Framework Contract No ECHA/2008/2 - Reference Number ECHA/2008/2/SR25

Service Request on Providing Actual Data on the European Market, Uses and Releases/Exposures for 2,4-Dinitrotoluene

Revised Final Report

prepared for

the European Chemicals Agency (ECHA)

DHI

TNO

RPA

August 2010

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prepared for

European Chemicals Agency (ECHA)

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EXECUTIVE SUMMARY

Introduction

2,4-dinitrotoluene (2,4 DNT) was identified as a Substance of Very High Concern (SVHC) according to Article 57(a) of the REACH Regulation. According to Annex VI, part 3, Table 3.2 of Regulation (EC) No 1272/2008 it is classified as a carcinogen category 2, R45 (May cause cancer) and was therefore included in the candidate list for authorisation on 13 January 2010, following ECHA's decision ED/68/2009. This is a technical report prepared by the DHI consortium with RPA acting as the leading partner and TNO playing a supporting role on the manufacture, uses and releases of 2,4 DNT in the EU. The aim of the report is to support the prioritisation of the substance.

Manufacture, Imports and Exports

Manufacture: 2,4 DNT is commercially available as a purified isomer or as a component of dinitrotoluene mixtures. The total tonnage of 'technical grade' DNT (EC number: 246-836-1, CAS number: 25321-14-6), which is a mixture of isomers (approximately 80% of 2,4 DNT and 20% of 2,6 DNT), ranges between 540,000 and 810,000 tonnes per year. With a concentration of 75-80%, of 2,4 DNT, the tonnage of 2,4 DNT contained in the manufactured dinitrotoluene could range between 405,000 and 648,000 tonnes per year. The vast majority of this volume is used as a non-isolated intermediate for synthesis of toluene diisocyanate (TDI). Production of DNT 80 takes place in Germany, France, Hungary and Poland (note: the figure signifies the concentration of the 2,4 isomer in the mixture). Other identified uses of DNT 80 include the manufacture of DNT 95, DNT 65 and DNT 50 as well as the manufacture of propellants, as described below.

One further production plant was identified in Poland which uses DNT 80 to manufacture a range of products, DNT 95, DNT 65 and DNT 50. The quantities of DNT 95 and DNT 65/50 produced in the EU are very small compared to the overall EU production of DNT 80 and are in the 100-1,000 t/y range for DNT 95 and DNT 50, and the 10-100 t/y range for DNT 65.

DNT may also be produced as a by-product of the production of the explosive 2,4,6-trinitrotoluene (TNT) or be present as an impurity in the final TNT product. The available information suggests that two plants in the EU may currently produce TNT. DNT may also be present in TNT that is recovered from the decommissioning of old explosives and ammunition.

Imports: one company imports DNT 55 from an ex-USSR country. The quantity imported is very small in comparison to the overall EU production volume of DNT 80 as indicated above. Imports into the EU of mixtures that contain DNT may also take place, for example propellants for ammunition that contain DNT (of an unknown 2,4 DNT content). However, the DNT used in these mixtures appears to originate from the EU. Again, the relevant tonnage is small compared with the EU production tonnage of DNT 80.

Exports: some confidential information has been provided on the export of DNT 95 and DNT 50. The tonnages exported are in the 10-100 and 100-1,000 t/y ranges respectively.

Uses

The identified uses of DNT include:

- **use of DNT 80 in the manufacture of toluene diisocyanate (TDI)**: the substance acts as an intermediate; it is hydrogenated to yield TDA and this is then reacted with phosgene to yield TDI. This is then used to make flexible polyurethane (PU) foams that are used in furniture, bedding and automotive and airline seats. Smaller uses for TDI include PU elastomers and coatings;

- **use of DNT 80 in the manufacture of DNT 95 and DNT 65/50**: see above;

- **use of DNT 95, DNT 80 and DNT 65/50 in explosives and ammunitions**: DNT may be used in:

  - *intentional use in explosives*: in the past DNT may have been used in the manufacture of dynamites and Octol (a high explosive mixture consisting of HMX and TNT in different weight proportions)**;**
  - *unintentional presence in explosives*: impurities of DNT (as an isomer mixture) at a concentration of <1% may be found in TNT explosives;
  - *intentional use in ammunition*: DNT has two main uses in propellant formulations: (a) to provide a lower energy ingredient which lowers the calorific value, and therefore the flame temperature, of the final propellant; and (b) as a surface moderating agent to reduce the initial burning velocity and improve ballistic performance. Propellants may contain 2.5 – 17% DNT. The propellant consists of only a small percentage of the final shell;
  - *recycling of explosives and ammunition*: TNT recycled from old ammunition and explosives may still contain a small percentage of DNT isomer mixture. The recycling of old (smokeless) gunpowders is also possible and these may sometimes contain DNT-based propellants.

  The use of DNT in explosives and ammunition is likely to represent a small fraction (well below one per cent) of the total amount of DNT used in the EU. Users appear to be located at least in Austria, France, Germany and Spain. Sales elsewhere might be possible as a considerable amount of these grades is first sold to distributors.

- **use of DNT 50/55 in the non-ferrous metal industry**: DNT 50/55 is used as a temperature-specific cross-linking agent for refractories. Two relevant companies have been identified, one acting as a supplier to the other; both are located in the same EU Member State. The relevant products are used by around 30 users downstream in the following industry segments (as described in the IPPC BREF guidance note for non-ferrous metals):

  - 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; and
- tap hole clays – ferro-alloy furnace linings.

The IPPC BREF guidance note suggests that relevant companies are located in UK, Spain, France, Netherlands, Germany, Norway, Iceland, and Sweden.

A number of uses that have been mentioned in the literature (in airbags, azo dyes, engine fuels) have not been confirmed.

Releases from Manufacture and Use

Manufacture: information on releases of 2,4 DNT during the manufacture of DNT 80 is given in the Risk Assessment Report prepared under the Existing Substances Regulation. The Report indicates regional releases of 2,4 DNT to wastewater of 0.53 kg/day and continental releases of 0.34 kg/day.

Occupational exposure is expected in those activities where the system is breached such as collection of samples for quality control and maintenance. The exposure assessment in the Risk Assessment Report gave a reasonable worst-case inhalation exposure of 0.009 mg/m^3 and a reasonable worst-case dermal exposure of 0-2.1 mg/m^3 (90% protection by suitable gloves). Newer estimates produced for inhalation exposure using the Advanced REACH Tool show a reasonable worst case for dumping of 0.12 mg/m^3) and for vacuum transfer of 0.036 mg/m^3. The reasonable worst-case estimates for dermal exposure using the ECETOC TRA model are 0.77 mg (with LEV) and 77 mg (without LEV - assuming 90% reduction by protective gloves) for dumping and 3.8 mg (with LEV) and 38 mg (without LEV - assuming 90% reduction by protective gloves) for vacuum transfer.

On the other hand, during the manufacturing of DNT 95 and DNT 65/50, releases to the environment have been estimated to air and to wastewater in small amounts. In addition, releases to the workplace and therefore potential occupational exposure can occur during the manufacture at concentration much less than 1 mg/m^3 based on mean values of measurements.

Uses: generally, limited information is available. This can be summarised as follows:

- **manufacture of explosives and ammunition**: the Risk Assessment Report suggests no releases to air and an emission of 0.02 kg/day to water from a Spanish plant. Information from one company that handles propellants containing technical grade DNT suggests that emissions to air, wastewater, water bodies and soil are nil. Only a very small quantity of propellant may be lost as waste.

  With regard to occupational exposure, literature (Sabbioni *et al*, 2006) discusses exposure of workers to DNT in a factory manufacturing DNT and TNT, in China. The air concentration of 2,4 DNT was 43.1 ± 98.0 μg/m^3 and the concentration of 2,6 DNT was 13.9 ± 27.6 μg/m^3 (both expressed as 8h-Time-Weighted Averages). Other literature sources (Bodeau, undated) indicate that significant occupational exposure is possible during the mixing and shell-loading operations at plants manufacturing explosives.

Consultation suggests that occupational exposure during the handling of pre-prepared explosives is very low and a series of protective measures are taken (PPE, local extraction, automated filling plant). In addition to this information, we have also developed exposure estimates based on available information and expert judgement. Inhalation exposure was estimated using the Advanced REACH Tool (ART) and the reasonable worst-case estimate is 0.0026 mg/m^3 (2.6 µg/m^3). For dermal exposure, the reasonable worst case calculated with ECETOC TRA is 0.96 mg of DNT with LEV and 96 mg of DNT without LEV;

- **detonation of explosives and firing of ammunition**: literature suggests that during the thermal decomposition of TNT both 2,4 DNT and 2,6 DNT may be emitted to air and may also be detected in soil (at the ng/g level). The same applies for the thermal decomposition of RDX. Propellants contain energetic compounds such as nitroglycerine and 2,4 DNT, both of which are found at firing positions and propellant disposal areas. Some estimates of limited potential releases of DNT during detonation have been given by some consultees but are only available in the Confidential Annex 2. On the other hand, the German Federal Institute for Materials Research and Testing has noted that, if DNT is an ingredient of an explosive, it will be almost completely destroyed during detonation and only a very small part of it would be detectable after the blast (fractions of ppm to ppb).

  With regard to occupational exposure, limited information is available in literature. Among consultees, some companies and the German Federal Institute for Materials Research and Testing have argued that DNT will be almost completely destroyed during detonation. A company however has provided information based on a 1996 publication, which would suggest that exposure of humans may still be possible although the estimated exposure levels are expected to be considerably low;

- **demilitarisation of explosives/ammunition**: information from consultation suggests that the recycling of old TNT explosives and ammunition may indeed result in some releases to wastewater.

  With regard to occupational exposure, some information from literature (Letzel *et al*, 2003) suggests that occupational exposure to DNT during the disposal of military waste may occur. Eighty-two employees from a mechanical plant in Germany were studied, of whom 51 were regularly exposed to ammunition containing TNT and DNT, 19 occasionally, and 12 not at all. Air analyses yielded maximum concentrations of 20 µg/m^3 for 2,4 DNT. Some information on occupational exposure has been provided by consultees but is only available the Confidential Annex 2; and

- **use of DNT in the non-ferrous metals industry**: information from consultation suggests that some environmental releases of DNT to air during the relevant applications may occur. Some information on occupational exposure has been provided but is only available the Confidential Annex 2.

GLOSSARY

Term	Description
Actuator	An actuator is a mechanical device for moving or controlling a mechanism or system. It takes energy, usually transported by air, electric current, or liquid, and converts that into some kind of motion.
ART	The Advanced REACH Tool (ART) version 1.0 incorporates a mechanistic model of inhalation exposure and a statistical facility to update the estimates with the user's own data. This combination of model estimates and data produces more refined estimates of exposure and reduced uncertainty. The ART project has been conducted in close collaboration with a range of stakeholders from industry and member states. The use of ART for workers exposure assessment under REACH is described in ECHA' updated Guidance on Information Requirements and chemical safety assessment (see http://www.advancedreachtool.com/)
Azo dye	Any of a large number of yellow to red synthetic dyes that contain an azo or diimide (-N=N-) functional group
Calcination	The conversion of metals into their oxides as a result of heating to a high temperature
Carbon ramming paste	Ramming paste is used between the blocks at the bottom of the aluminium electrolysis cells
DNT	Dinitrotoluene
DNT XX	Dinitrotoluene mixture of isomers containing XX% of 2,4-dinitrotoluene
DoJELR	Irish Department of Justice, Equality and Law Reform
Dynamite	explosive material based on the explosive potential of nitroglycerine, initially using diatomaceous earth or another absorbent substance such as sawdust as an absorbent
EASE	Estimation and Assessment of Substance Exposure model
EASSP	European Association for Study of Safety Problems in production and use of propellants
ECETOC TRA	ECETOC Targeted Risk Assessment Tool (see http://www.ecetoc.org/tra)
Energetic compounds	Any material, chemicals, or end products used in the production of pyrotechnics, explosives, and propellants. A component of, or an item of ammunition, that is designed to produce the necessary energy required for ignition, propulsion, detonation, fire or smoke, thus enabling the item to function. Also a material (corrosive, oxidiser, etc.) that is inherently dangerous and capable of causing serious damage and which requires regulated handling to avoid accidents in connection with its existence and use
GDP	Gross Domestic Product; a measure of the economic production of a particular territory in financial capital terms over a specific time period
Grout	A thin mortar that can be poured and used to fill cracks in masonry or brickwork
Donarit	Ammonium nitrate explosive
HMX	Also called octogen, is a powerful and relatively insensitive nitroamine high explosive, chemically related to RDX. Like RDX, the name has been variously listed as High Melting eXplosive, Her Majesty's eXplosive, High-velocity Military eXplosive, or High-Molecular-weight RDX
Howitzer	A short cannon, intermediate between the gun and mortar
Loading hopper	A hopper in which free-flowing material is placed for loading by gravity into buggies or other conveyances
Nitrocellulose	A cotton-like material, made from cellulose by the action of nitric and sulphuric acids, used in the manufacture of explosives
Nitroglycerine	A heavy yellow poisonous oily explosive liquid obtained by nitrating glycerol; used in making explosives
Octogen	See HMX above
Octol	Octol is a melt-castable, high explosive mixture consisting of HMX and TNT in different weight proportions

Term	**Description**
Pre-tensioner	Seat-belt
Propellant	A low explosive composition, solid or liquid form, which burns and does not detonate. Propellants are used for propelling projectiles and rockets and to generate gases for powering auxiliary devices
PU	Polyurethane
Pyrotechnics	Mixtures of finely divided fuels and oxidizer powders, which may include various organic binders and colour intensifiers, used to produce sound, light, heat, smoke, delay, and gas
RDX	RDX (Royal Dutch Explosive), also known less commonly as cyclonite, hexogen (particularly in German and German-influenced languages), and T4, and chemically as Cyclotrimethylenetrinitramine, is an explosive nitroamine widely used in military and industrial applications
Refractory	A substance which is infusible at the highest temperature it may be required to withstand in service; heat-resistant material
RISKOFDERM	Risk Assessment of Occupational Dermal Exposure to Chemicals (model)
Slurry	Water resistance of explosives may be achieved by pre-dissolving ammonium nitrate in a small amount of water, thickening the solution with guar gum or starch and, optionally, cross-linking the gum thickeners to produce a gelled product. To this system, the fuel components are added as soluble or finely divided insoluble materials. Additional dry oxidisers may also be suspended, if desired, to lower the overall water content. The presence of these solids as well as ammonium nitrate crystals that precipitated upon cooling, the formulation led to the general designation of ‘slurries’ for these composite explosives
Smokeless powder	Smokeless powder is the name given to a number of propellants used in firearms and artillery which produce negligible smoke when fired, unlike the older gunpowder (black powder) which they replaced
TDA	Toluene diamine
TDI	Toluene diisocyanate
TNT	2,4,6-trinitrotoluene

1. INTRODUCTION

1.1 Objectives

In the framework of the authorisation process, Member States Competent Authorities or the European Chemicals Agency (ECHA), on a request by the Commission, may prepare Annex XV dossiers for the identification of substances of very high concern (SVHC). An Annex XV dossier has been prepared for 2,4-dinitrotoluene (2,4 DNT) by Spain (dated July 2009). The dossier concludes that 2,4-dinitrotoluene is a carcinogenic, mutagenic and reprotoxic (CMR) substance. It has, therefore, been put forward for consideration as a SVHC and potentially, subsequent inclusion in Annex XIV of the REACH Regulation.

The main objective of this project has been to provide background information on the markets, uses and releases of 2,4 DNT, with the aim to support priority setting of the substance on the candidate list for inclusion in Annex XIV.

The present analysis focuses on uses that exclude circumstances when the substance is used as an intermediate but include those uses that could potentially result in significant releases and exposure.

1.2 Methods

In undertaking this study, RPA conducted a desk-based review of literature as well as direct consultation with industry stakeholders. A dedicated web page was created within the RPA Internet site (http://www.rpaltd.co.uk/news-dnt.shtml) where a description of the project was provided as well as a link to a questionnaire in Microsoft Word format. Consultation encompassed manufacturers and users of the substance identified through literature review and Internet searches. Information was sought from:

- manufacturers of the substance;
- distributors and importers of the substance as well as of mixtures or articles that may contain them; and
- potential users of 2,4 DNT such as manufacturers of dyes, manufacturers of automotive airbags, manufacturers of explosives, and manufacturers of products for the non-ferrous metal industry.

We also contacted a series of trade associations relevant to the stakeholders mentioned above as well as a number of national authorities responsible for the safe handling of explosives and ammunition. It should also be noted that ECHA supported this consultation exercise by directly contacting those companies that have pre-registered the substance.

Finally, a second questionnaire was also formulated and used for consultation with Competent Authorities in the EU/EEA. This was disseminated by ECHA and responses were returned directly to RPA. Only a small number of Member State authorities made an input to this study.

2. NAME AND OTHER IDENTIFIERS OF THE SUBSTANCE

'Pure' 2,4 DNT can be identified as follows:

Substance Name: 2,4-dinitrotoluene

EC Number: 204-450-0

CAS Number: 121-14-2

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

According to the Annex XV report for the substance, 2,4 DNT is commercially available as a purified isomer or as a component of DNT mixtures. The commercial or technical grade, consists of approximately 80% 2,4 DNT and 20% 2,6 DNT. Manufacturers of the technical grade DNT (which has separate EC and CAS numbers - EC No: 246-836-1 and CAS No: 25321-14-6) have formed a consortium which intends to register only this form (rather than the 2,4 DNT isomer) as a strictly controlled transported isolated intermediate. The substance represented by the SIEF is described as follows:

Substance Name: Dinitrotoluene *or*

Reaction mass of 2,4-dinitrotoluene and 2,6-dinitrotoluene

EC Number: 246-836-1

CAS Number: 25321-14-6

Table 2.1: Dinitrotoluene (CAS No 25321-14-6, EC No 246-836-1) Substance Description

Constituents	**CAS No.**	**Concentration (% wt.)**
2,4-dinitrotoluene	121-14-2	75-80
2,6-dinitrotoluene	606-20-2	17-20
Impurities	**CAS No.**	**Concentration (% wt.)**
3,4-dinitrotoluene	610-39-9	2-3
2,3-dinitrotoluene	602-01-7	< 2.0
2,5-dinitrotoluene	629-15-8	< 0.8
3,5-dinitrotoluene	618-85-9	< 0.1
2,4,6-trinitrotoluene	118-96-7	< 0.1
Water		< 2.0
3-nitrotoluene	88-72-2	< 0.1
2- nitrotoluene	99-08-1	< 0.1
4-nitrotoluene	99-99-0	< 0.1

Source : Consultation

It should be noted that our research has confirmed the use of 'pure' 2,4 DNT in the EU. However, this is not 100% pure as it still contains a small percentage of other isomers. This is further discussed later in this report.

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

3.1 Production Process

According to the Annex XV for the substance, dinitrotoluene can be produced by a two-step nitration of toluene in a closed system process producing a mixture, the commercial or technical grade DNT. Hereafter, products that are mixtures of DNT isomers are referred to in this report as DNT XX where XX is a number representing the concentration of 2,4 DNT in the mixture. If the single 2,4-isomer is required, the nitration can be stopped at the mono-stage and pure p-nitrotoluene is obtained by crystallisation. Subsequent nitration of the p-nitrotoluene yields only 2,4 DNT.

No additional information was collected during this study with regard to the manufacture of the 'typical' technical grade DNT (hereafter referred to as DNT 80)[1]. However, we have identified one company (**NITRO 1**)[2] which is using DNT 80 to manufacture both 'pure' 2,4 DNT as well as less pure technical grade DNT products (DNT 65 and DNT 50) through a combination of crystallisation, centrifugation and drying. The 'pure' 2,4 DNT in fact contains around 95% of 2,4 DNT, therefore, we have opted for describing it as "DNT 95" in this report.

3.2 Production Sites

Information from ISOPA (2010), the association representing the European polyurethane industry, has submitted information on behalf of five EU-based manufacturers of DNT 80 located in France, Germany, Hungary, and Poland.

The number of individual sites is uncertain. As will be discussed later in this Section, the vast majority of DNT 80 manufactured by these large manufacturers (some of them with an extensive global presence) is apparently used in the manufacture of toluene diisocyanate (TDI). Literature suggests that, in 2004, there were seven plants manufacturing TDI in the EU, located in France, Germany (3), Hungary and Poland (ICB, 2008). There have been plans however to replace two of the German plants with a single world-scale plant (PU Magazine, 2010). Overall, it is believed that the production sites for DNT 80 are five to six. These companies do not manufacture 'pure' 2,4 DNT.

With regard to the production of DNT 95, DNT 65 and DNT 50, this is undertaken by a single plant located in Poland.

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1 Please note that whilst this product is described in this report as "DNT 80", in reality it contains a variable 2,4 DNT content of 75-80% (as shown in Table 2.1).

2 For confidentiality reasons, companies are referred to by codenames in this report.

3.3 Production Volumes

According to ISOPA (2010), the total tonnage of DNT 80 manufactured by its member companies and their affiliated companies ranges between 540,000 and 810,000 tonnes per year. Assuming a concentration of 2,4 DNT of 75-80%, the tonnage of 2,4 DNT contained in the manufactured technical grade product could range between 405,000 and 648,000 tonnes per year.

The quantities of DNT 95 and DNT 65/50 produced in the EU (by one company only) are very small compared to the overall EU production of DNT 80 and are in the 100-1000 t/y range for DNT 95 and DNT 50, and the 10-100 t/y range for DNT 65. Additional detail on the relevant tonnages is provided in the Confidential Annex 2 to this report.

As will be discussed later in this report, DNT may also be produced as a by-product of the production of the explosive 2,4,6-trinitrotoluene (TNT) or be present as an impurity in the final TNT product. The available information suggests that TNT may currently be produced by two plants in the EU. Additional detail is provided in the Confidential Annex 2 to this report.

Finally, DNT may also be present in TNT which is recovered from old explosives and ammunition. This recycling process is further discussed in Section 4.2.1.

3.4 Imports into the EU

Limited information was collected during the course of this study. A leading non-EU manufacturer of 2,4 DNT[3] (company **NITRO 2**) has indicated that it does not export 2,4 DNT to Europe although the mixture of isomers may be used to manufacture toluene diamine (TDA) which may find its way into the EU. TDA is subsequently fully reacted.

On the other hand, we have identified an EU-based company (**NITRO 3**) that imports DNT with a 55% content of 2,4 DNT from an ex-USSR country. The quantity imported is very small in comparison to the overall EU production volume of DNT 80 indicated in Section 3.3 above. Additional detail is provided in the Confidential Annex 2. It should be noted that the imports referred to in the Annex XV dossier for the substance are imports of the substance into Spain originating from country(ies) which did not belong at the time to the EU. The information on imports presented in the current report is new information.

Imports of mixtures that contain DNT into the EU may also take place. Some limited information on propellants for ammunition that contain DNT (of an unknown 2,4 DNT content) has been provided by an EU-based company (company **NITRO 4**). However, the DNT used in these mixtures appears to originate from the EU. Again, the relevant

3 At this point, it is not clear whether this is the pure substance or a technical grade but it is most likely to be the latter. The company did not clarify this issue within the timeframe of this study.

tonnage is small compared with the production tonnage of DNT 80; additional detail is provided in the Confidential Annex 2.

Finally, a chemicals distributor located in an Asian country (company **NITRO 5**) who contacted the study team has indicated that they have not shipped 2,4 DNT to EU customers in recent years and, following the substance's inclusion to the candidate list for authorisation, they have no plans to import it in the future.

3.5 Future Trends

We have not been provided specific information with regard to foreseeable trends. The Annex XV dossier refers to a production of ca. 630,000 tonnes of technical grade DNT in 2004 (containing ca. 504,000 tonnes of 2,4 DNT). The average production figure based on the most recent data is (405,000+648,000)/2 = 527,000 tonnes; that would indicate a small increase in production over the figure presented in the Annex XV dossier.

With regard to the production of DNT 95 and DNT 65/50, there has been a mixed trend in the production volumes over the last five years (between 2005 and 2010, 2,4 DNT production increased and then decreased and is now currently somewhat higher than the 2005 levels). Details of temporal changes in production volumes are provided in the Confidential Annex 2 to this report.

3.6 Information on Releases from Manufacture

Information on releases of 2,4 DNT during the manufacture of DNT 80 has not been provided in the course of this study. The Annex XV dossier and more importantly the Risk Assessment Report prepared under the Existing Substances Regulation provide a considerable amount of information. A summary of releases is given in **Table 3.1**. It should be remembered however that DNT 80 manufactured in the EU is mostly (but not exclusively) used as a transported isolated intermediate in the production of TDI.

Table 3.1: Summary of Regional and Continental Release Estimates of 2,4 DNT (kg/day) from Manufacture and TDI Production

Scale	Air	Waste water
Regional	0	0.53
Continental	0	0.34
Source: ECB (2008)		

Some additional information on releases and occupational exposure to DNT has been provided by the company manufacturing DNT 95 and DNT 65/50 (company **NITRO 1**). During the manufacturing of 2,4 DNT ('pure') and technical grade dinitrotoluene (with a content of 50/65% 2,4 DNT), releases to the environment have been estimated to air and to wastewater in small amounts. In addition, releases to the workplace and therefore potential occupational exposure can occur during the manufacture at concentration much less than 1 mg/m^3 based on mean values of measurements. Additional detail is available in the Confidential Annex 2.

4. INFORMATION ON USES OF 2,4-DINITROTOLUENE

4.1 Use in the Manufacture of Toluene Diisocyanate

4.1.1 Description of Use

According to the Annex XV dossier, the substance is hydrogenated to yield TDA and this is then reacted with phosgene to yield TDI. This is then used to make flexible polyurethane (PU) foams which are used in furniture, bedding and automotive and airline seats. Smaller uses for TDI include PU elastomers and coatings (ICB, 2009). PU foams account for about 90% of world demand in TDI (ICB, 2008).

A consultee based outside the EU (company **NITRO 2**) has further noted that uses of TDA other than the production of TDI may also exist.

4.1.2 Locations and Quantities Used

According to ISOPA (2010), DNT 80 manufactured by the five leading EU manufacturers is exclusively used in the manufacture of TDI in the EU. In relation to the locations of use, see information presented in Section 3.2. It should be noted however that, contrary to the assertion by ISOPA, two additional minor uses of DNT 80 have been identified: the manufacture of DNT 95, DNT 65 and DNT 50, and the manufacture of propellants for ammunition.

4.1.3 Structure of Supply Chain

The vast majority of DNT 80 is used in the manufacture of TDI by the manufacturers of DNT 80 and their affiliated companies. For the remaining minor uses, see discussion below.

4.1.4 Future Trends

A 2008 publication (ICB, 2008) suggests that world demand for TDI would grow by 3-4% per year, with the strongest growth in Asia, mainly China. Western Europe was expected to grow at GDP rates, but growth would be higher in Central/Eastern Europe and the Middle East/Africa. EU-based companies were making plans for expanding capacity both within the EU and elsewhere in the world.

A later publication (ICB, 2009) notes that demand for flexible PU foams fell in 2009 between 5% and 20% in Western Europe. Still, demand in Western Europe was expected to grow at GDP rates but would potentially be much higher in Eastern and Central Europe, driven by improving living standards. These projections could provide some insight to the likely future trends in the use of DNT in the production of TDI and thereon on PU foams; however, we cannot be certain that these projections will materialise in the current economic volatility and the ongoing credit crisis in the EU.

4.2 Use in Explosives and Ammunition

4.2.1 Description of Use

Use in Explosives

<u>Intentional Use of DNT in Explosives</u>

Literature: it is understood that DNT has been used as a component of explosives. Roemer *et al* (2002) indicate that, in the past, DNT-based explosives might have been used for technical and economic reasons instead of 2,4,6 trinitrotoluene (TNT).

Consultation: the Federation of European Explosives Manufacturers (2010) has advised us that they consulted their member companies (who cover more than 95% of the EU explosives market). The information received from the association would suggest that DNT is no longer used for many years as an additive in the manufacture of explosives (dynamite) (but it is possible that at least one company (company **NITRO 10**) might be using the substance in propellants). Similarly, the German Federal Institute for Materials Research and Testing (2010) has noted that, in Germany, all manufacturers of blasting explosives have replaced DNT by other substances.

Consultation with company **NITRO 17** suggests past use of DNT as an intentional component of explosives. More specifically, DNT was used in small concentrations in Octol (a melt-castable, high explosive mixture consisting of HMX[4] and TNT in different weight proportions) as a melting/solidification moderator. The company discontinued this use in the 1990s. Company **NITRO 16** has also confirmed that DNT may find use as an intentional component of explosives (but not by the company itself). Company **NITRO 18** also indicated a past use in dynamites. Additional detail on intentional uses of DNT in explosives is provided in the Confidential Annex 2.

More importantly, there is at least one EU-based company (company **NITRO 1**) that supplies DNT 95 and DNT 65/50 to EU and non-EU customers for the manufacture of explosives. Information on specific tonnages sold for specific explosive or ammunition applications have not been made available. However, the amount of DNT 95 sold in the EU for explosives/ammunition is in the 100-1,000 t/y range. For DNT 65/50, EU sales for the manufacture of explosives are currently in the 10-100 t/y range. Additional detail is provided in the Confidential Annex 2.

<u>Unintentional Presence of DNT in Explosives</u>

Literature: Singh (2009) notes that DNT is a by-product (impurity) of TNT manufacture.

[4] Also known as octogen.

Consultation: company **NITRO 18** confirmed that TNT may contain impurities of DNT but also suggested that in the past it produced technical grade DNT as a by-product of the TNT manufacturing process.

Another two companies (companies **NITRO 6** and **NITRO 17**) have also advised us that TNT (2,4,6 trinitrotoluene) explosive may also contain DNT as an impurity. In fact, company **NITRO 17** still holds a stock of TNT explosive that contains a low percentage of 2,4 DNT.

The available information points to the fact that the DNT is present in TNT in the form of mixed isomers rather than 2,4 DNT only. One of the two companies (company **NITRO 17**) has noted that as technical grade DNT was the starting substance for the synthesis of the TNT 80.4°C-quality[5], the DNT present in the TNT end product should be assumed to be a mixture of isomers.

It appears however that the use of TNT is apparently becoming less popular in Europe. It may still be used in Eastern Europe or Asian countries (China/India) but now finds limited use in Western Europe. Company **NITRO 6** noted that TNT is normally manufactured at a large scale (i.e. smaller producers are unlikely to be there in general) and production may still be ongoing at significant levels in countries such as the USA. The information received (and discussed in more depth in the Confidential Annex 2) would point to the presence of two current manufacturers of TNT in the EU.

Use in Ammunition

Description of Use

Literature: DNT acts as a stabiliser, flash and temperature suppressor in smokeless[6] propellants for ammunition. Wallace (2008) also notes that DNT acts as a stabiliser by combining with decomposition products and may be used as a muzzle flash suppressor by reducing the heat of explosion. Heramb & McCord (2007) suggest that deterrents such as DNT coat the exterior of the propellant granules to reduce the initial burning rate on the surface as well as to reduce initial flame temperature and ignitability. The coating also broadens the pressure peak and increases efficiency. Rifle powders, particularly when porous, can burn so rapidly that the initial rise of pressure can be faster than necessary. In this case, the grains can be surface moderated, or given a surface coating of a nitrocellulose gelatiniser, such as DNT. This process is often carried out at the same time as glazing, with a small amount of graphite, which improves the flow properties of the powder as well as increasing its loading density (Fordham, 1980). The role of DNT has also been described as (a) a plasticiser – Kosanke *et al* (2004) suggest compositions of double-based propellants containing DNT; Heramb & McCord (2007) agree that DNT may act as a plasticiser, and (b) a waterproofing agent (NTP, 1978).

5 This is believed to be the solidification point of the product.

6 The term smokeless powder refers to propellants used in firearms and artillery, which produce negligible smoke when fired. Older forms of gunpowder or “black powder” produced significant amounts of smoke.

Consultation: manufacturers of propellants are organised in the European Association for the Study of Safety Problems in the Production and Use of Propellant Powders (EASSP). According to the Association (European Association for Study of Safety Problems in Production and Use of Propellants, 2010), DNT has two main uses in propellant formulations:

- in some large calibre, single base formulations it is added to the propellant composition at the mixing stage in order to provide a lower energy ingredient which lowers the calorific value, and therefore the flame temperature, of the final propellant; and

- in some smaller calibre propellants, DNT is used as a surface moderating agent. That means it is applied to the outer surface of the already formed propellant granules in order to reduce the initial burning velocity and improve ballistic performance.

In both situations, DNT acts as a plasticiser for nitrocellulose so it is essentially bound to the base matrix of the propellant.

It is understood that propellants which contain DNT can be used for both military ammunition and recreational (hunting/sporting) ammunition. This has been suggested by the manufacturer of DNT 95/65/50 referred to earlier in this report and has been confirmed by an EU-based manufacturer of sporting ammunition (company **NITRO 9**) who coats its propellants with DNT. The sporting ammunition of company **NITRO 19** also contained DNT until a few years ago as a result of recycling of old smokeless powders but not any longer (recycling processes are discussed further below in this Section).

On the other hand, one of the market leaders in civilian ammunition, company **NITRO 26**, has suggested that DNT has largely been abandoned in civilian ammunition, although for military powders used in ammunition a requirement that DNT be part of the specifications[7] might still exist. In addition, we have received information from a company (company **NITRO 4**) that uses pre-prepared propellant containing a low percentage of DNT in the manufacture of propellant charge articles which are used for military applications. Additional detail on this use of DNT is provided in the Confidential Annex 2.

<u>DNT Concentration in Propellants</u>

Literature: Evans (2010) provides details of the compositions of propellants used by the British artillery in World War II that contained DNT. DNT was present in concentrations of 9-10%. Another source - with a US bias (Ammunition Pages (undated)) - presents a range of different US propellants (some of them rather dated) that may contain DNT. Several of these propellants contain 2.5-17% DNT and several others have a DNT coating.

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7 The company has noted that producers of powders in North America (USA & Canada) may still be using DNT in civilian products.

Consultation: information on current levels of DNT in propellants has been made available by consultees. Due to the sensitive nature of this information, it is discussed in detail in the Confidential Annex 2.

Recycling of Explosives and Ammunition

Consultation: company **NITRO 6** confirmed that old TNT may also be recycled from ammunition and then sold at low prices for commercial uses (mining, demolition, etc.).

We have spoken with two companies located in two different EU Member States, which are active in recycling of old TNT explosives. The first company (company **NITRO 7**) owns two sites. On one of them, TNT is extracted from old ammunition. This indeed contains a small percentage of DNT.

The second recycling company (company **NITRO 8**) disassembles mostly old ammunition and recycles its components, occasionally recovering TNT, which contains DNT as an impurity. This TNT is then sold to civilian companies within and outside EU for re-use in booster charges etc. for the mining industry.

The percentage of DNT in TNT appears to vary but is generally below 1%. More specific information received from consultees is provided in the Confidential Annex 2.

Finally, recycling of old (smokeless) gunpowders is also possible and these may sometimes contain DNT-based propellants. This has been confirmed by companies **NITRO 7** and **NITRO 19** (for the latter only in the past). Details of this process are provided in the Confidential Annex 2 to this report. It should be noted that these two companies are operating in the same industry sub-sectors: one is active in the military ammunition sector while the other is active in the sporting ammunition sector.

Transformation of DNT and Grades of the Substance Used

<u>Transformation of DNT</u>

There is limited information on whether DNT is transformed to another substance during its use in the preparation of explosive mixtures (only company **NITRO 4** that uses pre-prepared propellant advised that no transformation of DNT takes place during its use of the propellant). However, judging from the nature of DNT applications (mixing with other substances), it is most likely that the substance is not transformed during use in explosives and ammunition.

<u>Grades of DNT Used</u>

With regard to whether 2,4 DNT (DNT 95, as discussed above) or technical grade DNT is used in the above applications, information from the manufacturer of DNT 95 (company **NITRO 1**) suggests that DNT 95 can be used as an additive in explosives, in propellants for ammunition (military and hunting ammunition) as well as in applications for which limited additional information is available, such as an engine fuel additive. Especially for propellants, only DNT 95 is sold by company **NITRO 1** for this use. Company **NITRO 17** noted that, when intentional use of DNT in explosive manufacture took place in the past, this was 2,4 DNT rather than a mix of isomers. In fact, as the quantities required were small, these were purchased in the pure form from a supplier of reagents and pharmaceutical products. Information received from company NITRO 28, which is located outside the EU further suggests that 'high purity' DNT is used in their manufacture of propellants, in accordance with a relevant Standard. The percentage of 2,4 DNT in the DNT grade used exceeds 99%. Additional information is provided in the Confidential Annex 2. In support of this information, Bodeau (undated) suggests that military-grade DNT requires "*highly purified 2,4 DNT flakes*".

However, other sources suggest that 'lower' DNT grades may also be used. Company **NITRO 10** confirmed that it uses DNT 80 in the manufacture of propellants. Also, the European Association for Study of Safety Problems in Production and Use of Propellants (2010) noted that DNT used by propellant manufactures is the commercial grade, so it will most likely be a mixture of isomers (nevertheless, no suggestion could be made of the composition of the grades used).

Information relating to the presence of DNT in TNT explosives (from companies **NITRO 8** and **NITRO 17**) also suggests that a mixture of DNT isomers is present rather than 'pure' 2,4 DNT. Company **NITRO 1** has confirmed that 2,4 DNT is predominant in the mixture.

We have not been offered an adequate explanation on why one grade may be preferred over the other. A suggestion that has been made (by company **NITRO 4**) is that users may be particularly aware of the freezing points of different grades: 'pure' 2,4 DNT has a freezing point of 70-71°C, DNT 65 has a freezing point of 50°C and DNT 50 has a freezing point of 35°C. It is possible that different users may use different production technologies which depend on the freezing point of the materials used. A possible explanation could be the difference in the price of DNT 95 and DNT65/50. This is elaborated further in the Confidential Annex 2.

4.2.2 Locations and Quantities Used

Information on locations of use has been provided by some companies and is presented in the Confidential Annex 2. This suggests that the use of DNT in explosives and ammunition is likely to represent a small fraction (well below one per cent) of the total amount of DNT used in the EU. With particular regard to sales of DNT 95 and DNT 65/50 sold to the explosives and ammunition sectors, users appear to be located at least in Austria, France, Germany and Spain. However, sales elsewhere might be possible as a considerable amount of these grades is first sold to distributors and detailed information on their supply chains is not available.

Some information was received by authorities of a limited number of EU Member States. The Mines Service of Cyprus (2010) advised us that manufacture of explosive substances and pyrotechnic articles does not exist in Cyprus. The explosives that are used in Cyprus are imported from Spain and Greece. They are dynamites and slurries (ammonium nitrate gels) packed in cartridges and the explosive substance does not come in contact with persons. Information presented above would suggest that DNT was used in dynamites in the past; we do not have sufficient information on whether DNT-based dynamites are currently used in Cyprus.

In addition, the Weaponry Fund of the Republic of Lithuania (2010) noted that the Lithuanian explosives industry is very small. There is only one company producing explosives for their own needs and two more using commercially available explosives. Reportedly, none of these uses materials of relevance to this study.

The Spanish Ministry of Health and Social Policy (2010) reiterated information available in the Risk Assessment Report and Annex XV for the substance. Apparently, the 'pure' form of the substance has been used, in the past at least, by a Spanish manufacturer of explosives. The company (company **NITRO 10**) had reported that they used the 'pure' form in the solid state but according to the Spanish authorities consulted, this does not mean that using the technical grade would not be possible. The use of the pure substance was considered in the Risk Assessment Report as a worst-case scenario. Some up-to-date information collected from the company itself is provided in the Confidential Annex 2.

Finally, the Irish Health and Safety Authority (2010) has relayed to us information from the Irish Department of Justice, Equality and Law Reform (DoJELR). The Department indicated that the questionnaire for DNT was circulated to explosive manufacturers and it was concluded that neither of the two substances are currently used in Ireland. The DoJELR also indicated that the explosives industry does not use, or does not intend to use DNT in Ireland.

4.2.3 Structure of Supply Chain

Limited information is available, mostly on the supply chains of the manufacturer of DNT 95, a past user of DNT in explosives manufacture and one user of propellant mixtures (these are discussed in the Confidential Annex 2).

We assume that the number of companies that manufacture military and sporting ammunition may not be particularly large (for example, there is a limited number of companies that place propellant powders on the market to be used in sporting ammunition, according to the Internet site of the Association of European Manufacturers of Sporting Ammunition[8] and of them only some may still use the substance).

With regard to the number of companies, which may recycle TNT, at least two of them exist and are located in two different EU Member States. Consultation suggests that the total number of relevant companies is likely to be fewer than ten.

8 See the website of the Association of European Manufacturers of Sporting Ammunition (http://www.afems.org/).

4.2.4 Future Trends

No specific trend was identified; however, there are strong indications that the use of DNT in explosives and ammunition may be in decline. The Federation of European Explosives Manufacturers has indicated so; also certain companies have confirmed that they have used the substance in the past but not any longer (for example, companies **NITRO 17** (explosives) and **NITRO 19** (sporting ammunition)).

4.3 Use in the Non-Ferrous Metals Industry

4.3.1 Description of Use

Technical grade DNT (DNT 50/55) is used as a temperature-specific cross-linking agent for refractories. Company **NITRO 11** is involved in the use of DNT in this field and has claimed that, in this process, DNT is transformed into another substance. More detailed information on the processes involved is provided in the Confidential Annex 2 on the company's request.

OECD also suggests that DNT may be used to stain refractory bricks and causes the prominent yellow of calcinated refractory bricks (OECD, 2004).

4.3.2 Locations and Quantities Used

Two relevant companies have been identified, one (company **NITRO 3**) acting as a supplier to the other. Both are located in the same EU Member State, as explained in the Confidential Annex 2.

4.3.3 Structure of Supply Chain

Regarding the use in the non-ferrous metals industry, two companies have been identified and are both located in the same EU Member State. The relevant products are used by around 30 users downstream in the following industry segments (as described in the IPPC BREF guidance note for non-ferrous metals):

- 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; and
- tap hole clays – ferro-alloy furnace linings.

The IPPC BREF guidance note suggests that relevant companies are located in UK, Spain, France, Netherlands, Germany, Norway, Iceland, and Sweden. Some limited additional information is available in the Confidential Annex 2.

4.3.4 Future Trends

The companies consulted have explained that consumption may somewhat vary from year to year depending on customer (downstream user) demand. No specific foreseeable trend for the future could be described.

4.4 Use in Automotive Airbags

4.4.1 Description of Use

Literature: the Annex XV dossier for the substance suggests the possible use of 2,4 DNT in automotive airbags. Several other sources (typically of a US bias) mention this use. It is not entirely clear where and how 2,4 DNT may be used, although it is fair to assume that the substance could be used in pyrotechnic devices. ACEA *et al* (2009) suggests that the term "pyrotechnic device" should be taken to be any vehicle component whose function relies on the ignition of one or more pyrotechnic charges. Examples include but are not limited to the following:

- airbags;
- seat belt pre-tensioners;
- pyrotechnic actuators; or
- gas generators/inflators and pyrotechnic initiators for any of the above-mentioned products.

Consultation: we have attempted to contact the European Automobile Manufacturers' Association (ACEA), the European Association of Automotive Suppliers (CLEPA) and several individual companies, which may be involved in the manufacture of automotive airbags and similar safety systems. Information has been received from CLEPA (European Association of Automotive Suppliers, 2010) as well as from individual companies (companies **NITRO, 12**, **NITRO 13** and **NITRO 14**) that manufacture airbags. The companies have confirmed that they do not use DNT in the products they place on the European market. Some additional background information that has been made available by individual companies is provided in the Confidential Annex 2.

4.4.2 Locations and Quantities Used, Structure of Supply Chain & Future Trends

Not relevant.

4.5 Use in Dyes

4.5.1 Description of Use

Literature: the Annex XV dossier for the substance suggests that the use of DNT as an intermediate in azo dyes is a historical one. NTP (1978) also notes that 2,4 DNT has been a precursor in the synthesis of azo dyes.

Consultation: communication with the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (2010) suggests that 2,4 DNT is not used for the synthesis of azo dyes and organic pigments. The substance has not been used in the past either; only amines are being used as intermediates for the synthesis of azo dyes.

Additional information has been received by a single dye manufacturer (company **NITRO 15**). The company confirmed that the substance has not been used in the manufacture of azo dyes but rather in the manufacture of other types of dyes. On the request of the company and for reasons of confidentiality, the limited amount of information that has been provided is presented in the Confidential Annex 2.

Overall, the available information provides strong indications that DNT is not used in the manufacture of dyes in the EU; however, it is possible that such use may be undertaken by companies that did not make a contribution to this study.

4.5.2 Locations and Quantities Used, Structure of Supply Chain & Future Trends

Only some limited information on future trends is presented in the Confidential Annex 2.

4.6 Other Uses

Another use which has been mentioned by consultees but for which no substantial information has been collected include engine fuel additive when used in its DNT 95 grade.

4.7 Summary of Uses

Table 4.1 provides an overview of manufacture, uses and recycling of the substance as well as the NACE codes for the relevant activities.

Table 4.1: Overview of Manufacture / Uses of Dinitrotoluene in the EU

Use	NACE code	Transformation during use?	Form of DNT	Stage of use	Presence of DNT in final product
Manufacture of TDI	C20.5.9: Manufacture of other chemical products n.e.c.	Yes	Technical grade (DNT 80)	Formulation	Assumed to be nil
	C31.0.3: Manufacture of mattresses C31.0.9: Manufacture of other furniture C30.3.0: Manufacture of air and spacecraft and related machinery			Product use	Assumed to be nil
Manufacture of DNT 95 and DNT 65/50	C20.1.4: Manufacture of other organic basic chemicals	No (?)	Technical grade (DNT 80)	Formulation	50-95% 2,4 DNT
Manufacture of explosives (intentional)	C20.5.1: Manufacture of explosives	No	'Pure' 2,4 DNT (DNT 95+) & technical grade DNT (65/50))	Formulation	<1% as a melting/ solidification moderator; a few % in dynamite (old use); more details in the Confidential Annex 2
	B7: Mining of metal ores F43.1.1: Demolition			Product use	
Manufacture of TNT explosives (impurity)	C20.5.1: Manufacture of explosives	No	Technical grade	Formulation	<1% as impurity (some source suggest a potentially higher percentage); more details in the Confidential Annex 2
	B7: Mining of metal ores F43.1.1: Demolition			Product use	
Manufacture of propellants	C25.4.0: Manufacture of weapons and ammunition	No	DNT 95 (or higher) & technical grade (DNT 80)	Formulation	2.5-17% or coating; more details in the Confidential Annex 2
	A1.7.0: Hunting, trapping and related service activities Warfare, military training			Product use	Unknown but well below 1% (as propellant will only be a small proportion of shells)
Recycling of explosives and ammunition	C20.5.1: Manufacture of explosives	No	Technical grade	Recovery	<1% as impurity; more details in the Confidential Annex 2
	C25.4.0: Manufacture of weapons and ammunition			Recovery	
	B7: Mining of metal ores F43.1.1: Demolition			Product use	
Manufacture of refractories for the non-ferrous metal industry	C23.2.0: Manufacture of refractory products	Yes – according to consultees	Technical grade (DNT 50/55)	Formulation	Trace
	C19.1.0: Manufacture of coke oven products	Yes – according to consultees	Technical grade (DNT 50/55)	Recovery	Use of off-specification material to produce coke or as a fuel

Table 4.1: Overview of Manufacture / Uses of Dinitrotoluene in the EU					
Use	**NACE code**	**Transformation during use?**	**Form of DNT**	**Stage of use**	**Presence of DNT in final product**
Manufacture of engine fuel	C19.2.0: Manufacture of refined petroleum products	No (?)	DNT 95	Formulation	Probably yes, but unknown
Obsolete uses or uses irrelevant to the EU					
Manufacture of propellants for automotive airbags	C20.5.1: Manufacture of explosives C29.3.2: Manufacture of other parts and accessories for motor vehicles	No	Unknown	Formulations	Assumed to be 10% (as above for propellants for ammunition)
Manufacture of special dyes	C20.1.2: Manufacture of dyes and pigments	Yes	'Pure' 2,4 DNT	Formulation	Very low

4.8 Quantification of Releases from Uses of 2,4-Dinitrotoluene

4.8.1 Releases of 2,4-Dinitrotoluene to the Environment

Releases from Manufacture and Use as an Intermediate in the Manufacture of Toluene Diisocyanate

No information was collected in the course of this study. Please see emission data from the Risk Assessment Report presented in **Table 3.1**. The substance is used as an intermediate.

Releases from Manufacture of Explosives and Ammunition

Very little information is available from consultation. The Risk Assessment Report presents the releases of 2,4 DNT from one plant located in Spain, which a few years ago was using 'pure' 2,4 DNT in the manufacture of explosives. The Report suggests no releases to air and a release of 0.02 kg/day to water (ECB, 2008).

Information from one company (company **NITRO 4**) handling propellants that contain technical grade DNT suggests that emissions to air, wastewater, water bodies and soil are nil. Only a very small quantity of propellant may be lost as waste. Some additional (but limited) information is provided in the Confidential Annex 2.

Releases from Detonation of Explosives and Firing of Ammunition

Information from Literature

Explosives: thermal degradation of high explosives under normal detonation conditions when detonation goes to completion is relatively straightforward. The major compounds remaining post-detonation of explosives such as TNT, RDX (Royal Dutch Explosive, the explosive cyclotrimethylenetrinitramine), HMX (also known as octogen) are water, carbon dioxide, nitrogen gas and carbon monoxide. Results are not as straightforward for open burning due to lower temperatures, greater time periods for reactivity and greater oxygen availability. Information on releases during the thermal decomposition of TNT suggests that both 2,4 DNT and 2,6 DNT may be emitted to air and may also be detected in soil (at the ng/g level). The same applies for the thermal decomposition of RDX ((Becker, 1995).

Szostak & Cleare (2007) refer to a case study where six kilotons of energetic materials were detonated in 1996. These included nitrocellulose (55%), trinitrotoluene (30%), nitroglycerine (5%), nitroguanidine (4%), DNT (3%), and RDX (3%). Based on previously reported test data (BangBox), energetic detonation emissions of environmental concern were calculated to be less than 1%. This residue contained nitrogen oxides (88%), a mix of volatile organic compounds (11%), and possibly undetonated RDX (<1%).

Ammunition: the Defence Research and Development Canada (DRDC) Valcartier has performed environmental site assessments on the live ranges of the major Canadian Forces training bases to evaluate the contamination by explosives at target and firing points. It was found that most of the fixed firing positions are contaminated with propellant residues. In 2006, DRDC Valcartier began to assess the dispersion of residues at firing points during 105 mm howitzer live firing exercises. Residues of nitrocellulose fibres collected in front of the muzzle showed measurable amount of 2,4 DNT. After discussion with the soldiers, it was determined that the gunners may be affected by the gaseous emissions.

In the Spring of 2006, researchers from DRDC Valcartier contacted researchers from DRDC Toronto to undertake further investigations on airborne substances emitted during live gun firing. Preliminary tests were conducted in September 2006 at the muffler installation of the Munitions Experimental Testing Centre (METC) in Nicolet (Quebec) both inside the muffler and outdoors on the C3 105 mm howitzer. Samples were analysed for particulate matter, hydrogen cyanide, nitroaromatic compounds, dinitrotoluene compounds, benzene, toluene, ethylbenzene and xylene. New testing was performed in February 2007 at Canadian Forces Base (CFB) Valcartier during a live training exercise on the anti-tank Carl Gustav 84 mm weapon for the same parameters. According to the results, most of the chemicals were not detected during the trial (although for both sets of samples, particles were found at concentrations much higher than the recommended environmental standards and these findings suggested that there is a potential risk to health associated with exposure to particles for artillery soldiers) (Quémerais *et al*, 2008).

DNT has been found in the soil, surface water, and groundwater of at least 122 hazardous waste sites that contain buried ammunition wastes and wastes from manufacturing facilities that release DNT (Global Security, 2006). FRTR (undated) indicates that the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and the Missouri River Division (MRD) have been involved with numerous explosives-contaminated sites and have compiled data on the frequency of nitroaromatics and nitramines detected in explosives-contaminated soils from Army sites. TNT is the most common contaminant, occurring in approximately 80% of the soil samples found to be contaminated with explosives. 2,4 DNT and 2,6 DNT, which are impurities in production-grade TNT, were found in less than 40% of the soils.

According to Walsh *et al* (2010), military training with howitzers and mortars produces excess propellant that is burned on the training range and can result in point sources containing high concentrations of unreacted propellant constituents. Propellants contain energetic compounds such as nitroglycerine and 2,4 DNT, both of which are found at firing positions and propellant disposal areas.

<u>Information from Consultation</u>

Mixed views have been received from consultees in relation to the releases of DNT during the detonation of explosives and firing of ammunition. For instance, according to the German Federal Institute for Materials Research and Testing (2010), if DNT is an ingredient of an explosive it will be nearly completely destroyed during detonation. Only a very small part of it would be detectable after the blast (fractions of ppm to ppb). On the other hand, some estimates of potential releases of DNT during detonation have been given and these are provided in the Confidential Annex 2.

Releases from Demilitarisation of Explosives/Ammunition

Information has become available by company **NITRO 8**; this suggests that rather small amounts can be released to the environment via wastewater in TNT-recovery operations. Some additional detail is presented in the Confidential Annex 2.

Releases from Use in the Non-ferrous Metals Industry

Information has become available by one company; this is presented in the Confidential Annex 2. This information suggests that some environmental releases of DNT to air during the relevant applications may occur.

4.8.2 Releases of and Exposure to 2,4-Dinitrotoluene in the Working Environment

Introduction

In this sub-section, we present the available information on occupational exposure to DNT. This includes information from the Risk Assessment Report, estimates based on modelling software (using information in the report and expert judgement) which have been undertaken by the study team, and information from consultation.

No estimates have been made for situations for which too limited information was available and expert knowledge could not compensate the lack of information. In addition, no estimates have been made for situations with relatively well-described estimates from literature or confidential information.

Releases and Exposure from Manufacture and Use as an Intermediate in the Manufacture of Toluene Diisocyanate

The reader is referred to the analysis presented in the Risk Assessment Report for the substance. The Annex XV dossier summarises the relevant information. The relevant scenario is Scenario 1: Production and further processing of 2,4 DNT. Exposure is expected in those activities where the system is breached such as collection of samples for quality control and maintenance.

The exposure assessment was based on measured data obtained from industry or from the literature and modelled data derived from EASE model (EASE for Windows Version 2.0) and RISKOFDERM potential dermal exposure model (EXCEL version 2.0, October 2005). The results are shown in **Table 4.2**.

Table 4.2: Summary of Occupational Exposure Levels During Manufacture of TDI								
Scenario	**Inhalation exposure**						**Dermal exposure**	
	RWC		**Typical**		**Short- term**		**RWC (mg/day)**	**Method**
	mg/m^3	**Method**	**mg/m^3**	**Method**	**mg/m^3**	**Method**		
Manufacture of TDI (sampling and maintenance)	0.009	Measured	0.0007	Measured	0.018	Calculated	0-2.1	EASE (90% protection by suitable gloves)
Source: Annex XV dossier for 2,4-dinitrotoluene (July 2009)								

In addition to this information, we have also developed exposure estimates based on available information and expert judgement. **Inhalation exposure** was estimated using the Advanced REACH Tool (ART)[9]; the parameters used in the model are presented in Annex 1 to this report. The 75th percentile of the exposure distribution with the interquartile confidence range is calculated with ART:

- for **dumping**:
  - 75th percentile = 0.061 mg/m^3;
  - interquartile range = 0.032 mg/m^3 to 0.12 mg/m^3; and
  - reasonable worst-case estimate of inhalation exposure by ART is 0.12 mg/m^3 (120 $\mu g/m^3$);

- for **vacuum transfer**:
  - 75th percentile = 0.0019 mg/m^3;
  - interquartile range = 0.00098 mg/m^3 to 0.0036 mg/m^3; and
  - reasonable worst-case estimate of inhalation exposure by ART is 0.0036 mg/m^3 (3.6 $\mu g/m^3$).

Dermal exposure has been estimated with ECETOC TRA v2[10]; the parameters used in the model are presented in Annex 1 to this report. The ECETOC TRA estimates can be summarised as following:

- for **dumping**:
  - dermal exposure full product with LEV: 10 $\mu g/cm^2$ on 960 cm^2 à 9.6 mg product = 7.7 mg DNT;
  - dermal exposure full product without LEV: 1000 $\mu g/cm^2$ on 960 cm^2 à 960 mg product = 770 mg DNT;
  - assuming 90% reduction by protective gloves leads to 0.77 mg (with LEV) and 77 mg (without LEV);

9 Available at http://www.advancedreachtool.com/.

10 Available at http://www.ecetoc.org/tra.

- for **vacuum transfer**:
  - dermal exposure full product with LEV: 100 µg/cm^2 on 480 cm^2 à 48 mg product = 38 mg DNT;
  - dermal exposure full product without LEV: 1000 µg/cm^2 on 480 cm^2 à 480 mg product = 380 mg DNT; and
  - assuming 90% reduction by protective gloves leads to 3.8 mg (with LEV) and 38 mg (without LEV)

Releases and Exposure from Use in Explosives

Exposure from Manufacture of Explosives (e.g. TNT and others)

Literature: Sabbioni *et al* (2006) looked into the exposure of workers to DNT. The population group chosen were exposed (n = 104) and control (n = 72) workers in a factory manufacturing DNT and TNT, situated in Liaoning (Liaoning Province, China). The industrial synthesis of DNT and TNT was done by continuous batch nitration of nitrotoluene (NT) and subsequently DNT with sulphuric acid and nitric acid. The air concentration of 2,4 DNT was 43.1 ± 98.0 µg/m^3 and the concentration of 2,6 DNT was 13.9 ± 27.6 µg/m^3 (both expressed as 8h-Time-Weighted Averages). We do not have information that would allow us to conclude whether the working conditions in this plant are comparable to conditions in plants in the EU.

Bodeau (undated) indicates that significant occupational exposure is possible during the mixing and shell-loading operations at plants manufacturing explosives (this source does not provide specific quantified information).

Exposure from Handling Pre-prepared Explosive Mixtures

The exposure patterns during the handling of DNT-containing propellants in the manufacture of propellant charges for military ammunition are described in **Table 4.3**.

Table 4.3: Exposure Patterns for Technical Grade DNT Released during handling of Propellant Material

Activity	Relevant process step where exposure occurs	Route of occupational exposure	Occupational exposure level	Exposure control measures taken	Number of employees exposed
Manufacture of propelling charges	Handling of propellant materials	Skin	Not known; estimated to be very low	PPE; local extraction; automated filling plant	8 - 10

Source: Consultation with company ***NITRO 4***

It is suggested that the propellant is loaded by scoop transfer from the drum in which it is delivered to a hopper for auto weighing and dispensing into containers. The opening in the container is closed after loading. Any propellant granules spilt to the floor at any stage of the process are treated as waste and placed in a waste bin for disposal.

Eye protection and leather gloves for transfer to hopper are used and extraction ventilation is used in transfer area, which is separate from other operations. Weighed increments of propellant are loaded directly into containers and extraction ventilation is used at the loading position. Finally, extraction ventilation is used at container closing stage.

Latex disposable gloves are used for direct handling propellant at any stage of the process. Workers wear overalls during all operations and personal clothing is minimised to underwear.

The company estimates that workers may potentially be exposed to DNT during these operations for well below one hour every day. Some additional information on the duration of this process is provided in the Confidential Annex 2.

In addition to this information, we have also developed exposure estimates based on available information and expert judgement. Inhalation exposure was estimated using the Advanced REACH Tool (ART); the parameters used in the model are presented in Annex 1 to this report. The 75^{th} percentile of the exposure distribution with the interquartile confidence range is calculated with ART:

- 75^{th} percentile = 0.0014 mg/m³;
- interquartile range = 0.00071 mg/m³ to 0.0026 mg/m³; and
- reasonable worst-case estimate of inhalation exposure by ART is 0.0026 mg/m^3 (2.6 $\mu g/m^3$).

Dermal exposure has been estimated with ECETOC TRA v2; the parameters used in the model are presented in Annex 1 to this report. ECETOC TRA estimates the dermal exposure to the full product as 10 $\mu g/cm^2$ on 960 cm^2 à 9.6 mg product. This would mean 0.96 mg DNT. However, the effect of LEV in ECETOC TRA is not well founded. Without LEV the model estimates 1000 $\mu g/cm^2$ on 960 cm^2 à 960 mg product à 96 mg DNT. The use of proper protective gloves can reduce the dermal exposure by a factor of 10 to 0.096 mg or 9.6 mg (depending on whether the use of LEV is considered to have substantial effect).

<u>Exposure from Detonation of Explosives and Firing of Ammunition</u>

Literature: dated information that has been presented in the Risk Assessment Report for the substance (e.g. Brüning *et al* (1999), Stayner *et al* (1993), Woollen *et al* (1985)) is not reproduced here.

Some additional information has been retrieved in relation to a 72-year-old man who was diagnosed with a highly malignant non-Hodgkin's B-cell lymphoma. The man had worked from 1948 to 1952 in the former Wismut uranium mining company in Saxony, Germany, as a hewer. Working conditions were notoriously poor at the time. The miner handled the explosive Donarit (contains dinitrotoluene, DNT), which for technical and economic reasons was used in the former German Democratic Republic instead of trinitrotoluene (TNT). As a miner, he had had to break the Donarit bars with his bare hands to obtain the required amount of explosive. He was therefore intensively exposed to the highly skin-penetrating DNT. 'Dynamite headache' is a commonly reported adverse effect of high occupational exposure to DNT (Roemer *et al*, 2002). However, as discussed earlier, use of DNT in dynamites appears to no longer occur in the EU.

Consultation: companies **NITRO 6** and **NITRO 8** initially argued that under typical conditions of detonation of explosive materials, DNT, which is a very energetic material, should not remain but rather be fully consumed in the explosion (assuming that the detonation is organised and executed appropriately). The German Federal Institute for Materials Research and Testing (2010) has also argued that DNT is no longer used in Germany, so there should be no exposure at all of workers in the factory or users of explosives, respectively. If DNT is an ingredient of an explosive it will be nearly completely destroyed during detonation. Only a very small part of it would be detectable after the blast (fractions of ppm to ppb).

However, upon closer inspection, company **NITRO 8** suggested that exposure may indeed be possible during the detonation of explosives (apart from skin exposure during handling of explosive materials). The Confidential Annex 2 presents these estimates in more detail. The estimated exposure levels are expected to be considerably low as the estimated percentage of DNT released during detonation is low.

<u>Exposure from Demilitarisation of Explosives/Ammunition</u>

Literature: a study by Letzel *et al* (2003) has been identified. The researchers investigated the exposure to DNT and TNT and the resulting effects in workers which occur during the disposal of military waste. Eighty-two employees from a mechanical plant in Germany were studied, of whom 51 were regularly exposed to ammunition containing TNT and DNT, 19 occasionally, and 12 not at all. Air analyses yielded maximum concentrations of 20 $\mu g/m^3$ for 2,4 DNT (see **Table 4.4**) and 3,250 $\mu g/m^3$ for 2,4,6-TNT, respectively. The maximum concentrations in the urine of workers regularly exposed amounted to 5.0 µg/l of 2,4,6-TNT, 1,464.0 µg/l of 2-amino-4,6-dinitrotoluene, 6693.0 of µg/l 4-amino-2,6-dinitrotoluene, 2.1 µg/l of 2,4-DNT, 95.0 µg/l of 2,4-dinitrobenzoic acid, and 3.6 µg/l of 2,6-DNT. There was a highly significant linear correlation between the urinary concentrations of the two main metabolites of TNT, 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene. In 63 persons, TNT or DNT or metabolite concentrations above the analytical detection limit were found in urine. These persons reported more frequently symptoms like bitter taste, burning eyes, and discoloration of the skin and hair than persons (n = 19) without detectable TNT and/or DNT exposure. The air concentration of levels of 2,4 DNT that were documented in this research are reproduced in **Table 4.4**.

Table 4.4: Air Concentration Levels for 2,4 DNT During Disposal of Military Waste			
Work area	**Stationary air sample**	**Personal air sampling**	**2,4 DNT value or range (µg/m^3)**
Bending hand grenades (work rate approx.160/h)		ü	<0.1-10
Pressing bomblets (work rate: approx.110/h)		ü	0.4-2.5
Pressing bomblets (work rate: approx.110/h) (sampling: 2 hours; sample volume: 60 l)	ü		<0.5-3.2
Separating tablets		ü	0.2-2.3
Separating tablets (sampling: 2 hours; sample volume: 60 l)	ü		3.7
Opening bomblets		ü	<0.1-1.3
Opening bomblets (sampling: 2 hours; sample volume: 60 l)	ü		11
Water treatment, removing agglomerate	ü		<0.1-4.2
Water treatment, removing agglomerate		ü	<0.1-20
Sucking out		ü	4.4
Sucking out (sampling: 2 hours; sample volume: 60 l)	ü		4.4
Selection		ü	<0.1
Selection (sampling: 2 hours; sample volume: 60 l)	ü		<0.5
Emptying and piercing		ü	<0.1
Emptying and piercing (sampling: 2 hours; sample volume: 60 l)	ü		<0.5
Hand grenades (intermediate storage) (sampling: 2 hours; sample volume: 60 l)		ü	1.0
Rest room	ü		<0.5
Offices (sampling: 2 hours; sample volume: 60 l)	ü		<0.5
Source: Letzel et al (2003)			

5. REFERENCES

ACEA *et al* (2009): **Position of the Automotive Industry in regard to Imported Pyrotechnic Devices and Vehicles Containing said Devices and of Registration of Substances/preparations under Article 7.1 of REACH and "Guidance on Requirements for Substances in Articles"**, 6 November 2009, available online at http://www.acea.be/images/uploads/files/20091127_Automotive_industry_position_on_pyrotechnic_devices.pdf (accessed on 1 June 2010).

Ammunition Pages (undated): **Propellants**, available online at http://www.ammunitionpages.com/download/167/PROPELLANTS%20COMPOSITIONS.pdf (accessed on 1 June 2010).

Becker N (1995): **Fate of Selected High Explosives in the Environment: A Literature Review**, available online at http://www.fas.org/sgp/othergov/doe/lanl/lib-www/la-pubs/00276619.pdf (accessed on 15 June 2010).

Bodeau D (undated): **Military Energetic Materials: Explosives and Propellants**, available online at http://www.bordeninstitute.army.mil/published_volumes/occ_health/OHch9.pdf (accessed on 15 June 2010).

ECB (2008): **2,4-Dinitrotoluene, CAS No: 121-14-2, EINECS No: 204-450-0**, Risk Assessment, Final report (Final Approved Version), February 2008, European Chemicals Bureau.

Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (2010): Personal communication.

European Association of Automotive Suppliers (2010): Personal communication.

European Association for Study of Safety Problems in Production and Use of Propellants (2010): Personal communication.

Evans N (2010): **British Artillery in World War 2**, available online at http://nigelef.tripod.com/ammo.htm#PROPELLANT (accessed on 1 June 2010).

Federation of European Explosives Manufacturers (2010): Personal communication.

Fordham S (1980): **High Explosives and Propellants**, Pergamon Press.

FRTR (undated): **Common Treatment Technologies for Explosives in Soil, Sediment, Bedrock and Sludge**, available online at http://www.frtr.gov/matrix2/section2/2_10_2.html (accessed on 15 June 2010).

German Federal Institute for Materials Research and Testing (2010): Personal communication.

Global Security (2006): **Explosives – Nitroaromatics**, available online at http://www.globalsecurity.org/military/systems/munitions/explosives-nitroaromatics.htm (accessed on 9 June 2010).

Gunczar (undated): **Smokeless Powder**, available online at http://gunczar.com/smokeless.html (accessed on 3 June 2010).

Heramb RM & McCord BR (2007): **The Manufacture of Smokeless Powders and their Forensic Analysis: A Brief Review**, available online at http://firearmsid.com/Feature%20Articles/McCord_gunpowder/index.htm (accessed on 1 June 2010).

ICB (2009): **Toluene Di-isocyanate (TDI) Uses and Outlook**, available online at http://www.icis.com/V2/chemicals/9076541/toluene-diisocyanate/uses.html (accessed on 1 July 2010).

ICB (2008): **Chemical Profile: TDI**, available online at http://www.icis.com/Articles/2008/01/21/9093901/chemical-profile-tdi.html (accessed on 1 June 2010).

Irish Health and Safety Authority (2010): Personal communication.

ISOPA (2010): Personal communication.

Kosanke BJ *et al* (2004): **Pyrotechnic Chemistry**, Journal of Pyrotechnics, Whitewater, USA.

Letzel S *et al* (2003): *Exposure to Nitroaromatic Explosives and Health Effects during Disposal of Military Waste*, Occup Environ Med, Vol 60, pp483-488 (only abstract available).

Mines Service of Cyprus (2010): Personal communication.

Norwegian Climate and Pollution Agency (2010): Personal communication.

NTP (1978): **Abstract for TR-54 - 2,4-Dinitrotoluene (CASRN 121-14-2)**, available online at http://ntp.niehs.nih.gov/go/7187 (accessed on 1 June 2010).

OECD (2004): **Dinitrotoluene (isomers mixture) CAS N°: 25321-14-6, SIDS Initial Assessment Report for SIAM 18, Paris, France, April 20 – 23, 2004**, available online at http://www.inchem.org/documents/sids/sids/25321146.pdf (accessed on 1 June 2010).

PU Magazine (2010): **BMS Planning New World-scale TDI Plant in Germany**, 2 March 2010, available online at http://www.pu-magazine.com/nc/news/industry/newsdetails/article/bms-planning-new-world-scale-tdi-plant-in-germany7454.html (accessed on 1 June 2010).

Quémerais B *et al* (2008): **Characterization of Atmospheric Emissions Produced by Live Gun Firing: Test on the Carl Gustav Anti-tank, 84 mm Weapon**, available online at http://pubs.drdc.gc.ca/PDFS/unc72/p529452.pdf (accessed on 15 June 2010).

Roemer HC *et al* (2002): *Two Extrapulmonary Neoplasms in a Uranium Miner*, J R Soc Med, June 2002, Vol 95(6), p 302.

Sabbioni G *et al* (2006): *Biomarkers of Exposure, Effect, and Susceptibility in Workers Exposed to Nitrotoluenes*, Cancer Epidemiol Biomarkers Prev, March 2006, Vol 15(3), pp560-566.

Singh KA (2009): **Technology Sector – Security, Sub Sector – Detection, Segment – Explosives**, Institute of Nanotechnology, UK, May 2009, available online at http://www.observatorynano.eu/project/filesystem/files/TS%20Security%20Sub-Sector%20-%20Explosive%20Detection%20May%2009.pdf (accessed on 1 June 2010).

Spanish Ministry of Health and Social Policy (2010): Personal communication.

Spiritus-Temporis (2005): **Nitroglycerin**, available online at http://www.spiritus-temporis.com/nitroglycerin/instability-and-desensitization.html (accessed on 1 June 2010).

Szostak R & Cleare K (2007): *Emissions Related to Munitions Firing: A Case Study of Nitrogen Oxides, Volatile Organic Compounds, and Energetic Residue from Detonable Munitions*, Federal Facilities Environmental Journal, Vol 11(3), pp87-104 (only abstract available)

UK Department for Environment (1995): **Chemical Works - Explosives, Propellants and Pyrotechnics Manufacturing Works**, available online at http://publications.environment-agency.gov.uk/pdf/SCHO0195BJKB-e-e.pdf?lang=_e (accessed on 1 June 2010).

Wallace JS (2008): **Chemical Analysis of Firearms, Ammunition, and Gunshot Residue**, CRC Press, Boca Raton, USA.

Walsh MR *et al* (2010): *Energetic Residues from Field Disposal of Gun Propellants*, J Hazard Mater, January 2010, Vol 15, pp115-122.

Weaponry Fund of the Republic of Lithuania (2010): Personal communication.

Wilcox JL *et al* (1996): **Characterization of Emissions Produced by the Open Burning/Open Detonation of Complex Munitions**, September 1996.

ANNEX 1. EXPOSURE MODEL CALCULATION ASSUMPTIONS

A1.1 Releases and Exposure from Manufacture and Use as an Intermediate in the Manufacture of Toluene Diisocyanate

Table A1.1 summarises the parameters used in the Advanced REACH Tool (ART) model for estimating inhalation exposure from the manufacture and use of 2,4 DNT as an intermediate in the manufacture of toluene diisocyanate.

Table A1.1: Estimated Occupational Inhalation Exposure to 2,4 DNT during Use as an Intermediate

Input parameter	Value	Remark
Substance/product type	Powders, granules or pelletised material	
Dustiness	Granules, flakes or pellets	A slightly more conservative option than the least dusty product type in ART: "firm granules, flakes or pellets"
Moisture content	Dry product (< 5 % moisture content)	
Powder weight fraction	0.8	Technical DNT containing 80% of 2,4 DNT
Activity class (1)	Falling powders	
Activity class (2, alternative)	Vacuum transfer	More careful handling
Situation	Transferring 10-100 kg/minute	Value indicated for dumping of powders in ART
Handling type	Careful transfer involves workers showing attention to potential danger, error or harm and carrying out the activity in a very exact and thorough (or cautious) manner.	Careful handling due to the types of product handled
Drop height	< 0.5 m	Only for falling powders
Containment level (1)	Open process	Manual scooping
Containment level (2, alternative)	Handling that reduces contact between product and adjacent air.	Vacuum transfer
Process fully enclosed?	No	
Effective housekeeping practices in place?	Yes	Expected due to the type of substances handled
Work area	Indoors	
Room size	Any size workroom	
Primary localised control	LEV: fixed capturing hoot	
Ventilation rate	Mechanical ventilation giving at least 3 ACH	
Duration activity	120 min	
No exposure period	360 min	
Source: TNO calculations		

Table A1.2 summarises the parameters used in the ECETOC TRA v2 model for estimating dermal exposure from the manufacture and use of 2,4 DNT as an intermediate in the manufacture of toluene diisocyanate.

Table A1.2: Estimated Occupational Inhalation Exposure to 2,4 DNT during Use as an Intermediate		
Input parameter	**Value**	**Remark**
Substance/product type	Solid	
Activity (PROC) (1)	PROC 8a: Transfer of chemicals from/to vessels/large containers at non-dedicated facilities	Most relevant option for open dumping
Activity (PROC) (2, alternative)	PROC 8b: Transfer of chemicals from/to vessels/large containers at dedicated facilities	Most relevant option for vacuum transfer
Local Exhaust Ventilation (LEV)	Yes	
Powder weight fraction	0.8	Technical DNT
Source: TNO calculations		

A1.2 Exposure from Handling Pre-prepared Explosive Mixtures

Table A1.3 summarises the parameters used in the Advanced REACH Tool (ART) model for estimating inhalation exposure from the handling of pre-prepared propellant mixtures that contain DNT.

Table A1.3: Estimated Occupational Inhalation Exposure to 2,4 DNT during Explosive Mixtures Handling		
Input parameter	**Value**	**Remark**
Substance/product type	Powders, granules or pelletised material	
Dustiness	Granules, flakes or pellets	A slightly more conservative option than the least dusty product type in ART: "firm granules, flakes or pellets"
Moisture content	Dry product (< 5 % moisture content)	
Powder weight fraction	0.1	10% DNT in the imported propellant
Activity class	Falling powders	
Situation	Transferring 1 – 10 kg/minute	Value indicated for scooping of powders in ART
Handling type	Careful transfer involves workers showing attention to potential danger, error or harm and carrying out the activity in a very exact and thorough (or cautious) manner.	Careful handling due to the types of product handled
Drop height	< 0.5 m	
Containment level	Open process	Manual scooping

Table A1.3: Estimated Occupational Inhalation Exposure to 2,4 DNT during Explosive Mixtures Handling		
Input parameter	**Value**	**Remark**
Process fully enclosed?	No	
Effective housekeeping practices in place?	Yes	Expected due to the type of substances handled
Work area	Indoors	
Room size	Any size workroom	
Primary localised control	LEV: fixed capturing hoot	
Ventilation rate	Mechanical ventilation giving at least 1 ACH	
Duration activity	120 min	
No exposure period	360 min	
Source: TNO calculations		

Table A1.4 summarises the parameters used in the ECETOC TRA v2 model for estimating dermal exposure from the handling of pre-prepared propellant mixtures that contain DNT.

Table A1.4: Estimated Occupational Dermal Exposure to 2,4 DNT during Explosive Mixtures Handling		
Input parameter	**Value**	**Remark**
Substance/product type	Solid	
Activity (PROC)	PROC 8a: Transfer of chemicals from/to vessels/large containers at non-dedicated facilities	Most relevant option for open scooping
Local Exhaust Ventilation (LEV)	Yes	
Powder weight fraction	0.1	10% DNT in the imported propellant
Source: TNO calculations		