	• Risk to all populations addressed.	• Some impacts to importers of ammunitions containing 2,4-DNT. Low impacts to other actors as low number of articles foreseen to be in scope	• Efficient as test exist? Some decrease of the efficiency is possible in case Member States use article 2(3) of REACH to allow exemption to this restriction in the interest of defence.	• High, even though Member States may use article 2(3) of REACH to allow exemption to this restriction in the interest of defence.
2	Restriction of placing on the market of articles containing 2,4-DNT of use by general public or specified uses by workers (such as professional uses) under article 68(1) of REACH.	• Risk to most vulnerable populations and professional workers addressed.	• Low impact as low numbers of articles foreseen to be in scope	• Efficient as test exists?	• Medium as ammunition is not covered.
3	Restriction of placing on the market of articles containing 2,4-DNT of use by general public under article 68(2) of REACH.	• Risk to most vulnerable populations addressed.	• Low impact as low numbers of articles foreseen to be in scope	• Efficient as test exists?	• Medium as ammunition and other professional uses not covered.

In addition, the Dossier Submitter has assessed that the non-REACH legislation described in Table 11 is not suitable for managing the identified risks (taking account of potential exemptions).

Table 11: Considerations related to other EU legislation for control of Articles containing 2,4-DNT

EU legislation	**Considerations**
Directive 2009/48/EC of the European Parliament and of the Council of 18 June 2009 on the safety of toys	Substances classified as carcinogenic 1B are prohibited in toys in concentrations equal to or above 0.1 %, unless a safety assessment has been carried out showing it is safe. *Conclusion: Proposed limit will be the same as in the toys Directive.*
Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment	2,4-DNT is not currently restricted in electronic equipment and has not been identified in this report as being used in such articles. *Conclusion: If this situation changes it could be added to ROHS but it is more efficient to use this restriction to prevent its use.*
Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food	2,4-DNT is not currently allowed in plastic food contact materials (not in the positive list in Commission Regulation (EU) No 10/2011) but other materials are not covered. *Conclusion: It is more efficient to restrict in this measure.*
Regulation (EU) 2017/745 [33]of the European Parliament and of the Council of 5 April 2017 on medical devices, amending Directive 2001/83/EC, Regulation (EC) No 178/2002 and Regulation (EC) No 1223/2009 and repealing Council Directives 90/385/EEC and 93/42/EEC Regulation (EU) 2017/746 of the European Parliament and of the Council of 5 April 2017 on in vitro diagnostic medical devices and repealing Directive 98/79/EC and Commission Decision 2010/227/EU Regulation 2020/561 of the European Parliament and of the Council of 23 April 2020 amending Regulation (EU) 2017/745 on medical devices as regards the dates of	Devices, or those parts thereof or those materials used therein that are invasive and come into direct contact with the human body, (re)administer medicines, body liquids or other substances, including gases, to/from the body, or transport or store such medicines, body fluids or substances, including gases, to be (re)administered to the body, shall only contain substances which are carcinogenic of category 1B, in a concentration that is above 0,1 % weight by weight (w/w) unless its justified where justified based upon: (a) an analysis and estimation of potential patient or user exposure to the substance;

[33] Enters into force in June 2021.

EU legislation	Considerations
application of certain of its provisions	(b) an analysis of possible alternative substances, materials or designs, including, where available, information about independent research, peer-reviewed studies, scientific opinions from relevant scientific committees and an analysis of the availability of such alternatives; (c) argumentation as to why possible substance and/ or material substitutes, if available, or design changes, if feasible, are inappropriate in relation to maintaining the functionality, performance and the benefit- risk ratios of the product; including taking into account if the intended use of such devices includes treatment of children or treatment of pregnant or breastfeeding women or treatment of other patient groups considered particularly vulnerable to such substances and/or materials; and (d) where applicable and available, the latest relevant scientific committee guidelines in accordance with Sections 10.4.3. and 10.4.4. *Conclusion: Exempt the use in medical devices.*
Council Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work. Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004 on the protection of workers from the risks related to exposure to carcinogens or mutagens at work.	For substances classified as carcinogenic 1B, employers are obligated to minimize worker exposure to these agents as far as possible, and must arrange for medical surveillance of workers exposed to these substances. Self-employed persons are not covered.
Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products.	2,4-DNT is restricted in Annex II (Prohibited Substances) in the Cosmetics Products Regulation but this regulation does not cover articles. *Conclusion: No need for any exemption.*

5.3 Proposed restriction

Considering the initial analysis in section 5.2, the best option appears to be RO2. Further points to consider are:

- Related to the concentration limit, it is proposed to use the same concentration limit as in the notification of substances in articles according to article 7(2) (SiA notifications).
- Related to exemptions, according to the analysis presented in Table 11 it is proposed to exempt articles covered by Regulation (EU) 2017/745 on medical devices.
- Related to the transitional period, as there is no EU production of articles, there is no need to transition to alternatives or stocks. If there are any imported articles, time is needed for importers to transition to different articles not containing 2,4-DNT. Therefore, it is assumed 12 months would be sufficient.
- The proposed restriction would also decrease the exposure of humans via the environment.

5.4 Available information on alternatives

ECHA has not received any applications for authorisations. Two SiA notifications were received for which one use has been ceased and the other use is proposed to be derogated. Based on this the Dossier Submitter assumes that there are suitable alternative substances or technologies available for 2,4-DNT in articles covered by this proposal.

5.5 Economic impact

Overall, the compliance costs of EU actors in the supply chain are considered to be very small. No costs are expected for manufacturers, importers of the substance or mixture because there is no direct article manufacturing in the EU (as no applications for authorisation were received). There may be some costs for importers of articles, having to re-source different products but this is assumed to be negligible.

For consumer uses of 2,4-DNT in articles, it is assumed there are suitable alternatives; for professional uses of 2,4-DNT in articles the situation is less clear. An RIVM study on alternatives for phthalates plasticisers lists alternatives for its use in ammunition as a plasticiser and deterrent (burning rate regulators), which could also be considered for the similar use of 2,4-DNT (RIVM, 2013).

In addition to the above, the Dossier Submitter is of the view that the potential for loss of employment or changes in price for end users will also be negligible.

In sum, the economic impact of a restriction on 2,4-DNT in articles covered by this proposal would be minimal. The assumptions on the availability of alternatives, loss of employment or changes in price for end users were tested in call for evidence (https://echa.europa.eu/previous-calls-for-comments-and-evidence/-/substance-rev/27201/term) and no information was received that questioned the assumptions.

5.6 Human health impact

According to the EU RAR (2008), there is no valid human epidemiology study available. However, two studies (Seidler et al., 2014, Brüning et al., 1999) support the hypothesis that occupational exposure to DNT may be carcinogenic, since excess cancer mortality observed among DNT-exposed workers is similar to the findings from experimental studies of DNT exposed animals.

These studies associated an excess of hepatobiliary cancer and both urothelial cancer and renal cell cancer with jobs where workers were supposedly exposed to purified 2,4-DNT and miners supposedly exposed to technical grade DNT, respectively.

However, considering the assumptions made in the costs assessment, there are unlikely to be (m)any workers or consumers exposed. Therefore, the benefit of the proposed restriction is due to its preventive value as it would prevent future uses of the substance in articles, and thus avoid regrettable substitution and potential risks to workers and consumers in the EU.

5.7 Other economic issues

No social, wider economic and distributional impacts have been identified.

5.8 Other issues

5.8.1 Effectiveness:

Risk reduction capacity

The proposed restriction reduces potential risks from 2,4-DNT in articles covered in this proposal to an acceptable level within a reasonable period of time.

Targeted

The restriction is targeted to the effects or exposures that are of most concern, e.g. consumer and certain worker uses.

Proportional to the risk

The restriction is assumed to impose very low costs to reduce a potential risk; given the information at hand, it is assumed that the measure is proportionate to the risk.

5.8.2 Practicality

The proposed restriction is practical because it is implementable, enforceable and manageable as the proposed restriction is easy to understand and communicate down the supply chain and can be enforced.

Implementability

The restriction is implementable as companies can test for a concentration limit in an article or make it a condition of the contract for purchase not to have the substance present in the article. It is assumed that for any imported articles covered in this proposal containing the substance that there are alternative articles types. In addition, the proposed restriction gives sufficient time to the impacted supply chains to transition.

Enforceability

Enforcement authorities can set up efficient supervision mechanisms to monitor industry's compliance with the proposed restriction. Testing and sampling methods exist.

Manageability

The restriction is manageable by industry and authorities.

5.8.3 Monitorability

The efficacy of the restriction can be monitored through the EU Safety Gate (former Rapid Alert System for Non-Food Products (RAPEX)) system at EU level. National control campaigns may be launched as a mean to monitor the compliance, e.g. coordinated by Forum.

6. Assumptions, uncertainties and sensitivities

Assumptions in the cost assessment should be tested in the stakeholder consultation on the Annex XV dossier.

The completeness of the use assessment should also be tested.

7. Conclusion

The conclusion of the Dossier Submitter's assessment is to propose a restriction covering consumer and certain professional uses of 2,4-DNT to prevent any existing or future uses of the substance which would pose a risk to the users of the articles. To identify the most appropriate measure to address these risks, an analysis of risk management options (RMOs) was conducted, including regulatory measures under REACH, other existing EU legislation and other possible Union-wide RMOs and it was concluded that a restriction under REACH is the most appropriate risk management option.

A number of restriction options (RO) were assessed on the basis of the effectiveness, practicality and monitorability of these ROs and the following restriction is proposed: see Table 1.

References

AMPLEMAN, G., THIBOUTOT, S., MAROIS, A., GAGNON, A., GILBERT, D., WALSH, M.R., WALSH, M.E., & WOODS, P.J. 2009. Evaluation of the propellant residues emitted during 105-mm Leopard tank live firing at CFB Valcartier, Canada. *Defence R&D Canada-Valcartier. .*

ATSDR 2016. Toxicological profile for Dinitrotoluenes. U.S. Department of Health and Human Services. Agency for Toxic Substances and Disease Registry.

BRÜNING, T., CHRONZ, C., THIER, R., HAVELKA, J., KO, Y. & BOLT, H. M. 1999. Occurrence of urinary tract tumors in miners highly exposed to dinitrotoluene. *Journal of Occupational and Environmental Medicine,* 41**,** 144-149.

BRÜNING, T., THIER R & HM, B. 2002. Nephrotoxicity and nephrocarcinogenicity of dinitrotoluene: new aspects to be considered. *Reviews on environmental health,* 17**,** 163-172.

BRÜNING, T., THIER, R., MANN, H., MELZER, H., BRÖDE, P., DALLNER, G., & BOLT, H. M 2001. Pathological excretion patterns of urinary proteins in miners highly exposed to dinitrotoluene. . *Journal of occupational and environmental medicine,* 43**,** 610-615.

BUSBY, R. R., BARBATO, R. A., JUNG, C. M., MOROZOVA, K. A., BEDNAR, A. J., BRAY, A. L., MILAM, J. M., SMITH, J. C. & INDEST, K. J. 2018. Photoperiod and soil munition constituent effects on phytoaccumulation and rhizosphere interactions in boreal vegetation. *Water, Air, & Soil Pollution,* 229**,** 380.

ECHA 2010. Background document for 2,4-DNT - Document developed in the context of ECHA's second Recommendation for the inclusion of substances in Annex XIV.

ECHA 2012. Guidance on information requirements and chemical safety assessment, Chapter R.8: Characterisation of dose [concentration]-response for human health. ECHA.

ECHA 2016. Guidance on information requirements and chemical safety assessment, Part E: risk characterisation, Version 3.0. European Chemicals Agency.

EPA 2008. Drinking Water Health Advisory for 2,4-Dinitrotoluene and 2,6-Dinitrotoluene. EPA 822-R-08-010.

EPHW 2019. Environmental Protection of Heavy Weapon Ranges: Technical and Practical Solutions.

EU RAR 2008. European Union Risk Assessment Report on 2,4 – Dinitrotoluene

FOLLY, P. & MADER, P. 2004. Propellant chemistry. *Chimia,* 58**,** 374-382.

HOFSTETTER, C., MAITRE, M., BEAVIS, A., ROUX, C. P., WEYERMANN, C. & GASSNER, A. L. 2017. A study of transfer and prevalence of organic gunshot residues. *Forensic Science International,* 277**,** 241-251.

HUNT, J. & AND HUNTINGTON, G. 1999. A comprehensive environmental investigation of an active artillery range. *In:* AFFAIRS, M. D. O. M. (ed.).

JENKINS, T. & VOGEL, C. 2014. Department of Defense Operational Range Sustainability through Management of Munitions Constituents. THOMAS JENKINS ENVIRONMENTAL CONSULTING WEST LEBANON NH.

JOSHI, M., DELGADO, Y., GUERRA, P., LAI, H. & ALMIRALL, J. R. 2009. Detection of odor signatures of smokeless powders using solid phase microextraction coupled to an ion mobility spectrometer (vol 188, pg 112, 2009). *Forensic Science International,* 192**,** 135-135.

JRC 2015. Practical guidelines on the application of migration modelling for the estimation of specific migration – JRC Technical Report In support of Regulation (EU) No 10/2011 on plastic food contact materials.

KIILUNEN, M. 2017. Lyijyaltistuminen Suomessa 2000–2014 : Biologisen monitoroinnin tilasto. *Finnish Institute of Occupational Health 2017*.

LETZEL, S., GOEN, T., BADER, M., ANGERER, J. & KRAUS, T. 2003. Exposure to nitroaromatic explosives and health effects during disposal of military waste. *Occupational and Environmental Medicine,* 60**,** 483-488.

NISAR, N., CHEEMA, K. J., POWELL, G., BENNETT, M., CHAUDHARY, S. U., QADRI, R., YANG, Y., AZAM, M. & ROSSITER, J. T. 2018. Reduced metabolites of nitroaromatics are distributed in the environment via the food chain. *Journal of hazardous materials,* 355**,** 170-179.

PICHTEL, J. 2012. Distribution and fate of military explosives and propellants in soil: a review. *Applied and Environmental Soil Science*.

RIVM 2013. Analysis of alternatives for a group of phtalates
ROCHELEAU, S., KUPERRNAN, R. G., SIMINI, M., HAWARI, J., CHECKAI, R. T., THIBOUTOT, S., AMPLEMAN, G. & SUNAHARA, G. I. 2010. Toxicity of 2,4-dinitrotoluene to terrestrial plants in natural soils. *Science of the Total Environment,* 408**,** 3193-3199.
SEIDLER, A., HARTH, V., TAEGER, D., MOHNER, M., GAWRYCH, K., BERGMANN, A., HAERTING, J., KAHMANN, H. J., BOLT, H. M., STRAIF, K. & BRUNING, T. 2014. Dinitrotoluene exposure in the copper mining industry and renal cancer: a case-cohort study. *Occupational and Environmental Medicine,* 71**,** 259-265.
STAYNER, L. T., DANNENBERG, A. L., BLOOM, T. & THUN, M. 1993. Excess Hepatobiliary Cancer Mortality among Munitions Workers Exposed to Dinitrotoluene. *Journal of Occupational and Environmental Medicine,* 35**,** 291-296.
TECHNICAL REPORT 2010. Data on the European Market, Uses and Releases/Exposures for 2,4-Dinitrotoluene prepared for ECHA by DHI in co-operation with Risk & Policy Analysts Limited and TNO (Contract ECHA/2008/2/SR25).
US DEPARTMENT OF DEFENSE 1973. Military Standard: Propellants, Solid, for Cannons: Requirements and Packing. MIL-STD-652C (MU). U.S. Government Printing Office, Washington, DC.
WALSH, M. R. 2016. A Portable Burn Pan for the Disposal of Excess Propellants *In:* COLD REGIONS RESEARCH AND ENGINEERING LAB HANOVER NH HANOVER UNITED STATES. (ed.).
WALSH, M. R., THIBOUTOT, S., WALSH, M. E., AMPLEMAN, G., MARTEL, R., POULIN, I. & TAYLOR, S. 2011. Characterization and fate of gun and rocket propellant residues on testing and training ranges. *In:* ENGINEER RESEARCH AND DEVELOPMENT CENTER HANOVER NH COLD REGIONS RESEARCH AND ENGINEERING LAB (ed.).
WALSH, M. R., WALSH, M. E. & HEWITT, A. D. 2010. Energetic residues from field disposal of gun propellants. *Journal of Hazardous Materials,* 173**,** 115-122.

Annex 1: Use of 2,4-DNT in propellant mixtures

Summary

Propellants containing 2,4-DNT can be found both in small and large calibre ammunition. Trinitrotoluene (TNT) can contain 2,4-DNT either as an impurity or due to the recycling of 2,4-DNT containing ammunition or explosives for the use of manufacturing TNT. Some explosives may contain <1 % of 2,4-DNT as a melting/solidification moderator. 2,4-DNT may also have been used in some dynamite applications.

According to the screened literature, certain types of propellants utilised in artillery ammunition may contain up to 10-17 % of 2,4-DNT. The use and firing of artillery ammunition are a military activity. The vast majority of the literature on military uses of 2,4-DNT discussed in this report concerns practices and field experiments in the US and Canada. Exposure of military personnel or soil in EU is therefore unknown. However, in 2019, a group of Nordic countries together with experts from the US and Canada published a report that addresses the problem of field disposal of propellants and accumulation of 2,4-DNT in live-fire training fields.

Energetic residues containing 2,4-DNT can be found around the firing points of live-fire training places for the military because the combustion of the propellant is always incomplete. Furthermore, high levels of 2,4-DNT in the training areas can also be found in and around unexploded ordnances or places where unexploded ordnances are stored for disposal on the field. Training produces excess propellant as the amount of the propellant is adjusted for ballistic reasons at the range. Also, this excess is disposed at the field by burning, often on bare ground.

The risk of exposure for the military personnel handling and firing the artillery cannot be excluded on the basis of this assessment. There is a substantial literature (cf. Background) indicating that the incomplete combustion of propellants and the corresponding 2,4-DNT-related pollution on training ranges may lead to human exposure of 2,4-DNT. On military training ranges, 2,4-DNT is mostly accumulating in the top layer of the soil. Nitrocellulose fibres containing 2,4-DNT can be found on clothing of military personnel operating the artillery (i.e. artillerists). In addition to artillery firing points, small arms firing points have been found to be contaminated with 2,4-DNT. Environmental concerns relate to the fact that the substance, which is classified as Aquatic Acute 1 and Aquatic Chronic 1, is found in the top layer of the soil.

During the screening, a possible knowledge gap with regard to the extent of use and import of 2,4-DNT-containing artillery ammunition was identified. Also, a document summarizing the known and expected impacts of the European REACH regulation on the U.S. Department of Defence (DoD) by the Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) has stated that information on the propellants does not have to be registered or disclosed to ECHA[34]. More specifically, the referral was made in relation to the need for an Authorisation process, but it may also have implications to notifying substances in articles as producers and importers have to notify to ECHA the substances listed on the Candidate list which are present in their articles, if both the following conditions are met:

[34] Impact of European REACH Regulations on DoD and Military Equipment Manufacturers and Suppliers (2015): https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Surface-Engineering-and-Structural-Materials/Impact-of-European-REACH-Regulations-on-DoD-and-Military-Equipment-Manufacturers-and-Suppliers

- The substance is present in their relevant articles above a concentration of 0.1 % weight by weight.
- The substance is present in these relevant articles in quantities totalling over one tonne per year.

Background

Propellants are usually regarded as substances/mixtures within the context of the REACH Regulation and thus as such are not within the scope of this report. However, when they are as an integral part of an article (e.g. within an ammunition or artillery shell), they are regarded as part of the article. The ammunition cartridge containing the propellant is designed to launch a projectile and therefore the shape, surface and design of such ammunition cartridges determine their function to a greater degree than does its chemical composition[35].

Solid propellants are low-explosive with rapid or controlled burning[36] to produce gases to create the pressure to accelerate projectiles from guns or propel rockets toward targets (Folly and Mader, 2004). These types of propellants are often referred also as smokeless powders (e.g. Pichtel (2012)). DNT is used mostly in single-based or double-based solid propellants. Single-based powders contain nitrocellulose as the sole energetic material. According to Pichtel (2012), single base propellant has applications from small arms to cannons whereas double base propellants can have multiple applications.

Jenkins and Vogel (2014) did not list 2,4-DNT as an ingredient for double base propellants, and it seems that even if it can be found from this propellant type, it is not as often included in the principal ingredients as in single base propellants. Review of Pichtel (2012) lists 2,4-DNT in the composition of single and double based propellants. Common applications of 2,4-DNT containing propellants can be found in Table 11.

According to ECHA (2010) there are some literature referring to DNT in gunshot / post-blast residues (studies cited in Joshi et al. (2009)). Technical report (2010) refers to a study of Walsh et al. (2010) where it was shown how military training with artillery produces excess propellant that is burned on the training range and can result in point sources containing high concentrations of unreacted propellant constituents such as nitroglycerine and 2,4-DNT. Both are found at firing positions and propellant disposal areas.

Firing point or firing position residues are seen as a function of the efficiency of the weapon system and the composition of the propellant and especially larger weapon systems with longer barrels, rifled barrels or larger propellant loads consume propellants more efficiently whereas shorter barrels and smaller propellant loads leave relatively more residues (EPHW, 2019). Evidence of post-blast residues in the vicinity of the barrel (within meters) have been reported in the literature. 2,4-DNT is found embedded in fibrous propellant post-blast residues (Figure 2). A wipe sample of an artillery gun after shooting with 2,4-DNT containing propellant has shown 2,4-DNT residues, indicating a possibility for a particle deposition on the skin and the uniforms of artillery soldiers and their possible exposure through both dermal exposure and ingestion (Ampleman, 2009). Furthermore, handling of propellant bags and ammunition waste at the field, as well as burning excess propellant, are possible sources of human exposure.

2,4-DNT is mainly found on the topsoil layer where it accumulates (Walsh et al., 2011). Firing a large calibre gun also creates pressure waves that can mobilize dry soil effectively around the

[35] ECHA QA ID No 1059:
https://echa.europa.eu/support/qas-support/qas?p_p_id=journalqasearch_WAR_journalqaportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=2&p_p_col_count=3

[36] Known as deflagration (Jenkins & Vogel 2014).

firing point which then can lead to repetitive airborne 2,4-DNT containing particles and possible further exposure. Therefore, overall levels and aggregation of 2,4-DNT in firing points may have significance for the military personnel practising regularly at these points.

Excess propellant is created while training due to the habit of adjusting the number of propellant bags of artillery for ballistic reasons (Walsh, 2016). Propellants utilized in artillery ammunition are added or removed inside the ammunition shell according to the desired firing power and radius. Loading or unloading the ammunition includes manual handling of the propellant bags at the field (Figure 3). In US and Canada it is common that this excess in burned at the training field (Walsh, 2016). Soil samples adjacent to burning points of propellants have contained up to 48 mg/kg of DNT (Hunt and and Huntington (1999) in Walsh (2016)). Walsh et al. (2010) tested for residues from burning the propellants on both bare ground and in specifically developed propellant burning pans. Remaining DNT residues when burning on wet and dry soil were 1.0 % and 0.95 %, respectively. When burning three different types of propellants in burning pans the fraction of DNT-residues ranged from <0.001 % to 0.020 % (Walsh et al., 2010).

Disposing the excess propellant at the field is a practise of unknown magnitude in the EU member states. However, the presence of excess propellant due training has been mentioned in recently published guidance report *Environmental Protection of Heavy Weapon Ranges: Technical and Practical Solutions* (EPHW, 2019). EPHW as a project was initiated by Finland and consisted of environmental and legal experts from the defence administrations of Finland, Sweden, Norway, Denmark, the United States and Canada. The report addresses 2,4-DNT contamination of soil in ranges, especially at firing points for mortars and howitzers. The levels of 2,4-DNT in soil at the training range are mentioned to be measurable but low, except in areas where excess propellant has been burned on the ground. According to the report, in these areas high concentrations of energetics such as 2,4-DNT may be found (EPHW, 2019).

The EPHW-report (2019) recommends a portable burn pan for excess artillery propellant disposal at the field as it facilitates the burning process and increases the burning efficiency, resulting in less dispersal of the energetics in the environment and less remaining unburned energetics. The burn pan is mentioned to be in use at three military bases in the US and that reports of its performance describing the technology are fully available. No experience of the use of the burning pan in Nordic countries involved in EPHW-working group is mentioned (EPHW, 2019).

The use of 2,4-DNT containing propellants may also lead to occupational exposure in military waste disposal and recycling facilities (Letzel et al., 2003).

Table 12: Weapon systems producing releases of 2,4-DNT

Weapon system		Propellant	Rounds fired	Residues/ round (mg)	References	Consumption efficiency	Compound remaining
Howitzers	105-mm	M1-I & II	71	34	Walsh et al. 2009	N.A.	N.A.
	105-mm	M1	22	6.4	Walsh et al. in Ch 4 Jenkins et al. 2007	N.A.	N.A.
	155-mm	M1	60	1.2	Walsh et al. 2005	N.A.	N.A.
Tank (leopard)	105-mm	M1	90	6.7	Ampleman et al. 2009	99.998 %	0.0022 %
Machine gun	7.62-mm	WC846	100	0.0018	Walsh et al. 2012	99.95 %	0.05 %

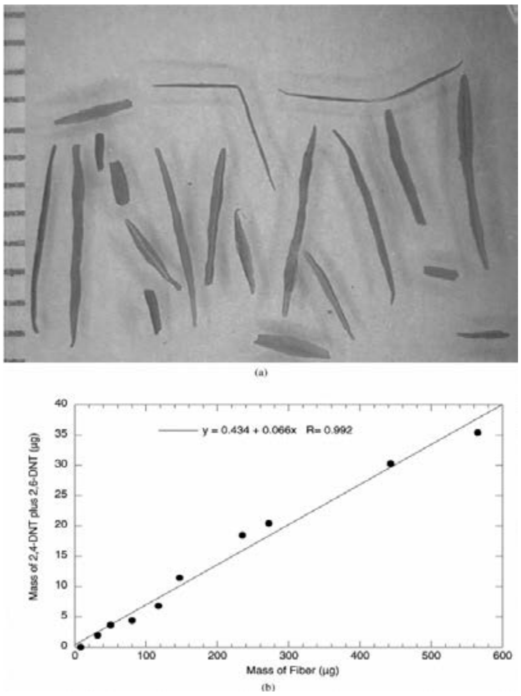


Figure 1: Single based propellant post-blast residues containing DNT (Source: Walsh, M. E., Ramsey, C. A., Taylor, S., Hewitt, A. D., Bjella, K., & Collins, C. M. (2007). Subsampling variance for 2, 4-DNT in firing point soils. Soil & Sediment Contamination, 16(5), 459-472.).

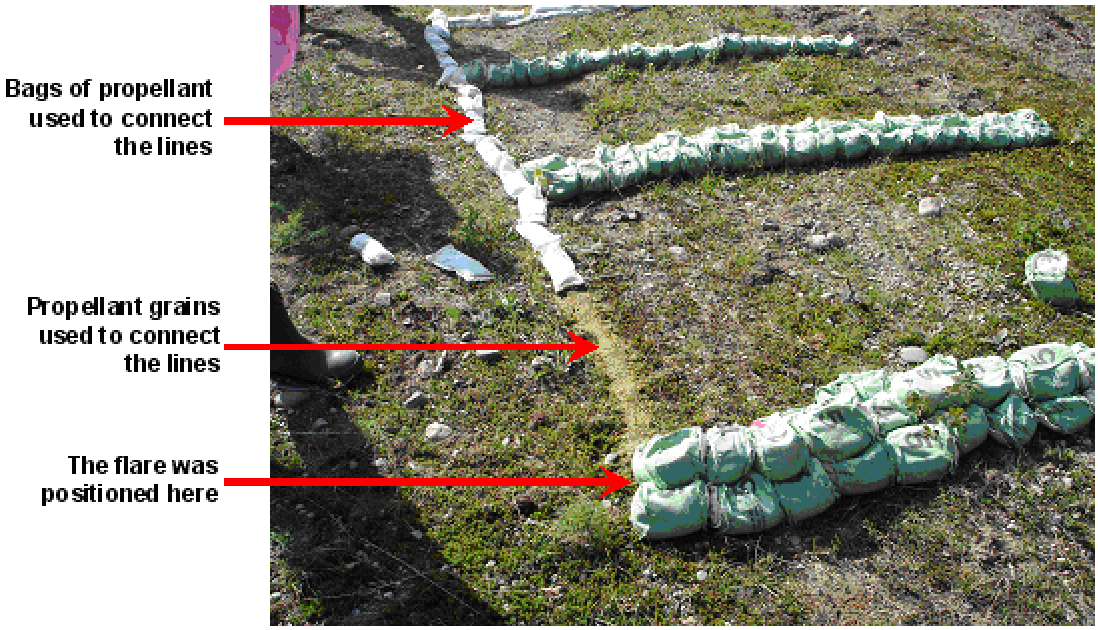


Figure 2: Excess Propellant bags for artillery ammunition (Source: *Poulin, I., Thiboutot, S., & Brochu, S. (2011). Production of dioxins and furans from the burning of excess gun propellant (No. DRDC-VALCARTIER-TR-2009-365). DEFENCE RESEARCH AND DEVELOPMENT CANADA VALCARTIER (QUEBEC).*)