CDI Best Practice Recommendation Regarding the use of Nitrogen

Contents

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For details of CDI Publications:
WITHERBY Seamanship INTERNATIONAL
www.witherbyseamanship.com

First Edition 2012

eISBN 978-1-85609-566-2

British Library Cataloguing in Publication Data
Chemical Distribution Institute, UK

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Published in 2012 by
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Edinburgh, EH54 8SB
Scotland, UK

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PREFACE

The CDI Foundation was formed in 1994 and is a non-profit making and non-commercial organisation funded by the chemical industry. www.cdi.uk.org

CDI is the voice of the chemical industry, representing 72 Chemical companies across the whole chemical logistic supply chain in the marine, terminal and container sectors of the industry and is responsible for the accreditation of inspectors and auditors to provide inspection and audit reports for use in the risk assessment process.

Driven by the expertise of the world's leading chemical manufacturers, CDI sets out to be the global source for data, information and advice specific to marine transportation and the storage of chemical products, whether that is in bulk or packaged form. The Business Objectives of CDI are set out in CDI's Quality Policy Statement as approved by the CDI Board of Directors, summarised as follows:

1. To constantly improve the safety, security and quality performance of marine transportation and storage for the chemical industry.
2. Through cooperation with industry and centres of education, drive the development of industry best practice in marine transportation and storage of chemical products.
3. To provide information and advice on industry best practice and international legislation for marine transportation and storage of chemical products to customers and stakeholders.
4. To monitor current and future international legislation and provide experience, knowledge and advice from the chemical industry to the legislators.
5. To provide chemical companies with cost effective systems for risk assessment, thus assisting their commitment to Responsible Care and the Code of Distribution Management Practice.
6. To provide a single set of reliable and consistent inspection data which chemical companies can use with confidence
7. To provide the chemical industry with an independent organization for:
   - Training; qualification and accreditation of inspectors.
   - Development and maintenance of databases on which inspection and risk assessment information can be promulgated.

With the above objectives in mind, and concern at the on-going number of fires and explosions on board chemical tankers: In spring 2012, The CDI Marine Executive Board instructed its Technical Committee to draw up a Best Practice Recommendation regarding the use of nitrogen on board chemical tankers for use by the chemical industry as appropriate. Consequently, the Technical Committee met on two occasions during 2012 and concluded its work in the form of this document.

The objective of the paper is to set out the Chemical industries recommendation regarding the use of Nitrogen on sea going chemical tankers and to supplement safer ways of working within the industry, fully recognising the dangers of Nitrogen, both to people and ships, and the means to address this: no more, no less. The paper is "not" intended to supplant any regulations that IMO may, at some time in the future, introduce. The document is an evolving living document that will be periodically reviewed by CDI. Any comments to the paper should be directed to the CDI General Manager howard.snaith@cdim.org

ABBREVIATIONS

IMO	International Maritime Organisation
CSB	US Chemical Safety Board(www.csb.gov)
TSG-C	Tanker Safety Guide Chemicals (3rd Ed, 2002)
IBC Code	International Bulk Chemicals Code (2007)

1. Introduction

The purpose of this document is to provide the chemical industry best practice recommendation for consideration during the inerting process and future revisions of legislation and industry guidelines. In addition, this document is directed towards any party involved with tank ships carrying chemicals, including, but not limited to, vessel personnel, shore personnel, surveyors, inspectors and charterers. This document will be periodically reviewed by CDI.

While not directed towards other vessel types, much of the information included here may be applicable when nitrogen is used. Any person who affects the policies, procedures or processes used in the carriage of chemicals should understand the implications of using nitrogen on board the vessel.

It is expected that the use of nitrogen will increase within the maritime industry (both ashore and on board), and this could lead to an increase in nitrogen related incidents if not properly managed. It is recognised that implementation of the recommended best practice could impact upon the commercial and operational aspects of both vessels, terminals, and the industry as a whole which could lead to other changes within the industry to help mitigate these impacts. As nitrogen generators on board chemical tankers become more prevalent, it could allow further alternatives to address these emerging issues.

Flue gas (inert gas generated through combustion of fuels) was introduced on-board large tank vessels by the oil industry as a barrier to tank explosions by reducing the tank's oxygen content safely below that level needed to support combustion. Rules governing the installation and operation of inert gas systems were subsequently developed by IMO under the SOLAS convention. Due to the high quality requirements for many chemicals, flue gas was not deemed suitable for use on chemical tankers which were exempt from having to comply with the SOLAS IG rules providing certain conditions were met. With the development of efficient nitrogen generators chemical tankers began to be fitted, or retrofitted, with this equipment. Many of these units were sized and installed for use in padding and topping up (and thus, of insufficient capacity to inert cargo tanks as they are being discharged), but it is expected that as the industry moves towards the greater use of nitrogen, more and more of these systems will be of sufficient capacity for this use, which potentially creates additional issues to be addressed. As it is recognised that vessels without a nitrogen generator can still be exposed to nitrogen through other sources (i.e. shore-supplied nitrogen, nitrogen bottles, etc.), this document also provides general precautions regarding nitrogen operations on-board vessels that do not have a nitrogen generator.

Nitrogen has been in use for many years on chemical tankers to reduce the oxygen content in empty tank spaces (and even occasionally adjacent void spaces) when carrying certain chemicals, which can be adversely affected by Oxygen. This is done either for safety reasons, such as to prevent a flammable atmosphere from developing (e.g. Propylene Oxide), for cargo quality reasons (e.g. Hexene 1 or Hexamethylene Di Amine), and for other uses on the vessel (e.g. cargo handling, or inerting void spaces or cofferdams).

Nitrogen is 78% part of the atmosphere, (with the remainder consisting of 21% Oxygen and 1% others) and is consequently undetectable to human senses

Increased CO_2 concentration in a person's lungs is the biological trigger to inhale; nitrogen asphyxiation kills by eliminating that trigger.

Nitrogen is

1. Inert
2. Non-flammable
3. Non-toxic
4. Colourless, odourless & tasteless
5. Marginally lighter than air

Nitrogen-related incidents have occurred, both ashore and aboard ships, over many years, many of which have resulted in fatalities when personnel have entered, or worked too close to spaces where the atmosphere had been displaced by nitrogen. Reports of such incidents can be found in various publications (see References for some of these documents)

The US Chemical Safety Board (CSB) issued the following statistics regarding nitrogen asphyxiation incidents, though not necessarily related to vessels. (http://www.csb.gov/assets/document/SB-Nitrogen-6-11-03.pdf)

1. 85 nitrogen asphyxiation incidents occurred in the decade between 1992 and 2002 resulting in an average of 8 deaths and 5 injuries per year
2. 80 people were killed and 50 were injured in these 85 incidents

Access to more recent statistics is not currently readily available. Information from maritime industry personnel point out that incidents continue to occur, thus leading to the need for further guidance within the industry.

2. Hazard Identification

There are particular hazards related to the properties of nitrogen. Some of the general hazards of nitrogen include:

1. There is NO warning when an atmosphere is oxygen deficient as a result of nitrogen displacement.
2. Any inhalation of nitrogen can cause a loss of consciousness and possible death. Even a small inhalation of nitrogen can lead to fatality (see also MSC.1/1401).

The following hazards have been identified with N_2 operations:

1. Oxygen depletion is most often associated within enclosed spaces.
2. Inhalation of N_2 is possible even when standing in the open.
3. Over pressurisation of cargo tanks (By uncontrolled/excessive volumes of nitrogen).
4. Sudden / Unexpected release of pressure when opening tanks which are under "pressure" with nitrogen

3. Best Practice Recommendations

1. Nitrogen should be used as an inert gas during cargo and tank cleaning operations involving low flash chemical cargoes. In keeping with the IMO definition, for purposes of this document, "low flash chemical cargoes" are defined as those which have a flashpoint of <60C, or any cargo with a flashpoint equal to or greater than 60 C that are carried or transferred at a temperature from 10 C below its flashpoint or higher.
2. In any situation where nitrogen is used, safety precautions should be in place in accordance with Section 5 of this document.
3. Oxygen levels must be maintained at or above the minimum level required by oxygen-dependent inhibitors[1] used with certain self-reactive chemical cargoes (examples: styrene and acrylonitrile). In such cases, padding (or blanketing) with N_2 during transit must be strictly controlled in accordance with the cargo requirements and/or inhibitor certificate as applicable. Using nitrogen during discharging

[1] IBC Code 15.13

and tank cleaning operations should also be strictly controlled to ensure the oxygen level is maintained within the appropriate limits.

In operational situations such as above, while handling a product that is oxygen dependant, a risk assessment should be carried out and possible mitigating controls,such as maintaining a certain level of oxygen, must be considered.

4. There maybe exceptional circumstances where nitrogen is incompatible with a particular chemical. In these circumstances, a risk assessment should be used to identify and mitigate any risks. It is recommended that ship owners work with the product owner or charterer to evaluate the use of nitrogen and associated risk management measures to be used in these situations.
5. Cargo tank gas freeing should only be carried out using the approved venting system on the vessel.
6. Not all vessels have access to nitrogen on board. However, as nitrogen may also be received from shore, the dangers identified and recommendations included within this document remain for these vessels as well.

4. Nitrogen Operations

4.1 Safety Precautions when Handling Nitrogen

Due to the hazards described in this document, nitrogen should be used with the following safety precautions in place:

1. The shipping company should have procedures to address the hazards of working with nitrogen, including those incorporated in this document, and the crew should be trained and familiarised with these procedures. Records of training should be maintained on-board and verified by office safety personnel.
2. The company safety procedures should prohibit the use of canister type filter masks during operations where personnel may be exposed to nitrogen.
3. A compressed air breathing apparatus should be used when a crew member could be exposed to nitrogen. This may include working in close proximity of an opening to any space designated as “inerted with nitrogen” or in the process of inerting with nitrogen.
4. Areas where personnel may be exposed to nitrogen should be restricted only to the personnel who are directly involved in the operation. Personnel working in these areas should wear a personal oxygen meter.
5. Personnel should be aware that deck structure/ lay-out may create areas that can allow nitrogen to accumulate near nitrogen-inerted spaces. This can result in an oxygen-deficient atmosphere, even on an open deck.
6. Enclosed spaces inerted with nitrogen should be tagged with suitable warning signs, such as: “Danger Nitrogen, do not enter”. (Other visual warning signs or symbols are depicted in Appendix 1), such warning signs, if exposed to weather, should be legible at all times.
7. If a space may be oxygen-deficient, all tank openings (besides those used as part of the gas-freeing operation) should be kept closed until the space has been cleaned, ventilated, and tested to ensure it is gas-free. Openings to other spaces, that could be oxygen-deficient, such as a nitrogen generator room, should be kept closed and secured, and verified as safe prior to entering.
8. All confined spaces on board, including cofferdams, void spaces and trunks, should be assumed to be oxygen-deficient until tested and proven otherwise.
9. Prior to entry into any space, personnel should verify that there are no connections into any part of the system that could allow nitrogen to enter the space that is to be entered, even if

not directly connected to the space (i.e. vapour return systems, common vent lines or other tanks connected through run-arounds, etc.).

10. Oxygen resuscitation units should be readily available in case of hypoxia due to nitrogen inhalation.
11. When nitrogen is provided from shore, the pre-transfer conference between the vessel and shore personnel must include a discussion addressing the operational and safety hazards related to the operations to take place as described in sections 4.3 and 4.4. All issues concerning the supply of nitrogen from shore, such as maximum pressures and flow rates, should be agreed and appropriate safety procedures implemented.

    When nitrogen is provided by the vessel itself, vessel personnel should also conduct a risk assessment to cover the same types of issues.

4.2 Entry into Enclosed Spaces Containing Nitrogen

See: IMO MSC.1/1401

Guidelines on Tank Entry for Tankers Using Nitrogen as An Inerting Medium
www.mardep.gov.hk/en/msnote/pdf/msin1127anx1.pdf

4.3 Purging/Inerting Operations: (definitions)

It is important to recognise that in the chemical industry, the words "inerting" and "purging" are often used interchangeably. To avoid confusion, especially with personnel who may shift between different types of products and/or vessels, it is recommended that the definition of the terms should be aligned with those incorporated in ISGOTT. It is preferred to use "inerting" to refer to the displacing of oxygen or moisture with nitrogen prior to loading. "Purging" should refer to the use of an inert gas to further reduce the oxygen or flammable gas concentration in a tank containing product residue to a level below the lower flammability range. It is important that instructions and procedures are clear and specific as to the operation to be conducted. In any context that the terms are used, the precautions and hazards regarding the use of nitrogen remain the same.

Clean and empty cargo tanks may be inerted with nitrogen prior to loading cargo. The flow rate may be as low as 100 m^3/hr or as high as several thousand m^3/hr, and it should be ensured that there is sufficient venting capacity to avoid over-pressuring the cargo tank or space. Whenever possible, the nitrogen mixture should be released through the approved venting arrangement. When this nitrogen mixture must be released through some other means, a risk assessment should be completed as described earlier in this document.

4.4 Padding Operations

Vessels may receive nitrogen after loading in order to reduce the oxygen content in the ullage space of the cargo tank or to apply a positive pressure to prevent the ingress of moisture or oxygen during the voyage. Numerous tank over-pressurisation incidents have occurred during padding operations. Often the nitrogen is supplied by shore through the cargo line resulting in a large volume of nitrogen being released into the bottom of an already loaded cargo tank. The pressure in the tank may increase rapidly above the venting capacity of the P/V valve or the liquid level in the tank forced to rise blocking the vent line. This can result in extensive structural damage to the tank as well as a loss of containment. The following precautions should be considered:

1. When possible, padding operations should be conducted through the vapour side of the vessel system rather than through the liquid in the cargo line and tank.
2. Nitrogen (or any other gas) flow should never be controlled through the main cargo or vapour line manifold valve. Instead, flow should be

controlled through a small diameter line fitted with a ball valve, enabling the vessel to control the flow of nitrogen.

3. In all cases, the delivery rate of nitrogen (m^3/hr) should not exceed the operational limits of the tank venting system at any time.
4. It is preferable for the shore to provide a dedicated pressure control system fitted at the junction between the shore inlet line and the ship to manage the pressure and flow coming on board the vessel.
5. As previously stated, oxygen levels must be maintained at or above the minimum level required by oxygen-dependent inhibitors[2] used with certain self-reactive chemical cargoes (examples: styrene and acrylonitrile). In such cases, padding (or blanketing) with N_2 (either at the berth or during transit)must be strictly controlled in accordance with the cargo requirements and/or inhibitor certificate as applicable. Using nitrogen during discharging and tank cleaning operations should also be strictly controlled to ensure the oxygen level is maintained within the appropriate limits. Similarly, bubbling nitrogen through these types of products must be avoided, as this could drive oxygen out of the product.

4.5 Using Nitrogen During Discharge

1. During the discharge of cargo, nitrogen may be used to avoid ingress of air or moisture as the cargo is being discharged. This nitrogen may be supplied by the vessel or from shore.
2. All precautions noted in Section 4.4 apply to the use of nitrogen during discharge.
3. Furthermore, additional precautions must be in place to avoid under-pressure and over-pressurisation of the cargo tank during the discharge. This could include the proper setting of pressure/vacuum alarms, regulation and monitoring of pressure, and other similar precautions.

4.6 Tank Cleaning

4.6.1 Tank washing under nitrogen using fixed tank cleaning machines

It is recommended to use fixed tank cleaning machines when cleaning tanks containing flammable or toxic chemicals. All tank hatches or other openings should be closed during this operation, and the P/V valves should be at the appropriate setting. For flammable products, the oxygen level in the tank should be regularly monitored to insure it is within the appropriate range, and steps may be required to maintain it below the flammable range throughout the entire operation. Vessel personnel must ensure that the flammable range is based upon the particular cargo being carried, and the MSDS should be referenced for this information. When testing oxygen content, it is recommended that a sampling connection be installed at an appropriate location to allow the equipment to be attached to allow an accurate result without the need to open the tank to the atmosphere.

For vessels lacking fixed tank cleaning machines, the use of temporary fixed machines are also suitable, provided they are installed prior to loading the product.

4.6.2 Tank washing under nitrogen using portable tank cleaning machines

The opening around the portable tank cleaning hose can allow the release of nitrogen, flammable or toxic vapours as well as allowing the ingress of oxygen.

If a vessel is to carry toxic or flammable cargoes, it is recommended that owners consider the permanent installation of fixed machines, or conduct tank cleaning as defined in the Tanker Safety Guide Chemicals 3rd Edition for undefined atmospheres.

[2] IBC Code 15.13

4.6.3 Purging & gas-freeing operations

The purging and subsequent gas freeing of cargo tanks that have been inerted with nitrogen could expose personnel on deck to large quantities of nitrogen or product vapours. As such, purging and gas-freeing should only carried out utilising the approved venting arrangement, with additional precautions if the cargo in the tank is toxic[3].

5. Vessels without a Nitrogen Generator

Vessels without a nitrogen generator may still receive nitrogen from other sources. As such, these vessels should observe the relevant items listed in Section 4 of this paper.

6. Vessels with a Nitrogen Generator

If a vessel is fitted with a nitrogen generator and designed in accordance with SOLAS Chapter II-2 Regulation 4 section 5.5 for Inerting operations, the nitrogen generator should be used for low flash cargoes at all times.

When the nitrogen generator is used, all safety aspects of section 4 of this paper should be taken into consideration. Appropriate alarms to warn of any depletion of oxygen content should be fitted to spaces used for the bulk storage or production of nitrogen, as well as other spaces with nitrogen lines running through them.

7. Miscellaneous Operations with Nitrogen

7.1 Pigging and Shoreline Clearing Operations

Pigging and shoreline clearing operations can lead to a high volume of compressed gas that can suddenly be released into the cargo tank (vessel or shore), quickly overwhelming the venting arrangement and leading to an over-pressurized tank. Pigging should not be conducted towards a vessel.

7.2 Using Compressed Air or Nitrogen to Move Cargo (Pressure Loading)

Nitrogen or air is often used to pressurise cargo discharged from trucks or rail cars to marine vessels. If not closely monitored, a high volume of compressed gas can suddenly be released at the end of the discharge of the truck or rail car resulting in a surge of high pressure gas to the cargo tank which could exceed the tanks venting capacity. This method of cargo transfer must be closely monitored to avoid this situation.

7.3 Sampling and Gauging Operations

When a vessel is operating under nitrogen (even when not required under the IBC Code), opening of tank hatches is not recommended. As such, closed sampling and gauging devices should be used.

8. References

- IMO DSC 15/10
- MSC.1/Circ.1401
- SOLAS Chapter 3
- ISGOTT Chapter 21.2.5
- IBC Code 8.5
- Tanker Safety Guide – Chemicals 6.5.7, 7.3.3, 7.7.1
- CSB US Chemical Safety Board 25th June 2003
- Safety Bulletin – U.S. Chemical Safety and Hazard Investigation Board – No. 2003-10-B – June 2003

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[3] IBC Code 15.12

APPENDIX 1

Visual Warning Signs or Symbols as per 4.1.6

The pictogram consists of 4 signs and a shield containing specific supporting text.

The 1st sign is a blue circular mandatory sign depicting a human head wearing a full face mask attached to an inverted gas cylinder indicating that self-contained breathing equipment is necessary beyond this point.

The second sign is a triangular warning sign depicting a sedated human and "N_2" which is the internationally recognized atomic symbol of Nitrogen.

The third sign is a prohibition sign depicting a human entering through a man-lid/tank hatch indicating that entry is not allowed.

The supporting text is displayed in the 4th shield under the ANSI "Danger" format.

- N_2 is understood by chemists worldwide.
- **Nitrogen** (Latin nitrogenium, from Greek "forming native soda") is understood in English, Spanish, Hungarian, Croatian, Serbian, Swedish, Danish and Norwegian.
- **AZOT**, (from the Greek word αζωτος "lifeless") is understood in French, Italian, Portuguese, Polish, Russian, Romanian, Bulgarian ,Turkish, Lithuanian and Greek.
- **Dusik** is understood in Czech, Slovak and Slovene.
- **Stickstoff** (translates literally as "asphixiant") is understood in German and Dutch.
- 氮氣 is Chinese for nitrogen