# CODE OF PRACTICE
# NITROUS OXIDE

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# NITROUS OXIDE

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## 1 Introduction

Nitrous oxide ($N_2O$) has been produced and distributed by the industrial gases industry for many years. It is mainly used for medical purposes (anaesthesia). It is also used in the food (whipped cream) and electronic industries.

Severe accidents such as violent decomposition of $N_2O$ and rupture of $N_2O$ tanks have occurred at production, storage and distribution facilities.

This document has been prepared in order to draw useful conclusions from such accidents and to give advice for improvement of safety in the $N_2O$ supply chain.

A major cause of $N_2O$ accidents has been insufficient attention to the specific properties of $N_2O$ when designing equipment and developing operating procedures. For that reason, the first chapter of this document describes the properties and hazards of $N_2O$. On this basis, the principles and relevant details of safe production, storage and distribution of $N_2O$ are considered.

For medical N2O the relevant European Guide [61] and IGC Document [37] shall be followed.

## 2 Scope

This document is intended for use in the industrial and medical gases industry for the design, engineering, construction and operation of $N_2O$ production, storage and supply installations.

This document does not cover questions with regard to quality and analysis of $N_2O$ and also not $N_2O$ applications.

## 3 Definitions

Bundle (of cylinders): Assembly of cylinders that are fastened together and which are interconnected by a manifold and carried as a unit [1].

Cryogenic receptacle: Transportable thermally insulated pressure receptacle for refrigerated liquid gas of a capacity of not more than 1000 litres.

Cylinder: Transportable pressure receptacle of a water capacity not exceeding 150 litres [1].

Decomposition: Exothermic cracking of a chemical compound into its elements which can be caused by certain pressure and temperature conditions and / or by energy input.

Filling degree: Percentage of the volume of liquefied gas to the volume of water at 15 °C that would fill completely a pressure receptacle or tank.

Filling ratio: Ratio of the mass of gas to the mass of water at 15 °C that would fill completely a pressure receptacle or tank [1].

Liquefied gas: A gas which when packaged under pressure for carriage is partially liquid at temperatures above –50 °C [1].

Maximum allowable working pressure (MAWP): The maximum effective gauge pressure permissible at the top of the shell of a loaded tank in its operating position including the highest effective pressure during filling and discharge [1].

Net positive suction head (NPSH): Total head of liquid at the inlet to a pump above the equilibrium pressure head [32].

Oxypotential: The oxidizing power of a gas compared to that of oxygen, given as a dimensionless number, where oxygen has the oxypotential 1.

Pressure: In this publication “bar“ shall indicate gauge pressure unless otherwise noted – i.e. “bar abs“ for absolute pressure and “bar dif“ for differential pressure.

Pressure receptacle: Collective term that includes cryogenic receptacles, cylinders, bundles.

Refrigerated liquid gas: A gas which when packaged for carriage is made partially liquid because of its low temperature [1].

Shall: The use of the word “shall“ in this document implies a very strong concern or instruction.

Should: The use of the word “should“ in this document indicates a recommendation.

Stationary tank: Thermally insulated or non-insulated tank at a stationary place that can be filled with liquefied gas or refrigerated liquid gas under pressure for storage purpose.

Tank: Collective term that includes stationary tanks and transport tanks.

Transport tank (Synonym: Portable tank): Transportable thermally insulated tank for refrigerated liquid gas having a capacity of more than 450 litres.

## 4 Properties and hazards

### 4.1 Identification

| | |
|---|---|
| Chemical formula: | $N_2O$ |
| CAS No. | 10024-97-2 |
| EC No. | 233-032-0 |
| UN-No., ADR-name | 1070, Nitrous oxide<br>2201, Nitrous oxide, refrigerated liquid |

Other names of nitrous oxide are laughing gas, dinitrogen monoxide.

Note: UN 1070, Nitrous oxide is a liquefied gas. According to the definition in [1] it is a high pressure liquefied gas, because its critical temperature is between –50 °C and +65 °C.

### 4.2 Physical properties and hazards

Substance characteristics [2, 7]

| | | |
|---|---|---|
| Molar mass | 44,013 | kg/kmole |
| Vapour density at 1 bar abs, 15 °C | 1,853 | kg/m$^3$ |
| Relative vapour density at 1 bar abs, 15 °C (air = 1) | 1,532 | |

Vapour pressure and liquid density see table 1.

**Table 1** [2, 7]

| Temperature °C | Vapour pressure bar abs | Liquid density kg/litre | Remark |
|---|---|---|---|
| –90,82 | 0,878 | | Triple point |
| –88,47 | 1,013 | 1,2228 | Boiling point |
| –78,89 | 1,793 | 1,241 | |
| –67,78 | 3,172 | 1,201 | |
| –56,67 | 5,102 | 1,161 | |
| –45,56 | 7,722 | 1,110 | |
| –34,44 | 11,514 | 1,073 | |
| –23,33 | 16,547 | 1,036 | |
| –12,22 | 23,097 | 0,980 | |
| 0 | 31,290 | 0,904 | |
| 10,00 | 40,679 | 0,838 | |
| 15,00 | 45,120 | 0,818 | |
| 21,11 | 52,400 | 0,745 | |
| 36,41 | 72,450 | 0,452 | Critical point |

Hazards

Gaseous $N_2O$ under atmospheric conditions is heavier than air. If $N_2O$ is released to the atmosphere it will evaporate and disperse along the ground and may enter low lying areas or confined spaces. In these locations $N_2O$ displaces the air and thus an asphyxiation hazard can be created.

Liquefied nitrous oxide – UN 1070 – is handled in cylinders and non insulated tanks at ambient temperature and a pressure of about 50 bar. Refrigerated liquid nitrous oxide – UN 2201 – is handled in insulated tanks at temperatures around –20 °C and a pressure of about 18 bar. Due to these operating conditions $N_2O$ will form cold liquid or spray, if released from a tank. Skin contact with such liquid can cause severe frostbite.

Upon contact with cold $N_2O$, materials such as rubber or plastics can become brittle and are likely to break without warning.

## 4.3 Chemical properties and hazards

### 4.3.1 Oxidizing ability

Under the action of heat $N_2O$ decomposes into its elements irreversibly and exothermally (see 4.3.2), to produce a mixture which is richer in oxygen than air.

$$N_2O \rightarrow N_2 + \frac{1}{2} O_2 + 82 \text{ kJ / mol}$$

As “by-products” of $N_2O$ decomposition toxic nitrogen oxides can be formed.

Under these conditions $N_2O$ becomes an oxidizing gas with oxypotential higher than that of air. Consequently $N_2O$ is classified in standards and regulations as an oxidizing gas, see table 2.

**Table 2**

| Reference | Classification of nitrous oxide |
|---|---|
| [1] | 2O = liquefied oxidizing gas (UN-No.1070)<br>3O = refrigerated liquid oxidizing gas (UN-No.2201) |
| [53, 58] | Oxypotential 0,6 |

Due to the oxypotential of $N_2O$, a fire hazard can be created if the gas comes in contact with flammable gases or combustible substances in presence of an ignition source.

Metals

Burning of metals in contact with $N_2O$ is only possible with a strong ignition source such as $N_2O$ decomposition or by promoted ignition from a preceding fire involving non-metallic materials.

Non-metals

Ignition of non-metals such as plastics, elastomers and clothing materials in contact with $N_2O$ is possible by influence of heat or flame. Small particles in $N_2O$ can be ignited by a weaker ignition source such as heat from an adiabatic pressure shock.

Oil and grease

Oil and grease in a $N_2O$ installation can create a severe fire hazard. Such fire can be ignited due to particle shock, adiabatic pressure shock or high temperature.

Flammable gases

Flammable gases form explosive mixtures with $N_2O$. The explosion limits are influenced by the special chemical properties of $N_2O$:

- The lower explosion limit of flammable gases is much lower with $N_2O$ than with air or oxygen, since the heat release by decomposition of $N_2O$ supports the combustion of combustible-lean mixtures.
- The upper explosion limit of flammable gases is much higher with $N_2O$ than with air, since the higher oxypotential of $N_2O$ supports the combustion of combustible-rich mixtures.

Examples for explosion limits at normal atmospheric conditions see table 3.

**Table 3**

| | **Lower explosion limit, mole-%** | | | **Upper explosion limit, mole-%** | | |
|---|---|---|---|---|---|---|
| | **in air [10]** | **in oxygen [11]** | **in nitrous oxide [10]** | **in air [10]** | **in oxygen [11]** | **in nitrous oxide [10]** |
| Methane | 4,4 | 5,15 | 1,5 | 16,5 | 60,5 | 49,5 |
| Propane | 1,7 | 2,3 | 0,7 | 10,9 | 52,0 | 27,0 |
| Hydrogen | 4,1 | 4,0 | 2,9 | 77,0 | 94,0 | 82,5 |
| Ammonia | 15,4 | 15 | 4,4 | 33,6 | 79 | 65,0 |

Note: Other literature sources may provide slightly different values, but the general conclusion is, that $N_2O$ is more oxidizing than air. Safety precautions in respect of flammable gases see 5.11.

### 4.3.2 Stability

Under normal operating conditions $N_2O$ is a stable compound.

$N_2O$ has not been classified as an unstable compound in any standard or regulation. However accidents and experiments have shown that $N_2O$ as a result of its positive formation energy can decompose exothermally. This decomposition reaction can be self-sustaining and violent. The theoretical pressure ratio at decomposition – final pressure / initial pressure – can reach 10 to 1 [9].

The tendency for decomposition increases as temperature, pressure and energy input increase, but other factors such as catalysts (e.g. silver, platinum, gold, cobalt, copper and nickel oxides), product impurities, pressure, container size, cleanliness and heat loss rate can influence decomposition behavior. Figure 1 shows relevant experimental results. It should be noted, that the separation between “no decomposition“ and “decomposition“ is not as distinct as indicated by the curves. In practice, there is an extended area of probability around the curves where decomposition or no decomposition can occur.

The following conclusions can be drawn from figure 1:

In the presence of an ignition source $N_2O$ can decompose under varying pressure / temperature conditions. The higher the energy input, the lower the pressure and temperature required for decomposition. In laboratories has been shown, that under the influence of a very strong ignition source (“exploding wire“, 70 – 80 Watt), $N_2O$ can decompose even under refrigerated liquefied conditions [3]. Experiments with a glowing wire as ignition source showed decomposition at high temperatures (390 – 720 °C) as at low temperatures (150 – 240 °C). In the temperature region between 240 and 390 °C results were inconsistent, i.e. sometimes the gas exploded and sometimes it did not react [4].

Without any ignition source auto-decomposition of $N_2O$ can occur either at low pressure and high temperature (3,5 bar, 760 °C) or at medium pressure and temperature (21,4 bar, 325 °C). Other experiments, which were carried out without ignition source at 1 bar showed no decomposition at temperatures up to 575 °C, slow auto-decomposition between 600 and 900 °C and violent auto-decomposition above 900 °C [5]. Auto-decomposition of $N_2O$ generally occurs only in the gas phase.

The decomposition of nitrous oxide is purely propagated by a thermal process: This explains why the nitrous oxide flame propagation is much slower in comparison to a hydrocarbon / air mixture explosion and more likely to be quenched.

The investigation results according to figure 1 provide an important message for any $N_2O$ procedure: To prevent decomposition hazard any source of heat on $N_2O$ must be avoided under all circumstances.

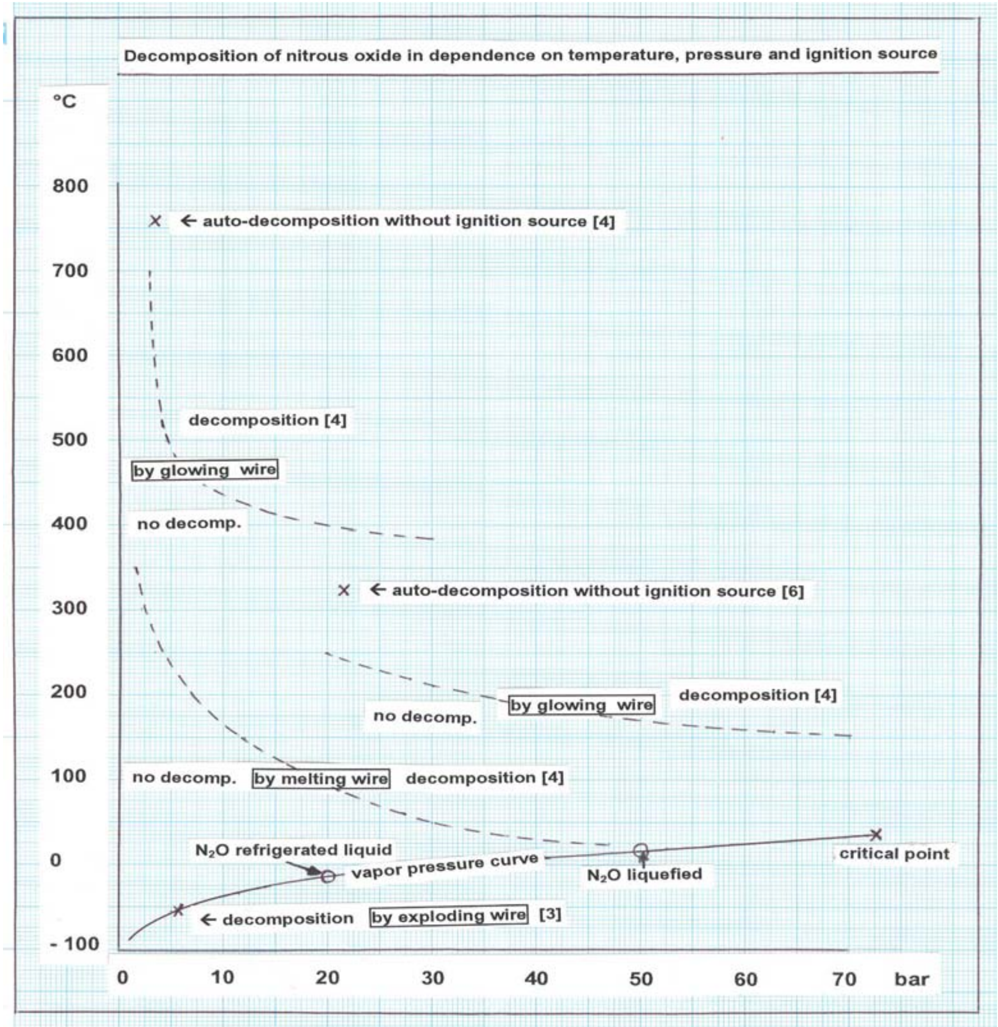


**Figure 1.**
**Decomposition of nitrous oxide. Dependence on temperature, pressure and ignition source.**

### 4.3.3 Other chemical properties

$N_2O$ is non-corrosive and does not form an acid in water. The solubility in water at 20 °C and atmospheric pressure is 0,665 litre $N_2O$ per litre $H_2O$.

### 4.4 Occupational exposure

The health effects of $N_2O$ are discussed only with regard to operators who are involved in production, transport and filling of $N_2O$. Medical exposure is not considered.

### 4.4.1 Short-term exposure

$N_2O$ is a colourless and odourless gas with slightly sweetish taste.

$N_2O$ if inhaled as a mixture with sufficient oxygen has no toxic effect. But inhalation in high concentration without the provision of sufficient oxygen creates the hazard of brain damage or fatal asphyxiation.

### 4.4.2 Long-term exposure

$N_2O$ has been associated with several side effects from long-term exposure. Epidemiological studies suggest feto-toxic effects and higher incidents of spontaneous abortion in exposed personnel [8]. Although no cause-and-effect relationship has been firmly established, exposure to the gas should be minimised. The occupational exposure limits for eight hours daily (25 to 100 ppm according to different national regulations) shall not be exceeded. Under normal operating conditions with natural or mechanical room ventilation this limit should be kept.

If $N_2O$ is produced, stored or filled in insufficiently ventilated rooms a gas monitoring system should be installed in order to monitor the room concentration of $N_2O$.

### 4.5 Environmental issues

The emission of $N_2O$ to the earth atmosphere is originated for 20 % from anthropogenetic sources, mainly by burning biomass and for 80 % from natural sources. The emission from medical application of $N_2O$ is absolutely irrelevant versus the overall environmental impact of $N_2O$.

The releases of $N_2O$ to the atmosphere are not restricted by law so far. However European Directives [60, 62] shall be considered and $N_2O$ releases shall be avoided as far as possible.

The Seveso II Directive applies to $N_2O$, if the quantity which is present at one time on the site exceeds the following quantities [27]:

- Greater than 50 tons: A notification on the quantity of substance and a Major Accident Prevention Policy is required.
- Greater than 200 tons: An official Safety Report is required.

## 5 Equipment and procedures – general considerations

### 5.1 Principles

The equipment used to handle $N_2O$ must be designed, constructed and tested in accordance with the regulatory requirements in the country in which the equipment is operated. The equipment must be designed to withstand the maximum pressure and temperature to which it is to be operated.

Because of the properties and hazards of $N_2O$ consideration shall be given to avoid combustible materials and any uncontrolled heat input.

General rules described hereunder apply to $N_2O$ systems where the pressure is below 70 bar. Above this pressure, i.e. in the supercritical state of $N_2O$, rules defined for pure oxygen concerning material compatibility, equipment selection etc. shall be applied to $N_2O$ as well. The oxygen rules are also applicable to nitrous oxide / oxygen mixtures whatever the pressure or percentage of $N_2O$ is.

### 5.2 Materials of construction

Materials shall be selected with consideration of the oxypotential of $N_2O$.

Metals
There is no restriction regarding the use of common commercial metallic materials for $N_2O$ installations. Primarily carbon steel, Mn steel, Cr-Mo steel, stainless steel, brass, copper, copper alloys and aluminum are considered to be suitable for use with $N_2O$ [2, 35].

Non-Metals
Examples of non metallic materials exhibiting the best compatibility with gases having a high oxypotential [55]:

- Plastic products such as Polytetrafluoroethylene (PTFE), Polychlorotrifluoroethylene (PCTFE), Fluorinated Ethylene-Propylene (FEP) Polyetheretherketone (PEEK) and ethylene propylene diene monomer (EPDM). Others such as Polyvinylchloride (PVC), Poly-vinylidenfluoride, Polyamide (Nylon 66®),Vespel SP21®) and Polypropylene can be used with due regard to the external fire risk.
- Elastomer products such as Viton®, Neoflon®, Kalrez®, Fluorel® should be tested for compatibility. Certain grades of Viton® are known to swell in pressurised nitrous oxide and non-swelling grades are preferred.
- Non metallic materials to be used in high pressure ($p > 30$ bar) nitrous oxide / oxygen mixture application shall conform to special requirements considering toxicity risks [28].

### 5.3 Valves

Materials for high pressure $N_2O$ valves such as cylinder valves shall be selected according to [54, 55]. Commonly used metals are brass, copper alloys, carbon steel. Acceptable non-metallic materials are the plastics PTFE, PCTFE, polyamides and the elastomer Silicon rubber.

Valves for refrigerated liquid $N_2O$ shall meet the requirements regarding design, testing and marking for cryogenic service [59]. Metallic and non-metallic materials for such valves shall have passed a test for oxygen compatibility according to [41]. Ball valves used for liquefied $N_2O$ are recommended to be bored or otherwise designed for pressure relief towards the tank to prevent trapping liquid inside the ball.

### 5.4 Filters

Filters or strainers shall be designed with consideration of the oxypotential of $N_2O$. Filters containing combustible materials shall not be used. Mesh filters made from stainless steel or copper alloys can be used. No glue or similar combustible material shall come into contact with $N_2O$.

Liquid nitrous oxide should be filtered as fine as possible. Hole size of the filter is a compromise between allowable pressure drop, space available and acceptable thermal mass of the filter body [17]. Gaseous nitrous oxide should be filtered using mesh sizes between 30 and 100 corresponding approximately to a 500 to 150 micron particle size capture [18].

### 5.5 Cleaning of installation

Any equipment and installation designed for $N_2O$ service shall be cleaned according to [22, 43]. Where it is necessary to change the product service of equipment from any gas to $N_2O$, same rules apply for cleaning. Pressure receptacles which are to be changed to $N_2O$ service shall be cleaned using a proper procedure. For cylinders see [40] and for transport tanks see [31].

The surfaces that come into contact with $N_2O$ shall be cleaned to remove all combustible particles and oil and grease, that may have been introduced into the system during its construction, fabrication or maintenance. The equipment shall be cleaned, as for oxygen service, using detergents or suitable cleaning agents that are free from non-metallic or metallic particles.

The maximum quantities of foreign matter (oil, grease, organic materials) in the installation shall not exceed 500 mg/m$^2$ for pressure range < 30 bar or 200 mg/m$^2$ for pressure range > 30 bar. Visible particles, fibres or drops of water shall not be accepted [22].

### 5.6 Prevention of contamination

Hoses and filling connections or other pieces of equipment that are not continually connected, shall be protected against the ingress of dirt and moisture by caps and / or nuts, when not in use.

### 5.7 Avoiding high temperature

Considering the potential hazard of $N_2O$ decomposition, temperature above 150 °C shall be avoided by all practical means, e. g.:

- Internal electrical heaters shall not be used in tanks or vaporizers.
- Pumps and compressors shall be protected from running hot (e.g. because of blocked discharge pipe or no flow).
- Hot work on equipment containing $N_2O$ shall not be performed, unless $N_2O$ has been removed and the equipment purged. Hot work close to a $N_2O$ installation may also require removal of $N_2O$ and purging, depending on the risks and type of work. Such work shall require a work permit issued in accordance with company requirements [24].
- Heat from a flame shall not be applied to any part of a $N_2O$ installation for de-icing, releasing threaded couplings or for increasing pressure in cylinders.
- Thermal mass flow meters shall not be used.
- $N_2O$ installations shall be earthed before use in order to avoid electrostatic sparks.
- As required, filters (or strainers) will be conveniently located in order to avoid migration of particles within specific devices (e.g. compressor, pump).

### 5.8 Restriction of flow velocity

The $N_2O$ flow can create locally heating of a material by particle impact or flow friction, particularly in areas with narrow passages. This heat can initiate a local combustion if the ignition temperature of the material in contact with $N_2O$ is reached. The $N_2O$ velocity should therefore be limited to avoid this temperature being achieved. In the absence of specific $N_2O$ data, the velocity limits which are defined for oxygen [18], should be considered when designing a new installation.

### 5.9 Operating procedures

As with any operation associated with a hazardous substance, written operating procedures shall be prepared. Proper training of operators regarding these procedures shall be performed.

Management shall ensure operators clearly understand that the equipment has to be operated within its design parameters, so as not to cause a hazard to personnel or damage to the equipment or environment.

Included in the procedures shall be a statement to indicate that no part of the installation shall be heated higher than the normal operating temperature.

### 5.10 Maintenance procedures

$N_2O$ equipment shall be maintained by qualified and properly trained personnel in a routine, controlled and safe manner following written procedures.

Any non routine maintenance work shall be subject to a work permit procedure [24].

Modifications to a $N_2O$ installation shall not be made without proper risk assessment [25].

Particular consideration shall be given to ensuring that the integrity of the cleanliness of the system is maintained and that spare parts and lubricants that come in contact with $N_2O$ are compatible with $N_2O$.

Pressure equipment shall be depressurised and purged with air or inert gas prior to any maintenance or repair. Regarding hot work see 5.7.

### 5.11 Isolation from flammable gases

To ensure that there is no hazard of inadvertent mixing of $N_2O$ with flammable gases or liquids, $N_2O$ equipment and pressure containers shall be dedicated to $N_2O$ service.

Where $N_2O$ has to be mixed with other gases, precautions shall be taken to ensure that no flammable gas is unintentionally mixed with $N_2O$, see [23]. Mixtures of $N_2O$ with flammable gases shall only be produced if the concentration lies outside the explosion limits.

Mixing of $N_2O$ with self-igniting gases such as silane shall be prevented under all circumstances, since immediate ignition and explosion can occur.

### 5.12 Use of carbon dioxide equipment

Any equipment designed for carbon dioxide service shall not be used for $N_2O$ service, unless a proper procedure has been followed for the change of service. The procedure shall meet the relevant requirements of this Code of Practice. Special care is required with regard to design, material, insulation, cleanliness, lubricants, sealing and avoiding high temperature.

***WARNING***: *Unlike carbon dioxide, nitrous oxide can not be used as pneumatic energy to actuate pneumatic cylinders or valve actuators or as sealing gas.*

## 6 Production process

### 6.1 Introduction and general description

The most usual industrial process for the manufacture of $N_2O$ is based upon thermal decomposition of ammonium nitrate (AN). There are a number of other $N_2O$ production processes, which are not covered in this document, e.g. direct oxidation of ammonia or purification of off-gas from adipic acid production (polyamide chain).

Chemical background of the thermal decomposition process

$N_2O$ is produced from AN in hot solution with water at a concentration varying from 80 to 95% at a temperature of approximately 250°C to 255°C. Thermal decomposition of AN is complex and may follow different routes. The main and desired reaction is $NH_4NO_3 \rightarrow N_2O + 2\ H_2O$. This reaction is exothermic, generating 59 kJ / mole at approximately 250°C and it is a first order reaction with an estimated energy of activation of 150 - 200 kJ / mole at standard conditions (273 K, 1013 mbar).

With these values it has to be understood that the kinetics of decomposition and the related heat release and gases produced ($N_2O$ + water vapour) double for each 10°C of temperature increase (or is multiplied by 1,07 for each °C). As an order of magnitude, a mass of molten AN producing 200 kg/h of $N_2O$ in a reactor at 250 °C develops a thermal power of about 70 kW; at 255 °C the same reactor would produce 280 kg/h (40% more), with a heat production of 98 kW.

Side reactions:

In addition to the first order reaction there are side reactions:
- Evaporation of water.
- Chemical side reactions leading to decomposition of AN with formation of $HNO_3$ + $NH_3$, and, to a less extent, to $N_2$ and nitrogen oxides:

$$NH_4NO_3 \leftrightarrow NH_3\ (\text{gas}) + HNO_3\ (\text{gas}) \qquad \Delta H = +\ 159{,}9\ \text{kJ/mole at } 250^\circ C$$

$$12\ HNO_3 + 16\ NH_3 \rightarrow 30\ H_2O + 3\ O_2 + 14\ N_2$$

$$12\ NH_4NO_3 \rightarrow 23\ H_2O + N_2O_3 + 2\ HNO_3 + N_2O_4 + 9\ N_2 \qquad \Delta H = -\ 69{,}75\ \text{kJ/mole.}$$

From a safety point of view, and even if some of these reactions are endothermic and may become predominant at high temperature, none of them are able to control, or even moderate, abnormal temperature increase of a reactor due to improper thermal balance.

These side reactions have great importance upon the purification system and the quality of $N_2O$, as they lead to the formation of significant amounts of the toxic nitrogen oxides $NO_x$.

Chloride catalyzed decomposition

The decomposition of AN in the melted phase will be faster and can occur at temperatures below the melting point when the AN contains chloride components or when the added water contains chloride ions. The reactions in presence of chloride components produce principally nitrogen.

Other components have a similar catalytic effect , see 4.3.2.

Corrosion – Use of Stabilizers

AN solution is very corrosive with several metals. Even stainless steel after prolonged periods of contact undergoes limited attack, which transfers ferric ions into the solution. Addition of di-ammonium phosphate $(NH_4)_2HPO_4$ or ammonium dihydrogen phosphate $NH_4H_2PO_4$ (also known as mono-ammonium phosphate) in AN limits this reaction. Historically phosphoric acid has also been used but there is no technical basis for this choice of material.

Where the purity of ammonium nitrate or water quality could lead to corrosion in the melter or reactor, phosphoric acid is often used to prevent corrosion.. This treatment is applied to new plants and re-applied annually. For treatment to be effective a 10% of solution at 85°C is applied for 8 hours.

Contamination

Accidental contamination of ammonium nitrate by combustible materials e.g. oil shall be avoided by appropriate measures.

AN shall be controlled thoroughly (see 6.3.1). Traces of anticaking substances from cross contamination with fertilizer grade AN will make the reaction violent and produce high amounts of CO, $CO_2$ and $N_2$. Therefore quality control of raw AN is required.

### 6.2 Abstract of the production process

Several different design of $N_2O$ process plant exist, but the general schematic overview of production is as in figure 2.

For the production of $N_2O$ the AN can be used in two forms:

- Liquid ammonium nitrate (LAN), which means AN is supplied as heated solution in water. To avoid solidification or crystallisation, heating is required.
- Solid ammonium nitrate (SAN) which has to be melted and some water added directly in the melter of the $N_2O$ plant. (It has been reported that some solid feed plants melt and decompose SAN without any addition of water. This technology is not recommended and not described in this Code of Practice).

Solid storage and a melter (1) are required for solid feed plants. Liquid hot solution tanks are required for liquid feed plants. In both cases, technical grade of AN, with low amounts of chloride and metals, is required. The liquid is injected into the reactor (2). Here the LAN undergoes a thermal decomposition into $N_2O$ and water vapour.

Control of the reaction is achieved by maintaining the substance and thermal balances by monitoring and adjusting the flow rate of ammonium nitrate and / or the heating power.

Other control parameters are:

- LAN level in the reactor.
- Temperature of the LAN or pressure control in the gas phase.

The temperature of the LAN is then maintained by heating and cooling the reactor.

The heat produced by the reaction may be used for preheating the LAN in the melter or the LAN before entering the reactor.

The produced gas is cooled and the water vapour is condensed in a counter-current water cooled condenser (3). The gas stream passes next through a number of chemical purification steps using towers (4). Impurities, e.g. $NO_x$, $HNO_3$, $NH_3$ are washed out in a sequence of absorption towers employing water, a mixture of potassium permanganate and sodium hydroxide, sulphuric acid and finally water. Some plants operate without the sulphuric acid purification step.

The purified $N_2O$ is accumulated in a gasholder (5). This accumulation device acts as a compensator for variations in production. The gas is compressed to liquefaction pressure (6) and, after drying (7), it is liquefied (8 )with cooling water (10) or other non-flammable refrigerant. The product is then stored (9, 11) and ready for filling cylinders or for bulk transport.

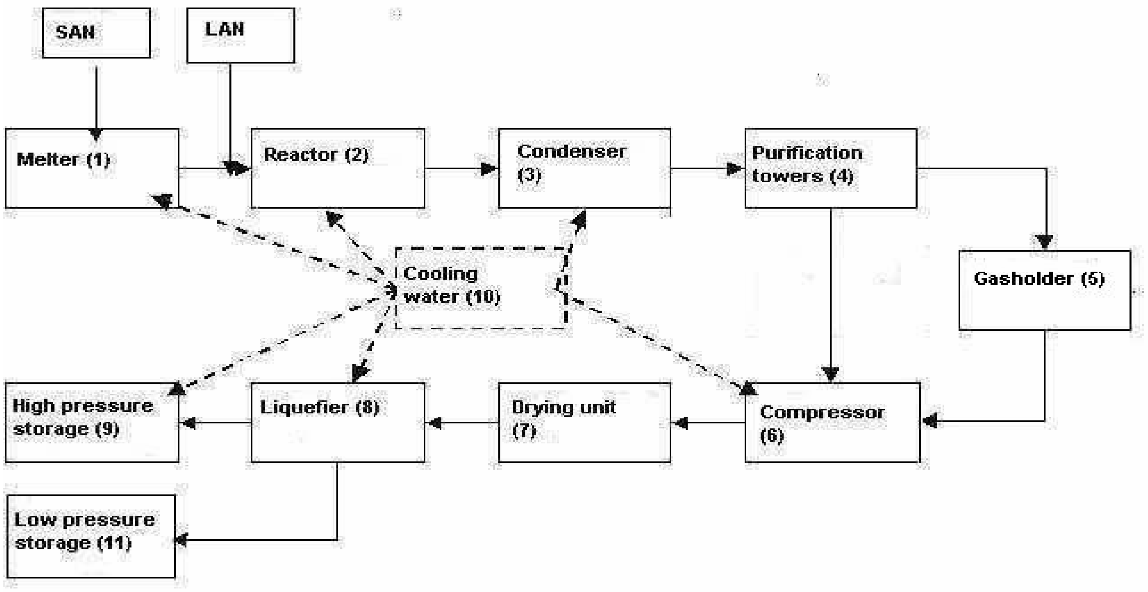


**Figure 2: Scheme of nitrous oxide production**

## 6.3 Equipment components

### 6.3.1 Feedstock

Both forms of the feedstock SAN and LAN must be considered as oxidizing substances with relevant properties and requiring safety precautions, see table 4.

**Table 4**

| | **Solid ammonium nitrate (SAN)** | **Liquid ammonium nitrate (LAN)** |
|---|---|---|
| Identification<br>Chemical formula<br>CAS No.<br>EC No.<br>UN-No:<br>Name according to [1] | <br>$NH_4NO_3$<br>6484-52-2<br>229-347-8<br>1942<br>ammonium nitrate | <br>80 – 93 % $NH_4NO_3$ in water<br>6484-52-2<br>229-347-8<br>2426<br>ammonium nitrate, liquid |
| Class according to [1] | 5.1 | 5.1 |
| Classification according to [1] | O2 (oxidizing substance solid) | O1 (oxidizing substance liquid) |
| Properties | Contact with combustible material may cause fire.<br>Explosive when mixed with combustible material.<br>Decomposes when heated to about 170 °C.<br>Fire may cause generation of toxic nitric gases. | LAN has in principle the same properties as SAN. But due to its water content it is slightly less sensitive. |
| Safety precautions | Keep away from sources of ignition – no smoking.<br>Avoid contamination by combustible liquids, powdery substances, oxidizing substances, alkalis and acids.<br>Avoid contact with skin and eyes. | |

LAN and SAN are dangerous substances according to legislation, but LAN has following safety advantages compared with SAN:

- Cross contamination with anti-caking substances is less likely with LAN.
- It is easier to maintain quality.
- The operation of the plant is safer.
- Consequently LAN has a lower hazard rating in ADR and in environmental law.
- Handling is minimized.

A) Liquid ammonium nitrate (LAN)

Quality requirements

- Depending on the process 80 % to 96 % $NH_4NO_3$ solutions are being used.
- For transportation purposes the concentration is limited to 93 % (UN 2426).
- A quality certificate with purchase is required.
- The supplier should be qualified and approved by consumer.
- Approved transport container, insulated, with possibility of external heating (steam, not electrical) are required for long distances, see e.g. [1].
- The product quality shall be analysed by either the supplier or consumer.

Typical specification for LAN transported by road:

| | |
|---|---|
| $NH_4NO_3$ concentration range | min. 91,0 – max. 93,0 % |
| N-content | min. 31,8 – max. 32,6 % |
| $NH_3$ (free ammonia) | min. 50 – max. 100 mg/kg |
| Organic matter (e.g. oil) | max. 5 mg/kg (as carbon) |
| Chloride (Cl) | < 5 mg/kg |
| Iron(Fe) | < 1 mg/kg |
| Nitrogen oxides ($NO_x$) | < 10 mg/kg |
| Phosphate ($PO_4$) | < 10 mg/kg |
| Calcium (Ca) | < 1 mg/kg |
| Sulphate ($SO_4$) | < 50 mg/kg |
| Acidity of 10 % solution | 5 < pH < 7 |
| No anti-caking agent or additive | |

Storage requirements:

- Arrangements for heating (e.g. steam, re-circulation of LAN) are required. No direct electrical heating is allowed. Hot points like electric wiring shall be avoided.
- The temperature shall be controlled to prevent crystallisation.
- If necessary the actual ammonium nitrate concentration shall be controlled and diluted to the required specification. Additional water should have low chloride and iron content.
- Storage quantity shall be according to local regulations.
- The LAN storage tank area shall be protected against spillage and the tank discharge system shall be protected to prevent inadvertent discharge into drains, e.g. by a retention area.
- Asphalt and other combustible material shall not be present in the area where spillage may occur.
- The LAN unloading system, including the transfer system, needs to be cleaned thoroughly to avoid any solid ammonium nitrate build-up; good practice is to use water of low chloride content.
- If possible LAN shall be transferred from the trailer to the tank by pressurization and to the $N_2O$ plant by gravity. Pumping LAN requires specific design to avoid dry running.

B) <u>Solid ammonium nitrate (SAN)</u>

General requirements:

- Depending on local regulations special permissions may be needed for purchase, transport and storage due to the fact that explosives can be produced from SAN.
- Safety distances to public roads and residential areas shall be performed according to local regulations.

Quality requirements:

- A quality certificate with purchase is required.
- The supplier should be qualified and approved by the consumer.

Typical specification:

| | |
|---|---|
| • Moisture | < 0,5 % |
| • N-content (free of water) | >34,8% |
| • Acidity (when diluted in a 10% solution) | 5 < pH <7 |
| • Non solubles | < 0,002% |
| • Ashes | < 0,002% |
| • Chloride and halogen | < 0,0002% |
| • Iron | < 0,0002% |
| • Total organic carbon | < 0,001% |
| • No anti-caking agent or additive (means no fertilizer quality) | |

Storage requirements:

- According to the chemical properties of AN (harmful, oxidising) a dry and special dedicated fire resistant area is required for storage. In addition nothing else is allowed to be stored in the same room. Strict housekeeping is necessary.
- Used bags shall not be kept inside the storage building and shall be disposed of properly.
- Access to the storage room shall be controlled.

### 6.3.2 Melter

The SAN is melted by addition of approximately 8% water and by heating up to a temperature of 125 to 130 °C. Addition of di-ammonium phosphate or ammonium dihydrogen phosphate (also known as mono-ammonium phosphate) is made to stabilize reaction (see also Section 6.1).

The melter is divided into two vessels:

- The melting or dilution vessel.
- The transfer vessel from which the LAN is fed to the reactor.

Each vessel is heated independently.
Passage of LAN from dilution to transfer vessel can be achieved by hydrostatic pressure or special pneumatic pumps.

Requirements:

- Insure the dilution vessel is at ambient temperature before introducing the ammonium nitrate and always introduce the water first, never introduce SAN in an empty and hot melter.
- Insure a high / low level control (e.g. by procedure or automatically).
- Heating system will be such that there is no contact between the heating source and the LAN.
- There must be a system for re-circulating / homogenizing the solution during the heating and melting process, to make sure there is no hotter point than the measured temperature.
- The melter shall be equipped with temperature control (T = 125 - 130 °C in production mode). Such temperature to be controlled by a minimum of two sensors (one controlling the other one) in each of the two vessels (dilution and transfer).
- Heat the injection line (pipe connection between melter and reactor) to avoid re-crystallization.
- The melter shall never exceed 130 °C during non production periods and 140 °C during production.
- For the preparation of the aqueous solution the water shall have low chloride and iron content (each < 10 ppm).
- If drinking water with a possible presence of chloride ions has to be used to prepare the aqueous solution, the melter and the reactor shall be drained and cleaned regularly to avoid accumulation of the chloride ions.
- Use of a strainer against unwanted solids (e.g. plastic bag parts) should be considered.

### 6.3.3 Reactor

The reactors shall be operated such that the risks to personnel are minimized. The installation of the reactors behind concrete walls or similar protection should be considered.

Reaction start-up

The ammonium nitrate is decomposed in the reactor according to the formula:

$$NH_4NO_3 \rightarrow N_2O + 2\ H_2O + 59\ \text{kJ / mol}$$

This decomposition of AN in water may start at temperatures around 210°C depending on reactor design, concentration and purity of AN, catalysers and stabilizer (see Section 6.1 Corrosion – Use of Stabilizers) concentration). It would take a relatively long time to naturally reach the thermal equilibrium set point (generally between 250 and 255°C). To accelerate the starting process the ammonium nitrate solution is heated in the reactor until approximately 240°C.

Process thermal equilibrium

Since the reaction is exothermic, the temperature in the reaction mass has to be strictly controlled. The optimum temperature for decomposition is around 250 °C at a pressure slightly higher than atmospheric pressure. The reactor thermal balance is a competition between an exothermic reaction, and the sum of the cooling effects coming from:

- Water vaporization.
- Heat capacity of fresh LAN feed.
- Heat losses through the reactor walls.

Reactors are designed for nominal temperature, level and water content of the AN feed. Any significant deviation of these operating conditions shall not be permitted, unless the new operating conditions have been properly validated.

The control of the reaction by injection of LAN is regulated by the static pressure in the reactor or the temperature, which depend on the quantity of gas produced by the reaction.

A properly designed system should allow for this natural thermal balance to be in close equilibrium. The final thermal balance and reactor control is achieved by moderate additional heating and cooling.

Reactors are designed to operate close to 250 °C; it is generally agreed that this temperature optimises both the kinetics of decomposition (not too fast, not too slow), and a minimum of side reactions.

Reactors are also designed to operate close to a nominal level: A substantial deviation from this nominal level will result in important additional heating or cooling and difficulties in controlling the process.

Ideally, temperature and level should be controlled and stable. In this process, mass and thermal balances are linked: Addition of fresh AN not only varies the level, but also acts as a cooling agent.

Due to this coupled effect, it is difficult to obtain and maintain stable conditions exactly at the nominal level and the nominal temperature. More likely, the reactor can be stabilized at a number of set points with temperatures and levels close to the nominal. This stability point may fluctuate slightly with time, subject to external temperature and the concentration or temperature of fresh LAN.

Heating and cooling equipment

Heating equipment could be either electrical or by direct or indirect flame burners. The heating system shall be designed for both the high thermal load required during start-up and for the smooth control during steady state operations.

Cooling power is required for both smooth control of reactor temperature during production, for stopping the production and for emergency situations. Cooling can be provided either by internal heat exchanger (internal coils) or external spray of fresh water on the reactor's wall.

A second cooling device shall be provided for emergency cooling. Should an abnormal high temperature be detected the cooling device shall automatically quench the reaction. This water supply shall be designed and frequently checked such that in the event of a water and / or power supply break-down the emergency cooling water is still operational.

Temperature measurements

Temperature indicators are located on the control board and indicate the temperature in the ammonium nitrate mass in the reactor. The corresponding temperature sensors (at least 2, one controls the other one) should be immersed in the bulk LAN and are connected to the temperature control system.

Sensors are selected according to how they are used. Accuracy, reliability and sensitivity are important, if the signal is to be used for the process regulation. The temperature control system shall be reliable and independent from electrical power fluctuation.

Pressure control and release

Reactors shall be designed to be operated slightly above atmospheric pressure. They will be equipped with appropriate pressure relief devices: Bursting disk and / or hydraulic overpressure safety device.

Process monitoring based on pressure can also be used instead of temperature monitoring. In this case pressure fluctuations are measured and these can be correlated with reactor thermal evolution.

Reaction interrruption

Sometimes the reaction has to be interrupted:

- Temporarily for stand-by mode (eg week-end or night).
- Completely for maintenance or cleaning.
- Immediately at emergency.

The normal procedure in discontinuous operations is to stop the reaction temporarily by decreasing the temperature of AN in the reactor to a level under which the reaction can not spontaneously restart

This operation must be carried out in a cautious way. Since the reaction kinetics are roughly doubling with each 10°C temperature increment, a reaction seemingly stopped, may restart after 45 to 60 minutes. It is consequently very important that during this procedure the operations are under constant surveillance until confirmation of the definite interruption of the reaction has been ascertained (below 180 °C). To avoid crystallization of AN the temperature in the reactor shall not decrease below 160 °C.

During this operation as well as during the stand-by period, all the safety systems must remain operational.

When the reactor is in a stand-by position for less than approximately 48 h, the temperature within the reactor shall be kept below 180 °C. When the reactor remains in a stand-by position for a longer period, water evaporates and AN concentration increases. Special attention through adequate procedure must be taken for controlling both temperature, level and concentration during stand-by and before restarting the reactor. Any increase in this temperature during stand-by, e. g. at 190°C, should trigger an alarm and quench the reaction.

When the reactor is completely stopped e. g. for maintenance, the reactor and piping system shall be cleaned by water.

When the reactor is restarted after a complete shut-down, the ammonium nitrate level has to be checked to be sufficient. Then the reactor has to be slowly warmed-up in order not to get local hot points inside the reactor and other equipment. In case of crystallized AN in the reactor a very careful heating is required.

### 6.3.4 Condenser

The gas leaving the reactor is water saturated and passes through a condenser for removal of the water.

The condensed water contains ammonium nitrate and nitric acid and can be reused. It should be purified before discharge, according to national regulations.

### 6.3.5 Purification towers

The gas leaving the condenser contains impurities produced by decomposition of the AN. The purification is done in absorption towers by washing the gas with chemical solutions re-circulated by pumps in a closed circuit.

Requirements:

- The system should be fitted with an alarm to stop the reaction, if
  → no flow of purification liquid in any tower,
  → no $N_2O$ gas flow through and / or pressure in the purification towers.
- The handling of both the raw substance and their solutions must be done in a safe way. Due to the fact that these are chemical substances, which can cause severe burns, the preparing of the solutions shall be performed by trained personnel only. According to relevant rules, the personnel involved shall use proper personal protective equipment.
- The storage of the solutions and their raw substances shall be done in a safe way, to prevent spillage or leakage from entering open drain systems. They shall be stored in a defined covered dry and ventilated area, away from any open drains and away from AN.
- The following substances may be needed:
  → Sulphuric acid.
  → Sodium hydroxide (solid or liquid).
  → Potassium permanganate.
  → Water (drinking quality) to prepare solutions.

### 6.3.6 Gasholder

The gasholder can be either a gasometer (water sealed bell) or a balloon. It acts as a compensator for the variations between the gas production from the reactor and the consumption by the compressor in order to ensure a constant gas flow to the compressor.

Requirements:
- Gasometer low level sensor and low pressure sensor to stop the compressor.
- Gasometer high level sensor to alarm before the excess gas is escaping.

### 6.3.7 Compressor

Product from the gasometer is fed to the compressor.

Requirements:
- Filter (strainer type) at the compressor's inlet side for removal of accidental particles.
- Compressor designed according to oxygen requirements [16, 21], dry running or water lubricated.
- For parts in the compressor where a contact with $N_2O$ is not possible, conventional oil can be used for lubrication; for parts where contact is possible, water lubrication should be used to avoid explosion and contamination for medical grade of the $N_2O$.
- Any contact between $N_2O$ and conventional mineral oil or synthetic oil must be avoided.
- Pressure relief to the outdoor atmosphere.
- Each stage of the compressor should be equipped with a temperature sensor.
- Compressor to be tripped to prevent vacuum being pulled on gasometer or balloon.
- Oil from the compressor should not reach the drying unit (because of high explosion risk).

### 6.3.8 Drying unit

The drying unit removes by adsorption the water vapour from the compressed gas. The unit contains two adsorbers filled with alumina, silica-gel or molecular sieve. The parallel arrangement of the adsorbers allows a continuous operation, with one adsorber in adsorption mode and the other in regeneration mode.

For regeneration the adsorber shall be depressurised; the gas is returned to the gasometer or should be used. Regeneration is accomplished by means of hot oil-free air or nitrogen. After sufficient heating regeneration is completed by the use of cooled air or nitrogen.

Requirements:

When using a drying unit with a solid adsorbent, care must be taken to avoid introducing $N_2O$ at temperature higher than 150 °C. Never start operation on a warm adsorber: Ensure sufficient cooling before drying unit switching. A written procedure is not sufficient and a surface thermometer with light indication is recommended. Particular care should be taken with internal heaters in the adsorbers. The temperature of the gas and the heating elements should be controlled to ensure that the local temperature is lower than the limiting temperature of $N_2O$ at operating pressure.

- Never regenerate or cool the dryer with $N_2O$ or with oil contaminated pressurised air.
- Avoid any backflow of $N_2O$ into the hot heater.
- Pressure relief valves sized according to flow rate capacity of the compressor.
- Filter at the outlet side.
- Analyse the product after the drying unit for moisture.

Another method is to use a heat free drying unit which utilizes $N_2O$ as the regeneration gas. The $N_2O$ is then returned to the gasholder.

### 6.3.9 Liquefaction and pressure storage

$N_2O$ is cooled and condensed by water or other non-flammable refrigerant and then stored in pressure tanks. In case of using a refrigerant, care to be given to avoid contamination of $N_2O$.

A) High pressure storage

For high pressure storage, the $N_2O$ is liquefied by water cooling (10 to 15°C) and stored at ambient temperature and pressure between 45 and 55 bar. In most cases, this type of storage is an intermediate storage prior to transfer to a low pressure tank.

Requirements:
- High-pressure alarm and shut off alarm on intermediate storage tanks (if not installed at the compressor) to shut down the compressor.
- Pressure relief valves sized according to the compressor's flow rate capacity.
- Method to measure product content, e.g. level or weight.

B) Low pressure storage

Low-pressure liquefaction and storage is a safer option than high pressure storage because of the properties of $N_2O$ and the large volumes involved.

For low pressure storage, the nitrous oxide is liquefied by a refrigerant to temperatures between –20°C and –30°C and stored under pressure between 15 and 20 bar in an insulated tank.

An alternative process for transferring $N_2O$ to low pressure storage is to remove product from the intermediate high pressure storage and pass it through an expansion valve.

Requirements:
- For non vacuum insulated tanks: Internal cooling coil operated with refrigerant to maintain $N_2O$ as a liquefied gas.
- Avoid the refrigerant coming into contact with the product.
- Pressure relief valves sized according to the compressor's flow rate capacity.
- Method to measure product content, e. g. level or weight.

## 7 Stationary tanks

Stationary tanks are used in $N_2O$ production plants, filling plants and customer installations. This chapter refers to all these types of tanks.

### 7.1 Design

There are two different tank types:

Non-insulated high pressure tanks, made of carbon steel, for storage of liquefied $N_2O$ at ambient temperature with corresponding vapour pressure in the range of 45 to 55 bar. The high operating pressure of this tank type requires high-pressure filling pumps and sometimes the use of two pumps in series. This increases the hazard of heat production and subsequent decomposition. Furthermore in case of an external fire, the tank content can be heated up quickly. For these reasons non-insulated tanks shall not be used in hospital installations.

Insulated tanks for storage of refrigerated liquid $N_2O$ at temperatures below –20 °C and corresponding vapour pressure in the range of 18 bar. There are two types of insulated tanks:

- Vacuum insulated tanks with the inner tank made from stainless steel or fine grain carbon steel and the outer tank from carbon steel. Vacuum insulated tanks present the best insulation against heat input to the inner tank.

- Non-vacuum insulated tanks with the inner tank made of low temperature steel, e.g. fine grain carbon steel and the outer cladding made of steel or aluminium.

Insulation material:
- The insulation system shall be non-combustible or fire resistant, e.g. the material itself shall not continue to burn when the external flame is extinguished.

- An insulation system made of polyurethane with cladding made of steel or aluminium is considered to be fire resistant.
- If the insulation system of an existing tank has to be replaced, it should be rebuilt using a fire resistant insulation system (e.g. polyurethane with cladding) or non-combustible material such as glass wool, foam glass or rockwool.

Safety requirements for all fixed tank types:

- Support and foundation of the tanks is recommended to be non-combustible.
- Tanks shall be installed outdoors. In the very rare cases where indoor installation is necessary, proper ventilation and easy access for filling shall be provided. $N_2O$ or oxygen deficiency levels in the ambient air shall be monitored. Further information on the hazards in indoor installations is documented in e. g. [35, 47, 51].
- Tanks shall be located away from any potential fire situation. Local regulations concerning safety distances shall be observed [19].
- All parts of $N_2O$ tanks shall be bonded to ensure electrical continuity and properly earthed. The electrical potentials between the tank and the ground should be equalised during service.

## 7.2 Accessories

If transport tanks are to be filled, a ground mounted pump shall be installed adjacent to the stationary tank, see 9.2. Pumps mounted on trucks and trailers shall not be used for filling transport tanks.

A refrigeration unit should be installed at non-vacuum insulated tank installations if the normal boil-off rate could be higher than the regular consumption. The refrigeration unit is controlled by the tank pressure. The cooling coil in the tank should be made of seamless pipe or longitudinally welded steel tube, which has undergone non-destructive testing and shall not have any demountable connections in the tank.

An internal heating unit shall not be installed because of the inherent danger of nitrous oxide decomposition caused by overheating.

A small ambient air heated pressure build-up coil may be sufficient to maintain the required pressure, depending on the ambient temperature. Liquid is evaporated and the vapour re-introduced at the top of the stationary tank.

An external vaporizer is required in the withdrawal system at customer installations if $N_2O$ is to be used in the gaseous state. This should be an ambient air heated vaporizer.

If an external indirect heated vaporizer has to be used, then the heating shall be controlled to limit the temperature to a maximum of 150 °C. Indirect heating such as warm water, steam, warm air, other non-reactive substances or non-contact electrical heat with a temperature limit of 150 °C, which safeguards against overheating, shall be used.

An economizer may be used to prevent tank from pressure increase, as sometimes the withdrawal rate is less than the boil-off rate.

## 7.3 Piping, instrumentation, valves

The piping and instrumentation shall enable the following functions:

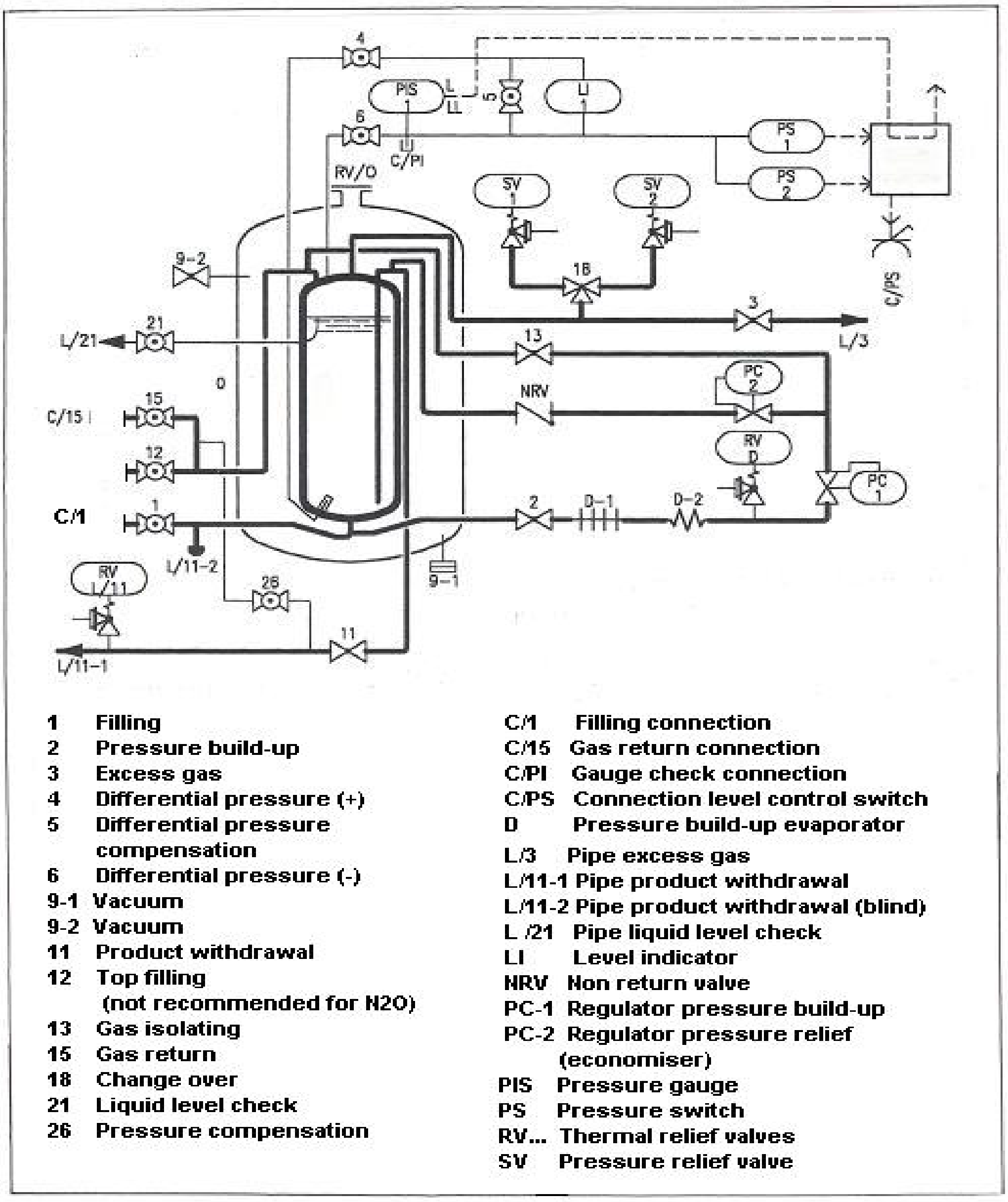
- Filling of liquid into the bottom of the tank is recommended. This would allow a potential decomposition starting at the pump to be quenched in the liquid phase.
- Product withdrawal should be by bottom line or via dip tube or through a vapour line if used to maintain tank pressure.
- Gas return to / from the top to accommodate two hose filling procedure with pressure compensation between stationary tank and transport tank.

***WARNING**: If there is any known risk of back contamination e.g. by impurities coming from customer tanks this method can only be used if proper mitigating measures have been taken.*

- Level indicator as an option (e.g. scale, load cell or differential pressure gauge). The admissible filling weight shall be marked.

- Pressure gauge to monitor the tank pressure. It can be combined with an alarm function for high and low pressure.
- Liquid level check (”full try cock“) to observe the maximum filling level. In some specific tank design the gas return line can be used as for liquid level check.
- Precaution against overpressure as a result of overfilling. Appropriate procedure and / or equipment shall be installed after a risk assessment has been performed [26].

An example of a P & I diagram of a stationary $N_2O$ tank is provided in Fig 3. The piping and instrumentation of $N_2O$ tanks can be different, depending on company standard and user’s demands.



| | |
|---|---|
| 1 | Filling |
| 2 | Pressure build-up |
| 3 | Excess gas |
| 4 | Differential pressure (+) |
| 5 | Differential pressure compensation |
| 6 | Differential pressure (-) |
| 9-1 | Vacuum |
| 9-2 | Vacuum |
| 11 | Product withdrawal |
| 12 | Top filling (not recommended for N2O) |
| 13 | Gas isolating |
| 15 | Gas return |
| 18 | Change over |
| 21 | Liquid level check |
| 26 | Pressure compensation |

| | |
|---|---|
| C/1 | Filling connection |
| C/15 | Gas return connection |
| C/PI | Gauge check connection |
| C/PS | Connection level control switch |
| D | Pressure build-up evaporator |
| L/3 | Pipe excess gas |
| L/11-1 | Pipe product withdrawal |
| L/11-2 | Pipe product withdrawal (blind) |
| L /21 | Pipe liquid level check |
| LI | Level indicator |
| NRV | Non return valve |
| PC-1 | Regulator pressure build-up |
| PC-2 | Regulator pressure relief (economiser) |
| PIS | Pressure gauge |
| PS | Pressure switch |
| RV... | Thermal relief valves |
| SV | Pressure relief valve |

**Figure 3: P & I diagram of a nitrous oxide vacuum insulated stationary tank**

### 7.4 Pressure relief valves

Each stationary tank for $N_2O$ should have two pressure relief valves that are connected in the vapour space. They shall conform to regulations and standards e.g. [20, 49].

### 7.5 Admissible filling degree / filling ratio

The admissible filling degree or filling ratio shall be verified for each stationary $N_2O$ tank.

Non-insulated tanks can be filled to the same maximum filling ratio as applied to cylinders and bundles see 9.1.

Insulated tanks should be filled to a level that prevents them to reach a liquid full condition before the vapour pressure is reaching the pressure relief device setting. When liquid nitrous oxide is stored in a tank and there is no product withdrawal, heat leak causes the temperature and pressure to rise and the liquid to expand. If the tank becomes liquid full, the hydrostatic pressure rise can cause its catastrophic failure.

The safe filling degree depends on the temperature of the liquid being transferred into the tank and on the pressure at which the pressure relief device is set to open. The colder the liquid, the more vapour space is required for liquid expansion. According to some national regulations and practical experiences the filling degree of insulated tanks shall not exceed 95 %.

The maximum filling level can be easily controlled by the ”full try-cock“.

### 7.6 Filling of stationary low pressure tanks

When stationary tanks are filled by a pump, for safety reasons the two-hose procedure should be applied in order to minimize pressure and mechanical stress. Filling shall be made through the bottom fill line. After it has been checked that there is no possibility of back contamination the gas phase shall be routed back to the transport tank. Tanks should not be filled by pump through the top equalizing line or any other line to the top. If filling is performed by pressure difference only without the use of a pump, the tank may be filled through the top line.

The differential pressure between the transport tank and the stationary tank shall be maintained at a level normally not exceeding 3 bar dif to ensure a smooth pump operation and to prevent creating any hot spots. Pump discharge pressure or flow shall be monitored to ensure that the pump is operated within the foreseeable performance conditions. The pressure and the level indicator of the stationary tank shall be monitored to avoid overfilling. The full try cock shall be opened at the end of filling to verify that the tank is not overfilled.

### 7.7 Product withdrawal

$N_2O$ shall be withdrawn as liquid and vaporized in an external vaporizer or taken from the gas phase of the tank. Requirements for the vaporizer see 7.2.

### 7.8 Product return

This operation occurs when product needs to be returned to the supplier and the tank to be emptied. This can only be performed under supervision of a qualified operator, observing specific procedure. Precautions shall be taken to avoid temperatures lower than the design temperature of the tank. Truck pumps shall not be used for emptying stationary tanks. If no suitable pump is available, pressure transfer shall be used.

## 8 Supply equipment

### 8.1 Cylinders

It is recommended to dedicate a stock of cylinders to the $N_2O$ service.

Suitable materials for $N_2O$ cylinders are carbon steel, Cr-Mo steel, stainless steel and aluminium alloys, see [54]. Cylinders made of non-metallic materials e.g. full composite, shall not be used.

Valve outlet connections shall be in accordance with national standards, where available and applicable, to avoid mix up of connections. The design and testing of valves shall follow the standards [56, 57] and valve materials shall meet the requirements in [54, 55].

Dip tubes made of non-metallic materials shall not be used. Electrical continuity shall be ensured for all parts of the cylinder and its accessories. For that purpose it is recommended to weld or to solder the connection between the dip tube and the cylinder valve. The valve shall be mounted such that electrical continuity is guaranteed.

To avoid accidental overpressure in the cylinder by overfilling, it is recommended to fit the valve with a bursting disk, that is designed to open at a pressure not exceeding, including all tolerances, 1,15 times the test pressure of the gas cylinder, see [15].

## 8.2 Bundles

Where bundles are used for transporting and storing $N_2O$ the individual cylinders in the bundle are usually manifolded together and terminate with one connection point for filling and discharge. Bundles are fitted with a main isolation valve. It is recommended that isolation valves are not fitted on each individual cylinder in a bundle to avoid overfilling of individual cylinders. Where non-closable fittings are used on each cylinder in the bundle only one bursting disc may be used to protect the bundle. If cylinders are equipped with individual valves, these valves shall be locked in an open position and equipped with a bursting disk.

The bundle shall be designed, manufactured and tested according to a proper code, e.g. [50].

Each individual cylinder shall be in accordance with 8.1. Pipes or hoses of metallic materials shall be used for the manifold. Connections within the manifold should preferably be welded or soldered.

## 8.3 Transport tanks

Insulated transport tanks are used for the transport of $N_2O$ refrigerated liquid. They shall fulfil the requirements of local transport regulations such as ADR or RID for Europe or DOT for USA.

Requirements to build such transport tanks are specified for vacuum insulated transport tanks e.g. in [48] and for non-vacuum insulated transport tanks e.g. in [52].

Insulation

Vacuum insulated transport tanks are preferred, since they present the best insulation against heat input to the inner tank.

If non-vacuum insulated transport tanks are used, the insulation should be “fire resistant” (see 7.1) and any connection that could become untight, e.g. manhole-flange, pipe flanges, screwed pipe, shall be separated from that insulation material. The insulation material shall be completely covered by a protective metal cladding.

Material

Suitable materials are aluminium, fine grain carbon steel and stainless steel for the tank including the baffles and accessories. Transport tanks shall be designed for a working temperature of –40 °C or lower and are commonly designed for a maximum working pressure of 24 bar. Material that will come in contact with the transported product should be approved for nitrous oxide. If no data are available on nitrous oxide compatibility, oxygen compatibility rules should be applied, e.g. according to [41].

Piping, instrumentation

Pipes, valves, flanges, couplings etc. shall be metallic. Seal and gasket materials shall be selected according to 5.2.

The piping and instrumentation shall enable the following functions:

- Filling of liquid into the bottom of the transport tank. This would allow a potential decomposition starting at the pump to be quenched in the liquid phase.
- Product discharge through bottom line.
- Gas return to / from the top for two hose filling procedure with pressure compensation between transport and stationary tank. A spray line in the top shall only be used during the initial cooling of a warm tank with product transfer from differential pressure (without the use of a pump).
- At least one “full try cock” in order to check the filling level limit.
- Level indicator to monitor the tank content as an option; operating principle is differential pressure.
- Pressure gauge to monitor the tank pressure.
- Pressure gauge to monitor the pump discharge pressure.
- Connections to allow sampling of liquid and gas phases.

Grounding

All parts of the transport tank shall be bonded to ensure electrical continuity.

### 8.4 Pumps

For transfer of refrigerated liquid $N_2O$ the following pump types are currently used:
- Gear pumps.
- Sliding vane pumps.
- Centrifugal pumps.

Any pump should have at least a nominal pressure that is equal to the maximum allowable working pressure of the tank. The pump discharge pressure should be in the range of 5 bar dif.

The requirements, which are laid down for liquid oxygen pumps shall be considered, see e.g. [17, 45].

In addition the design of the pump has to take into account ways of avoiding sources of heat or sparks, that may lead to an ignition and / or decomposition of $N_2O$:
- Cold bearings which are lubricated by $N_2O$ should be avoided. Warm bearings should be preferred, which are running outside the product containing part of the pump.
- The consequences of failures and consumption of wearing parts shall be considered very carefully. The periods of maintenance shall be taken into consideration.
- The clearances between moving and stationary parts within the pump shall be as large as practical, consistent with hydraulic performance and sealing.
- Fastenings of construction elements shall be properly secured to prevent them loosening during service.
- Mechanical seals are recommended.
- Material combinations of moving and stationary parts shall be selected to ensure that there is a low probability of ignition and spark production.

Installation

The pump shall be installed at the lowest point of the line so that the pressure drop on the suction side is as small as possible in order to reach the required “Net Positive Suction Head” (NPSH):
- The suction head (that means the height difference between the tank and the pump) should be as large as possible.
- The suction line should be as short as possible and its diameter should be greater than the diameter of the pump’s suction inlet. The suction pipe shall be designed according to pump manufacturer’s instruction assuring a sufficient NPSH.
- The suction pipe shall have as few bends as possible.
- The suction line shall be fitted with an appropriate filter, which shall have as little pressure drop as possible.
- Valves in the suction line should be capable of providing a full flow passage, e.g. ball valves.
- An emergency shut off valve should be installed in the suction line. This valve should be tripped automatically by the temperature and pressure control of the pump or by an operator. This action should also stop the pump.

- The external forces on the pump should be minimised, e.g. by using flexible pipes within the suction and discharge lines.
- The pump should be separated from the pump motor, if it is driven hydraulically.

All parts of the pump shall be bonded to ensure electrical continuity.

Lubrication

If a nitrous oxide pump needs lubrication in contact with $N_2O$ only oxygen compatible lubricants shall be used, see [45].

Dry running protection

The primary hazard during pump operation is dry running, which leads to heating and damage of the pump. In the case of $N_2O$, over heat can cause a decomposition reaction, which can lead to an explosion. Dry running is most often experienced at start-up of the pump and when loss of prime occurs during operation.

The following control measure shall be implemented:
Provide an automatic shut-off system that authorizes to start the pump after it has been properly cooled down and filled with liquid product and which protects from the dry running of the pump. Depending on the type of pump and usage, the system may be activated by differential pressure, temperature control, motor current and/or a suitable mass flow measuring device.

### 8.5 Hoses, accessories, couplings

Hoses are used for the transfer of liquefied $N_2O$ at ambient temperature or refrigerated liquid $N_2O$ at low temperature.

Hoses have to be designed, manufactured and tested to withstand the specified loads e.g. pressure, external forces, temperature etc. for the intended service, see e.g. [44].

Suitable materials of construction for hoses and other accessories (valves, pressure relief valves, flanges, pipes) are carbon steel, stainless steel and copper alloys. If other materials are used, e.g. for seals etc. the oxygen compatibility shall be considered, see e.g. [55] (ambient temperature service) or [41] (low temperature service).

Transfer hoses shall be protected against the ingress of dirt and moisture by caps and / or nuts, when not in use.

Hose couplings shall meet standardized basic requirements such as ”leak tightness“ or ”application by hand tools in a controlled manner“, see [46]. The couplings should be designed to avoid confusion between different gases, see [33]. Bolted flange couplings only partly meet the requirements. Therefore the EIGA coupling DN 60/PN 40 [34] or other suitable standard connection that prevents unsafe connection with other gases should be used for filling transport tanks. The version of the EIGA coupling with code No.15 has been allocated specifically to $N_2O$ service. For filling customer tanks a smaller diameter coupling is required and therefore the EIGA coupling cannot be used.

The coupling for the liquid filling line shall be different from the coupling for the gas return line in order to avoid confusion between liquid and gas.

All hoses, accessories and couplings shall be constructed such that electrical continuity is ensured.

The fill and product discharge connections of small transportable cryogenic containers should be permanently attached to the container by welding or brazing, see [39].

## 9 Product transfer

### 9.1 Cylinders and bundles

Cylinder / bundle filling stations shall be designed and built to withstand the pressure loads and the external loads during service to allow safe filling.

Nitrous oxide cylinder / bundle filling stations consist of the following main elements:
- Vacuum- or non-vacuum insulated stationary tank, working pressure around 20 bar or non-insulated high-pressure tank, working pressure around 80 bar.
- Reciprocating pump, working pressure up to 100 bar. The pump should be equipped with protection against dry running, e.g. by means of a thermocouple to monitor the temperature on the discharge side. Only oxygen compatible lubrication, where the lubricant could be in contact with $N_2O$ shall be used.
- A pump by-pass if the pump is running continuously. The by-pass line should feed back into the gas phase of the tank (manual closing of the filling line).
- In case of no by-pass line the pump must be automatically switched off when the cylinders are full.
- Pipe from the pump to the filling point partly or completely insulated.
- Filling scales, with the required accuracy for large and small cylinders.
- Cylinder / bundle emptying manifold with vacuum pump.
- Filling hoses should be equipped with safety cable.
- Cylinder / bundle filling point.

The following additional requirements shall be met:
- The installation shall be designed and operated in accordance with local regulations for oxidizing and medical gases.
- Written operating procedures, which describe all steps of the filling process (prefill check and reconditioning of the cylinders, tare weight check, control of filling weight). For details of a recommended gravimetric filling procedure see e. g. [30]. Filling of non-empty cylinders (“top filling”) and filling by pressure without scale shall not be applied.
- The admissible filling ratio is dependent on the test pressure of the cylinder, see table 5 or by local regulations.

**Table 5**
[1, Packing Instruction P 200]:

| Minimum cylinder test pressure, bar | Maximum filling ratio |
|---|---|
| 180 | 0,68 |
| 225 | 0,74 |
| 250 | 0,75*) |

*) This means e.g. that a cylinder with 10 litre capacity and test pressure 250 bar may be filled with 7,5 kg nitrous oxide.

All parts of a filling installation shall be bonded and earthed to ensure electrical continuity. The electrical potentials between the cylinder / bundle and the ground should be equalised during filling (resistance < 10 $\Omega$). If necessary the cylinder / bundle should be bonded directly to ground.

### 9.2 Transport tanks

Refrigerated liquid $N_2O$ is normally transferred from a stationary tank at the production plant into the transport tank and then transported to the consumer.

A ground-mounted pump adjacent to the stationary tank should be used to fill the transport tank. The suction pipe shall be designed according to pump manufacturer’s instruction assuring a sufficient

NPSH. The on-board pumping system of the transport tank should not be used, as the pump suction is not designed for this type of transfer.

In addition, the transport tank filling area shall meet the following requirements:

- The ground in the filling connection area should be covered with non-combustible material such as concrete or natural stones. Wood is not acceptable.
- Transport tanks should be equipotentially bonded to the stationary tank during product transfer.
- Connections, seals and transfer hoses shall be kept clean by using caps, plugs etc.

Transport tanks should be filled by the two-hose filling procedure in order to minimize pressure differential and the hazard of decomposition. Filling shall be made through the bottom fill line and the gas phase shall be directed back to the stationary tank. Filling through the top equalizing line or any other line to the top is not recommended in order to avoid heat input into the gas phase by a hot running pump.

During filling the pump discharge pressure shall be monitored to ensure that the pump operates within the specified performance conditions. The pressure and the level indicator of the transport tank shall be monitored to avoid overfilling and at completion of filling the “full try-cock” shall be opened to verify that the filling quantity is correct.

Further operational requirements are laid down for vacuum insulated transport tanks in [48] and for non-vacuum insulated transport tanks in [52].

The principles of safe filling of transport tanks can also be applied for cryogenic receptacles.

Filling degree

ADR transport tanks can be filled to 98 % at the specified filling temperature and pressure. UN portable tanks can be filled to a level where the filling degree does not exceed 98 %, if the vapour pressure is equal to the maximum allowable working pressure. These requirements appear sufficient to avoid the pressure relief system of the tank releasing $N_2O$ during a normal delivery.

If the expected journey time is longer than the holding time, specified for the transport tank, the initial filling degree shall be reduced to 95 % or less. A more accurate procedure for calculating the correct filling degree is described in appendix 1.

## 10 Emergency response

### 10.1 Hazards

Regarding the hazards associated with $N_2O$ see 4. Hazards of $N_2O$ and other chemicals involved in the production of $N_2O$ are also described in the relevant Safety Data Sheets and in references [12, 13, 14].

### 10.2 Procedures for large leaks or spills of $N_2O$

Isolate the leak without putting oneself at risk. If possible, orientate leaking containers such that the gas escapes rather than the liquid.

Isolate the area affected by the spill or leak for at least 25 to 50 meters in all directions, keep unauthorized persons away and stay upwind. In the event of large spills consider initial downwind evacuation for at least 500 meters.

Prevent the leaking gas / liquid from reaching low lying areas and prevent entry into drains, sewers, basements or confined spaces.

Ventilate and check confined spaces and rooms before entering. The check must be conducted by competent personnel who are trained to detect potential atmospheric hazards.

Entering confined spaces, where potential $N_2O$ enrichment has occurred, requires the use of a portable oxygen sensor. If the oxygen content falls below 18 % a positive pressure self-contained breathing apparatus shall be required [36].

In the event of large $N_2O$ spills, use water sprays to reduce vapours or divert vapour cloud drift. Do not direct water at the spill or at the source of the leak. Avoid water contact with pressure relief valves, as icing may occur.

Do not touch or walk through spilled liquid.

Prevent contact of $N_2O$ with materials, which are sensitive to cold, such as rubber or plastics.

Never use sawdust or other combustible absorbent material on $N_2O$ spills.

### 10.3 Procedures at fire situations

Plant personnel should only be restricted to fight minor fires; only professional fire fighters can cope with large fires. Recommend evacuation of plant if there is a fire in the nitrous oxide area.

Fires involving combustible materials with $N_2O$

$N_2O$ can strongly support the combustion of materials such as wood, paper, oil, clothing, etc. In dealing with any fire situation these materials shall be kept at a safe distance from the fire.

Materials burning in $N_2O$ can produce irritating and toxic gases. Use respiratory protection while extinguishing fires.

Use a suitable extinguishing agent for the type of fire in question such as dry chemical, carbon dioxide or water spray.

Fire in the area of $N_2O$ tanks

Tanks and pressure receptacles that are exposed to fire or extreme heat can rupture due to increase of temperature and pressure. This can occur in spite of pressure relief equipment. Fragments of metal will be ejected through the air.

Transport tanks and pressure receptacles should be removed from the immediate fire area, if this can be achieved without risk to personnel. If this is not possible, the concerned equipment should be immediately cooled with water jets directed from a safe position, e. g. from behind heavy machinery or solid wall.

If fire involves any tanks or pressure receptacles it shall be fought from a safe position or by using unmanned water monitors. Water-cooling of the equipment should be continued after the fire has been extinguished. Retreat immediately if the pressure relief equipment emits a hissing sound or discoloration of the tank or pressure receptacle is observed. Consider initial evacuation around an 800 m perimeter.

In the event of a fire in the area containing either cylinders or bundles of $N_2O$, then the EIGA recommendations [38] should be followed.

### 10.4 Procedures at traffic accident involving a transport tank

See [29].

The actions required in the event of incidents or accidents involving $N_2O$ transport tanks depend on the circumstances.

The following is given as guidance only regarding the type of action that could be required from drivers.

Where practicable, company guidance should be obtained before any major action is taken and co-operation with the police and other emergency services shall be given at all times.

In the event of breakdown

- If a stop is required on the roadside due to a breakdown, look for a parking area as far away as possible from built up areas.
- Stop the engine and switch on hazard warning lights. Put warning signs on the road.
- If the position of the vehicle is likely to cause a serious traffic hazard or obstruction, notify the police.
- Report to the company for instructions regarding further actions required, such as arrangements for assistance with repairs, changes of tractor, transferring the product from the transport tank to another vehicle.

In the event of accident

- If involved in an accident, stay calm, give first aid if possible.
- Stop the engine. Avoid unshielded flames. Do not smoke. Switch on hazard warning lights and position warning signs in the road.
- Put on your high visibility clothing.
- Notify the police and, if necessary, the ambulance or fire brigade.
- Keep bystanders at a distance and report to the company.
- Frequently check transport tank pressure and, if necessary, vent $N_2O$ gas to the atmosphere in order to reduce the pressure below the maximum allowable pressure. Try to find a safe place for venting and remember to take additional precautions to prevent fire hazards.

In the event of leak or spill

- In the event of minor leaks, whenever possible, and if no hazards are involved, check and close any valves to isolate the point of leakage.
- If there seems to be no damage to $N_2O$ tank or pipework that could develop into more serious failures, report to the company and, unless instructed otherwise, drive transport tank to the nearest company premises. Check tank pressure regularly during the journey.
- If leakage appears to be increasing, stop in a suitable place away from built-up areas, and proceed as detailed below for major leaks.
- In the event of major leaks drive to a suitable place well away from built-up areas, major roads, railways, tunnels etc. The object of this manoeuvre is to ensure that the prevailing wind carries any $N_2O$ gas further away, allowing it to disperse without danger.
- Notify the police and report the situation to the company. Inform emergency service about the nature of the leak. Stay in attendance throughout any discharge of $N_2O$. Warn others of danger, ensure no one in the vicinity is working in cellars, basements or trenches and consider initial downwind evacuation for at least 500 meters.

In the event of transport tank overturning

- If a transport tank overturns, or is lying on its side, the gas and liquid valves may be reversed, so that the liquid $N_2O$ discharges from the gas valve and vice versa.
- Depending on the position of the transport tank in the overturned position, it may not be possible to vent gas from either the liquid valve or the gas valve.

In the event of fire

- If the transport tank is involved in a fire, notify the police and emergency service and report the situation to the company. If possible, drive the vehicle away from all inhabited areas and main roads.
- The company should assist the fire brigade by providing information about the hazards and properties of $N_2O$.

### 10.5 Personal protective equipment (PPE)

The following PPE is recommended for the emergency services:

- Structural fire fighters protective clothing is only recommended for fire situations, it is not effective in spill situations.
- Use respiratory protection while extinguishing fires, as fire in the presence of $N_2O$ may produce irritating and toxic gases.
- In the event of minor leakage, wear head protection, safety goggles, gloves and safety shoes. Ensure that the area is appropriately ventilated.
- In the event of major leakage, wear thermal protective clothing, face shields, cryogenic gloves, safety shoes and respiratory protection.

Requirement for the driver: Wear protective gloves, warning vest, safety goggles or face shield.

### 10.6 First aid

<u>In the event of inhalation:</u>

Move the victim to fresh air, call the emergency medical services. Apply artificial respiration if the victim is not breathing; administer oxygen if difficulty is experienced with breathing.

<u>In the event of contact with liquid</u>

Remove and isolate contaminated clothing and shoes. Clothing frozen to the skin should be thawed before being removed. Thaw the frosted parts with lukewarm water. Spray with water for at least 15 minutes, apply a sterile dressing, keep victim warm and calm and obtain medical assistance.

Ensure that medical personnel are aware of the product involved and take precautions to protect themselves.

<u>Ingestion</u>

Ingestion is not considered a potential route of exposure.

## Appendix 1 - Filling degree of transport tanks and cryogenic receptacles

Transport tanks and cryogenic receptacles are filled to a weight not exceeding the allowable mass and to a required volume related to the filling degree.

The maximum allowable mass of the transport unit is indicated on the marking plate or on the tank wall and depends on the design loads of the transport unit and the allowable loads according to the transport regulations, e.g. road regulations.

The volume related filling degree is required by the regulations for transport of dangerous goods and shall avoid the relief system of the tank / cryogenic receptacle opening during transport. The following applies according to the European transport regulations:

- The filling degree is limited to 98% under filling temperature and filling pressure for cryogenic receptacles and tanks [1].
- For portable tanks the filling is limited to a degree so that the volume occupied by the liquid $N_2O$ will not exceed 98% if the vapour pressure is equal to the MAWP of the tank. In addition the actual holding time has to be calculated for each journey and indicated on the tank. The expected duration of the journey shall not exceed the actual holding time of the transport tank.

These requirements are sufficient to avoid the pressure relief valves releasing $N_2O$ during a normal delivery of the relevant transport unit, e.g. a daily round trip of a transport tank to deliver $N_2O$ to customer tanks or a longer journey of a portable tank.

Nevertheless if any doubt exists as to whether the pressure relief valves will remain closed during the expected journey the following considerations should be made to verify the conditions of the filled tank and the conditions of the empty tank. For these calculations see also e.g. [42].

These considerations are made for transport tanks but they may also be applied to cryogenic receptacles.

The following data is required:

- Water capacity V of the tank (litres).
- MAWP of the tank (bar), which is equal to the set pressure of the pressure relief valves.
- $N_2O$ vapour pressure (bar) in the tank just immediately after filling.
- Heat leak performance of the tank (Joule/hour), based on the expected average ambient air temperature. This value may be supplied by the manufacturer of the tank or may be calculated taking into account the heat inleak through the insulation of the tank, the support system of the tank and the piping to the tank.

Tank filled with $N_2O$

For the heat consideration of the filled tank the vapour phase in the tank can be neglected.
The following shall be made to verify the filling degree for a certain journey:

- From the table, take:
  → enthalpy, liquid $h_{sl}$ (kJ/kg) at vapour pressure at filling,
  → enthalpy, liquid $h_{fl}$ (kJ/kg) at vapour pressure of MAWP.
- Heat leak Q (kJ/h) for the tank.
- Mass $m_{sl}$ (kg) of liquid $N_2O$ in the tank after filling.
- Expected duration $t_e$ (hours) of the journey.

Calculate the time $t_c$ (hours) for the pressure relief valves to open:

$$t_c = (h_{sl} - h_{fl})\, m_{sl} / Q$$

If $t_c$ is smaller than $t_e$ the vapour pressure of the tank has to be reduced, e.g. by releasing vapour from the tank.

Sometimes it is necessary to calculate the maximum allowable vapour pressure in the tank. The following formula should be used to calculate $h_{sl}$:

$$h_{sl} = h_{fl} + (Q^*t_e) / m_{sl}$$

and the vapour pressure that relates to $h_{sl}$ is taken from table 6.

In addition it has to be verified that the tank will not be completely filled with liquid before the vapour pressure reaches a value that is equal to the MAWP:

From table 6, take

- the density $\rho_{sl}$ (kg/dm³) of the liquid at filling related to $h_{sl}$,
- the density $\rho_{fl}$ (kg/dm³) of the liquid at MAWP related to $h_{fl}$.

Calculate the maximum allowable filling degree for the expected journey by using the formula

$$\text{Filling degree (\%)} = (\rho_{fl} / \rho_{sl}) \, 100$$

For UN portable tanks this value is limited to 98%, in this case the following formula must be used

$$\text{Filling degree (\%)} = 0.98 \, (\rho_{fl} / \rho_{sl}) \, 100$$

Example:
For a ADR tank with MAWP of 20 bar that will be filled with $N_2O$ with a vapour pressure of 15 bar (which is a tank pressure of 14 bar) the filling degree should be less than

$$(0.998/1.044) \, 100 = 95.6\%.$$

For an UN transport tank with MAWP of 20 bar that will be filled with $N_2O$ with a vapour pressure of 15 bar (which is a tank pressure of 14 bar) the filling degree should be less than

$$0.98^*(0.998/1.044) \, 100=93.7\%.$$

If the actual filling degree is greater than the allowable value the filling degree has to be reduced e.g. by discharging liquid $N_2O$.

In some cases it may be more useful to compare the masses:

Allowable mass of filling (kg):

$$m = V \rho_{sl} \text{ (filling degree)}$$

If the mass in the tank after filling will be greater than the allowable mass, liquid $N_2O$ has to be discharged.

Empty tank

It is very important to consider also the journey of the discharged tank back to the filling station because the heat capacity of the load is reduced by discharging the liquid $N_2O$. For this consideration the liquid and the vapour phase of the transported $N_2O$ has to be taken into account.
In addition to the information necessary for the consideration of a filled tank the following shall be available:

- Residual mass $m_{sl}$ in kg of liquid $N_2O$ in the tank
- From table 6, take
  - → enthalpy, vapour $h_{sg}$ (kJ/kg) at the vapour pressure of the discharged tank,
  - → enthalpy, vapour $h_{fg}$ (kJ/kg) at vapour pressure of MAWP,
  - → vapour density $\rho_{sg}$ (kg/dm³) at the vapour pressure of the discharged tank.

Calculate the mass $m_{sg}$ (kg) of $N_2O$ vapour within the tank:

$$m_{sg} = [V - (m_{sl} / \rho_{sl})] \, \rho_{sg}$$

Then calculate the time $t_c$ (h) for the relief valves to open:

$$t_c = [(h_{sl} - h_{fl})\, m_{sl} + (h_{sg} - h_{fg})\, m_{sg}\,] / Q$$

If $t_c$ is smaller than $t_e$

- the vapour pressure of the tank has to be reduced, e.g. by releasing vapour of the tank,
- or the residual mass of liquid has to be increased,
- or the duration of the journey has to be reduced e.g. by using an intermediate stop where the pressure in the tank can be released.

**Table 6**

| Vapour pressure (bar abs) | Temperature °C | Density, liquid (kg/dm$^3$) | Density, vapour (kg/dm$^3$) | Enthalpy, liquid (kJ/kg) | Enthalpy, vapour (kJ/kg) |
|---|---|---|---|---|---|
| 10 | -38.50 | 1.085 | 0.028 | -154.443 | 168.381 |
| 11 | -35.79 | 1.077 | 0.030 | -149.605 | 168.943 |
| 12 | -33.30 | 1.069 | 0.032 | -145.067 | 169.460 |
| 13 | -31.05 | 1.059 | 0.035 | -140.847 | 169.929 |
| 14 | -28.79 | 1.049 | 0.038 | -136.627 | 170.397 |
| 15 | -26.64 | 1.044 | 0.040 | -132.522 | 170.671 |
| 16 | -24.48 | 1.039 | 0.042 | -128.417 | 170.945 |
| 17 | -22.45 | 1.032 | 0.045 | -124.464 | 171.130 |
| 18 | -20.56 | 1.024 | 0.048 | -120.694 | 171.209 |
| 19 | -18.67 | 1.015 | 0.051 | -116.924 | 171.287 |
| 20 | -16.95 | 1.007 | 0.054 | -113.537 | 171.359 |
| 21 | -15.42 | 0.998 | 0.056 | -110.551 | 171.424 |
| 22 | -13.88 | 0.989 | 0.058 | -107.565 | 171.489 |
| 23 | -12.35 | 0.981 | 0.061 | -104.579 | 171.554 |
| 24 | -10.79 | 0.972 | 0.064 | 101.358 | 171.502 |

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EIGA's publications are subject to periodic review and users are cautioned to obtain the latest edition.

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[46] EN 13371 Cryogenic vessels – Couplings for cryogenic service.
[47] EN 13458/1-3 Cryogenic vessels – Static vacuum insulated vessels – Fundamental requirements / Design, fabrication, inspection and testing / Operational requirements.
[48] EN 13530/1-3 Cryogenic vessels – Large transportable vacuum insulated vessels – Fundamental requirements / Design, fabrication, inspection and testing / Operational requirements.
[49] EN 13648/1 Cryogenic vessels – Safety devices for protection against overpressure – Safety valves for cryogenic service.
[50] EN 13769 Transportable gas cylinders – Cylinder bundles – Design, manufacture, identification and testing.
[51] EN 14197/1-3 Cryogenic vessels – Static non-vacuum insulated vessels – Fundamental requirements / Design, fabrication, inspection and testing / Operational requirements.
[52] EN 14398/1-3 Cryogenic vessels – Large transportable non-vacuum insulated vessels – Fundamental requirements / Design, fabrication, inspection and testing / Operational requirements.
[53] ISO 10156 Gases and gas mixtures – Determination of the fire potential and oxidizing ability for the selection of cylinder valve outlets.
[54] ISO 11114/1 Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Metallic materials.
[55] ISO 11114/2 Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Non-metallic materials.
[56] ISO 10297 Transportable gas cylinders – Cylinder valves – Specification and type testing.
[57] EN 849 Transportable gas cylinders – Cylinder valves – Specification and type testing.
[58] EN 720-2 Transportable gas cylinders – Gases and gas mixtures – Determination of flammability and oxidizing ability of gases and gas mixtures.
[59] EN 1626 Cryogenic vessels – Valves for cryogenic service.

**EC Directives**

[60] IPPC 96/61/EC Integrated Pollution Prevention and Control Directive.
[61] EC Guide to Good Manufacturing Practice (GMP).
[62] 2003/87/EC Greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC.