Nitrogen and its use in bulk liquid transport

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A number of bulk liquid cargoes require the use of nitrogen blankets/inert gas during ocean-going carriage to ensure safety when carrying chemical cargoes that react in the presence of oxygen or moisture. The application of nitrogen blanketing for any purpose is usually requested by the charterer in the voyage instructions or is stated in the International Maritime Dangerous Goods (IMDG) code, but the crew should still carefully consider whether to proceed.

Many thanks to Adam Jackson for his contribution to this article while at CWA International.

Common terms associated with the use of nitrogen in shipping are inerting, purging and padding/blanketing. Purging and inerting are often used interchangeably throughout the maritime industry. However, the International Safety Guide for Oil Tankers and Terminals (ISGOTT) defines inerting as the displacement of oxygen or moisture prior to loading and purging as the use of inert gas to reduce oxygen and flammable gas concentration to below the lower flammability range. Nitrogen padding or blanketing refers to the receipt of nitrogen after loading to reduce the oxygen content and maintain positive pressure, thereby preventing the ingress of air or water (which would cause unwanted reactions and damage to the cargo).

Introduction

The use of nitrogen or inert gas systems has been required on all new tankers over 20,000dwt since 1978. Originally, inert gas systems were devised as a means to prevent explosions during tank cleaning operations. A static charge or sparks could be formed from the use of tank cleaning equipment, which is an enormous safety hazard in a flammable hydrocarbon-rich atmosphere. Inert gas was later required for application above cargoes with low flash points (SOLAS specifies below 60°C) and for grade changeovers in the burgeoning liquefied gas industry. Eventually, as the chemical industry started shipping more complex cargoes with stricter carriage requirements, the use of nitrogen blankets in the vapour space over chemical cargoes (and some edible oil cargoes) that react in the presence of oxygen or moisture became commonplace. Nitrogen is also used during custody transfer operations to clear cargo from shorelines after completion of the cargo transfer.

Chemical cargo reactions

The type of damage that can be sustained by ingress of air depends upon the chemical cargo itself. For example, olefinic cargoes (i.e. those that contain a carbon-carbon double bond) tend to react with oxygen to form aldehydes, ketones and peroxides.

Chemical cargoes such as methanol, aromatics, acetic anhydride, acetone, hexane, decane, isobutyl alcohol, pyrolysis gasoline and ethanol all require inert atmospheres to prevent the formation of explosive atmospheres. This is the most common reason why a nitrogen atmosphere is required during chemical cargo carriage.

Alternatively, some compounds will react with the moisture that may be present in air and form either contaminating side-products or toxic gases (for example, methyl diisocyanate, MDI cargoes). Some chemical cargoes are hygroscopic (such as monoethylene glycol), meaning they readily dissolve moisture from the air, causing an increase in the water content of the cargo, potentially leading to an off-specification cargo.

Polymerising cargoes such as styrene are often inhibited. Their carriage is somewhat unusual, in that the effectiveness of the inhibitor is increased in the presence of oxygen (because of the formation of peroxide radicals after reaction with dissolved oxygen molecules, which is involved in the inhibition/polymerisation termination process). However, styrene is a flammable cargo and will form explosive atmospheres in too high an oxygen content. Therefore, styrene

carriage is performed in a controlled nitrogen/oxygen atmosphere of between 5% – 8% oxygen atmospheric concentrations and, as such, if polymerisation is to occur in a styrene cargo on board a vessel, review of the vessel's tank atmospheric condition records will be critical to defending an owner's position against any possible claim. If an inhibition certificate is provided for this or similar polymerising cargoes, this document will usually specify the atmospheric oxygen range suitable for carriage.

How it works

Most chemical tankers are equipped with nitrogen generators, which can produce nitrogen via a pressure swing membrane-type generator at a purity above 95%. Shore-side cryogenic nitrogen generators can also supply a vessel with high-purity nitrogen prior to, during or after custody transfer, or alternatively, pre-bottled nitrogen can be used. For fire/explosion prevention purposes and tank purging, 95% – 98% purity nitrogen is sufficient. However, higher-purity nitrogen is needed for chemical cargoes, especially those liable to suffer from oxidative degradation.

When inerting a cargo tank, a vessel will have target atmospheric conditions (e.g. cargo tank pressure, atmospheric concentration of previous cargo components) depending upon the cargo being loaded and the cargo that has been discharged, which are often provided on the voyage instructions. For example, after discharge and tank cleaning following the carriage of a low flash point cargo such as gasoline, a vessel will need to reduce the tank atmospheric concentration of hydrocarbon species to below 2% volume in order to load a high flash point cargo such as diesel/gasoil or fuel oil. Therefore, during inerting, the atmospheric conditions are monitored using pressure sensors and electronic gas detectors (such as the Riken RX series of detectors) or indeed through manual monitoring of the tank atmospheric conditions using chemical detection apparatus (such as the common Draeger tube detectors).

After the loading and topping up of the cargo tanks with nitrogen/inert gas is complete, the pressure in the cargo tanks should be monitored throughout the voyage to prevent excessive under or over pressure in the cargo tanks. A vessel can encounter drastic temperature changes between day and night that can affect the pressure in the cargo tank. Careful monitoring of the pressure is therefore necessary. A vessel's cargo tanks will be equipped with high and low pressure alarms that indicate whether a tank needs venting or topping up with nitrogen/inert gas. During discharge of inerted cargoes, it is also necessary to continuously top up the tanks with nitrogen/inert gas to maintain an overpressure, which prevents the ingress of air into the cargo tanks while cargo is discharged.

Summary

Each individual chemical cargo's need for nitrogen atmospheres will be dependent upon the properties of the cargo. The charterer's instructions should be followed when provided, but if they are not provided or seem contrary to what is expected, then the IMDG code or a suitable commodities database should be consulted. This article is only a small summary of some of the technical and safety aspects of the use of nitrogen on board ships. If further information is required, reference should be made to the Chemical Distribution Institute's (CDI) nitrogen best practice advice.