1 July 2010

Background document for 2,4-Dinitrotoluene

Document developed in the context of ECHA's second Recommendation for the inclusion of substances in Annex XIV

1. Identity of the substance

Chemical name:	2,4 - Dinitrotoluene
EC Numbers:	204-450-0
CAS Number:	121-14-2
IUPAC Name:	1-methyl-2,4-dinitrobenzene

2. Background information

2.1. Intrinsic properties

2,4 - Dinitrotoluene was identified as a Substance of Very High Concern (SVHC) according to Article 57(a) as it is classified according to Annex VI, part 3, Table 3.2 of Regulation (EC) No 1272/2008 as a carcinogen category 2[1], 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.

2.2. Imports, exports, manufacture and uses

2.2.1. Volume(s), imports/exports

2,4-Dinitrotoluene (DNT) is commercially available as a purified isomer or as a component of dinitrotoluene mixtures. According to information collected during the consultation that was performed after the identification of DNT as SVHC (Technical report, 2010), the total tonnage of dinitrotoluene (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 540000 and 810000 tonnes per year. Assuming a concentration of 2,4 - DNT of 75-80%, the tonnage of 2,4-DNT contained in the manufactured dinitrotoluene could range between 405000 and 648000 tonnes per year. This volume is exclusively used as a non isolated intermediate for synthesis of toluene diisocyanate (TDI). In addition, at one manufacturing site 'pure' 2,4

[1] This corresponds to a classification as carcinogen 1B, H350 (may cause cancer) in Annex VI, part 3, Table 3.1 of Regulation (EC) No 1272/2008 (List of harmonised classification and labelling of hazardous substances)

dinitrotoluene (95% 2,4-DNT content) as well as dinitrotoluene mixtures (containing 65 or 50% of 2,4-DNT) are manufactured in the range 100 – 1000 t/y each.

Furthermore an EU company imports a dinitrotoluene mixture (50-55% of 2,4-DNT) in the range 100 – 1000 t/year for use as a binding agent (Technical report, 2010) for use in the non ferrous metal industry. Import of propellants that contain technical grade dinitrotoluene of an unknown 2,4–DNT content has also been reported in the range 1 – 10 t/year.

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

Dinitrotoluene can be produced by a two-step nitration of toluene in a closed system process producing a mixture, the commercial or technical grade, of an approximate ratio of around 80% of 2,4-dinitrotoluene and 20% of 2,6-dinitrotoluene. 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-dinitrotoluene (Annex XV report, 2009).

According to the Technical report (2010) dinitrotoluene (80:20) is manufactured at 5 or 6 sites in the EU (located in France, Germany, Hungary and Poland) where the substance is exclusively used in the manufacture of toluene diisocyanate (TDI). Those sites do not manufacture 'pure' 2,4-DNT. 'Pure' 2,4-DNT and dinitrotoluene containing 65 to 50% of 2,4-DNT are manufactured by a single plant using technical grade dinitrotoluene (80% 2,4-DNT : 20% 2,6-DNT) as starting material (Technical report, 2010).

Releases to the working place and subsequent occupational exposure during the manufacture of dinitrotoluene (as a non-isolated intermediate and its further use in the synthesis of TDA/TDI in closed installations) can occur. Exposure (dermal and inhalation) can be expected mainly during those activities where the system is breached, such as collection of samples for quality control and maintenance. Inhalation and dermal exposure values are reported in the Risk Assessment Report (EU-RAR, 2008) based on measured data obtained from industry as well as on modelled data.

Releases to the environment can potentially occur to air as well as to waste water. According to the on site data available in the RAR there seems to be no release to air and release to water is in the range of 0.22 – 16 kg/day (EU- RAR, 2008).

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 waste water in small amounts. In addition releases to the working place 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 (Technical report, 2010).

2.2.2.2. Uses and releases from uses

Description of uses

Use in the manufacture of toluene diisocyanate (TDI)

According to information available in the EU Risk Assessment Report, 2,4-dinitrotoluene is primarily used as a chemical intermediate in the synthesis of toluene diisocyanate (4-methyl-m-phenylenediisocyanate). 2,4-Dinitrotoluene is hydrogenated to yield TDA and this diamine is reacted with phosgene to yield TDI, which is used to make flexible polyurethane foams.

Use of technical grade dinitrotoluene (80:20) in the manufacture of DNT 95 and DNT 65/60

See above in section 2.2.2.1.

Use in explosives and ammunitions

The volume of 'pure' 2,4-DNT and dinitrotoluene mixtures manufactured by the company mentioned in section 2.2.2.1 and consumed in the EU in explosives and ammunition is in the range of 100 – 1000 t/y (Technical report, 2010). No specific information is available on the amounts of substance going specifically to each of the two sectors.

Use in explosives

The information available suggests that DNT is since many years not used anymore as an additive in the manufacture of explosives (dynamite). However, there is one EU based company which still supplies 2,4-DNT ('pure' DNT) and DNT 65/50 to EU and non EU customers for the manufacture of explosives (Technical report, 2010). There is however no clear indication of the amount of DNT used in or supplied to the explosives sector.
Some information on unintentional use of DNT in explosives is available (Technical report, 2010). It is reported that DNT isomers may be present as an impurity in TNT explosives. The use of TNT is apparently becoming less popular in Europe and therefore it is likely that only a small number of companies may still produce TNT. DNT is a by-product of TNT synthesis (Technical report, 2010).

Recycling of TNT ammunition

The information available from two companies recycling old ammunition (one of them specifically recycles TNT and the other one recycles all components of ammunition and therefore occasionally TNT which contains DNT as an impurity).
This TNT is sold to civilian companies within and outside EU for re-use in booster charges, etc. for the mining industry. The DNT content is a mixture of different isomers and not the 'pure' 2,4 DNT only (Technical report, 2010).

Use in propellants for gun powders

DNT acts as a stabiliser, flash and temperature suppressor in smokeless propellants for ammunition. The role of DNT has also been described as (a) a plasticiser and (b) as a waterproofing agent (Technical report, 2010).
According to the available information some propellants may contain 2.5 – 17% DNT whereas others have a DNT coating (Technical report, 2010).

The ‘pure DNT’ (95% 2,4-dinitrotoluene) is used as an additive in explosives, in propellants for ammunition (military and hunting ammunition) as well as in applications for which limited information is available, such as a fuel additive. DNT 65/50 may also be used as a component of explosive materials (Technical report, 2010).

From the information available it is most likely that dinitrotoluene is not transformed during use in the manufacture of explosives and ammunition.

There is no clear explanation why one grade of dinitrotoluene may be preferred over another one. A suggestion is that the different grades have different freezing points which might lead to the use of different technologies and applications (Technical report, 2010).

Use in the Non-ferrous metals industry

The technical grade DNT (50/55) is used as a temperature-specific cross-linking agent for refractories. Information from one company indicates that the amount of DNT (50/55) used is less than 1000 t/year (Technical report, 2010).

Use in automotive airbags

Information collected from automotive manufacturers and suppliers as well as from individual companies indicates that dinitrotoluene compounds are not used in the products they place on the EU market (Technical report, 2010).

Use in dyes

The Technical report (2010) reports that 2,4-DNT (‘pure’) is not used for the synthesis of azo dyes and organic pigments nowadays but also that it has never been used for this application. However, the substance has been used in the past in the manufacture of other dyes. The available information suggest that there is no use at present of 2,4-DNT in dye manufacture.

Releases from uses

2,4-dinitrotooluene has not been identified in consumer products. Human exposure to 2,4-dinitrotoluene occurs primarily through occupational sources.

Use in the manufacture of toluene diisocyanate (TDI)

As mentioned and described above (section 2.2.2.1), according to the EU RAR (2008), occupational exposure to 2,4-dinitrotoluene is possible during its use as a chemical intermediate essentially for TDI production (Annex XV report, 2009).

Use in explosives and ammunitions

Releases from manufacture of explosive mixtures

According to data in the Annex XV report (2009), exposure does mainly occur during tasks such as weighing and charging. The respective inhalation exposure values provided are: 0.15 mg/m^3 (RWC), 0.075 mg/m^3 (typical), and 0.3 mg/m^3 (short-term), with a modelled dermal exposure for unprotected workers of 3 mg/day.

Releases from Handling Explosive Mixtures

Information from one company, which handles 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 wastes (Technical report, 2010).

However, occupational exposure via the dermal route of 8 to 10 workers to technical grade DNT may occur due to handling of propellant materials for the production of propelling charges. Exposure levels are not known but assumed to be very low. Reported risk reduction measures comprise overalls, eye protection, gloves and exhaust ventilation (Technical report, 2010).

According to information provided in the Annex XV report (2009), during the manufacture of cartridges and munitions, exposure could be possible during charging of the system. Available inhalation exposure values regarding this application are as follows: 0.006 mg/m^3 (RWC), 0.003 mg/m^3 (typical), and 0.012 mg/m^3 (short-term), with a modelled dermal exposure for unprotected workers of 0.42 – 4.2 mg/day.

Dinitrotoluene, present either as additive or impurity, may also be released to some extent during the storage of explosive mixtures, for example as vapour or dust particles from the explosive material (DNT is often detected at small concentrations in the air nearby explosives, e.g. Harper et al., 2005).

Releases from activities associated to end-uses of explosives (handling and detonation) and ammunition (firing)

According to the Technical report (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.

Regarding human exposure, one old study reports health effects due to the use of explosives in the copper mining industry (Brüning *et al.*, 1999). The explosive rods used contained approximately 30% technical dinitrotoluene. 20 cases of cancer in a group of 500 miners may correlate with DNT-exposure as the type of tumours observed was similar to those found in 2,4- dinitrotoluene exposed mice. Professional contact with dinitrotoluene in mines is envisaged via two routes: inhalation of fumes after explosion and direct skin contact during handling of dinitrotoluene containing explosive sticks (EU RAR, 2008).

Regarding the residues of DNT after detonation, it can be noted that existing literature refers to DNT in gunshot / post-blast residues (studies cited in Joshi et al., 2009). As concerns the presence / concentration of DNT in fumes after explosion or the exposure via this route, no specific data were identified in the literature / provided during the consultation study. It can though be envisaged that the amount of releases may depend on the explosion / firing set-up, while occupational exposure will depend on factors such as the environment of detonation (e.g. underground or open pit mines) and risk management measures applied during / after the end uses of explosion and ammunition.

Releases from the Waste stage and from Demilitarisation of Explosives/Ammunition

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 (Technical report, 2010).

Information from one company suggests that rather small amounts can be released to the environment via wastewater in TNT-recovery operations (Technical report, 2010).

Regarding exposure to humans, 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. Air analyses yielded maximum concentrations of 20 $\mu g/m^3$ for 2,4-DNT 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. (Technical report, 2010).

Use in the Non-ferrous metals industry

One company indicates releases to air in an amount of <0.1% of its annual consumption from different activities (RPA, 2010). In addition, the same company indicated occupational exposure levels in the range of 0 to 0.2 mg/m^3 (RPA, 2010). (Technical report, 2010).

2.2.2.3. Geographical distribution and conclusions in terms of (organisation and communication in) supply chain

According to the data available, the manufacture of 2,4-dinitrotoluene in Europe as intermediate in the production of TDI is located in France, Germany, Hungary and Poland (Technical report, 2010). The number of individual sites is uncertain. Overall it is believed that the production sites for the technical grade DNT (80:20) are 5 or 6. In addition there seems to be one plant manufacturing the pure 2,4 DNT as well as DNT 50/65 (Technical report, 2010).

Regarding the recycling of TNT, at least two companies located in two different EU Member States exist. The total number is likely to be fewer than ten.

Information on manufacture of military and recreational ammunition has been gathered from some companies. From the information collected it can be assumed that the number of companies in the EU might not be very large but the exact number is unknown. However the end use of explosives in mines, quarries and construction sites is expected to occur at a high number of sites.

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

2.3. Availability of information on alternatives

There is no information available on alternatives.

2.4. Existing specific Community legislation relevant for possible exemption

None

2.5. Any other relevant information (e.g. for priority setting)

No data available

3. Conclusions and justification

3.1. Prioritisation

The volume used for applications in the scope of authorisation appears to be in the range of 100 - 1,000 t/yr. This relatively high amount, mainly used in explosives and ammunitions, is already of concern, as it appears to fulfil the criteria of wide dispersive use. The end-use of explosives in mines, quarries and construction sites is expected to happen at a high number of sites with possibly uncontrolled exposure of workers when handling the explosives and (after detonation, particularly in mines and subterranean construction sites) to fumes containing residues of the substance.

There are further uses with potential for worker exposure (e.g. use in the non-ferrous metal industry or manufacture of explosive mixtures and articles).

Verbal-argumentative approach

On the basis of the prioritisation criteria, the substance qualifies for prioritisation.

Scoring approach

Score			Total Score (= IP + V + WDU)
Inherent properties (IP)	Volume (V)	Uses - wide dispersiveness (WDU)	
1 Carcinogen, cat. 2	5 (Relatively high volume confirmed to be used for explosives and ammunition)	Overall score: 3 * 3 = 9 At least some uses wide dispersive Site-#: 3 (Use at a high # of sites) Release: 3 (Uncontrolled releases, (e.g. use in explosives and information on workplace exposure from other uses where it is not clear whether the risk management measures in place are sufficient to control the risk for workers)	15

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, the substance qualifies for prioritisation. No regulatory effectiveness considerations have been identified that would suggest to refrain from prioritisation.

Therefore, it is suggested to prioritise 2,4-DNT for inclusion in Annex XIV.

4. References

Annex XV report (2009) - 2,4 – Dinitrotoluene. Proposal for identification of a substance as a CMR Cat 1 or 2, PBT, vPvB or a substance of an equivalent level of concern. Submitted by Spain, 28.08.2009. http://echa.europa.eu/doc/consultations/svhc/svhc_axvrep_spain_cmr_2,4-dinitrotoluene_20090831.pdf

Brüning T, Chronz C, Thier R, Havelka J, Ko Y and Bolt HM (1999). Occurrence of Urinary Tract Tumors in Miners Exposed to Dinitrotoluene. JOEM, 41, 144-149.

EU- RAR (2008) – European Union Risk Assessment Report on 2,4 – Dinitrotoluene. CAS No: 121-14-2. EINECS No: 204-450-0. http://ecb.jrc.ec.europa.eu/esis/

Joshi, M., Delgado, Y., Guerra, P., Lai, H., Almirall, J. (2009) Detection of odor signatures of smokeless powders using solid phase microextraction coupled to an ion mobility spectrometer. Forensic Science International Volume 188, Issues 1-3, p 112-118 .

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).

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), 11 June 2010.