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## TECHNICAL INFORMATION ON SYSTEMS AND OPERATION TO ASSIST DEVELOPMENT OF VOC MANAGEMENT PLANS

1 The Marine Environment Protection Committee, at its fifty-ninth session (13 to 17 July 2009), approved the Guidelines for the Development of a Volatile Organic Compound (VOC) Management Plan for tankers carrying crude oil (resolution MEPC.185(59)).

2 In conjunction with consideration of the guidelines, MEPC 59 agreed that additional technical information on vapour pressure control systems and their operation would assist the industry in development of VOC management plans. Therefore, MEPC 59 agreed to the technical information on systems and operation to assist development of VOC management plans for tankers carrying crude oil, as set out in the annex to this document.

3 The technical information addresses the general equipment and systems involved, their operation and conditions on board a crude oil tanker with respect to the formation and emission of Volatile Organic Compounds (VOC) as well as the ability to control VOC formation and and emissions.

4 Member Governments are invited to bring this circular to the attention of their Administrations, relevant shipping organizations, recognized organizations, shipping companies and other stakeholders concerned and encourage them to take it into account when applying the Guidelines for the development of a VOC management plan for crude oil tankers.

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#### ANNEX

### TECHNICAL INFORMATION ON VAPOUR PRESSURE CONTROL SYSTEMS AND THEIR OPERATION TO ASSIST DEVELOPMENT OF VOC MANAGEMENT PLANS FOR TANKERS CARRYING CRUDE OIL

#### Introduction

This technical information is compiled pursuant to the requirements in MARPOL Annex VI Regulation 15.6, and describes the general equipment, operations and conditions onboard a crude oil tanker with respect to the emission and ability to control Volatile Organic Compound (VOC) emissions.

The Guidelines for the development of a VOC management plan state:

#### 1 **Objectives**

- .1 The purpose of the VOC management plan is to ensure that the operation of a tanker, to which regulation 15 of MARPOL Annex VI applies, prevents or minimizes VOC emissions to the extent possible.
- .2 Emissions of VOCs can be prevented or minimized by:
  - .1 optimizing operational procedures to minimize the release of VOC emissions; and/or
  - .2 using devices, equipment, or design changes to prevent or minimize VOC emissions.
- .3 To comply with this plan, the loading and carriage of cargoes which generate VOC emissions should be evaluated and procedures written to ensure that the operations of a ship follow best management practices for preventing or minimizing VOC emissions to the extent possible. If devices, equipment, or design changes are implemented to prevent or minimize VOC emissions, they shall also be incorporated and described in the VOC management plan as appropriate.
- .4 While maintaining the safety of the ship, the VOC management plan should encourage and, as appropriate, set forth the following best management practices:
  - .1 the loading procedures should take into account potential gas releases due to low pressure and, where possible, the routing of oil from crude oil manifolds into the tanks should be done so as to avoid or minimize excessive throttling and high flow velocity in pipes;
  - .2 the ship should define a target operating pressure for the cargo tanks. This pressure should be as high as safely possible and the ship should aim to maintain tanks at this level during the loading and carriage of relevant cargo;

- .3 when venting to reduce tank pressure is required, the decrease in the pressure in the tanks should be as small as possible to maintain the tank pressure as high as possible;
- .4 the amount of inert gas added should be minimized. Increasing tank pressure by adding inert gas does not prevent VOC release but it may increase venting and therefore increased VOC emissions; and
- .5 when crude oil washing is considered, its effect on VOC emissions should be taken into account. VOC emissions can be reduced by shortening the duration of the washing or by using a closed cycle crude oil washing programme.

### 2 Additional considerations

- .1 A person in charge of carrying out the plan
  - .1 A person shall be designated in the VOC management plan to be responsible for implementing the plan and that person may assign appropriate personnel to carry out the relevant tasks;
- .2 Procedures for preventing or minimizing VOC emissions
  - .1 Ship-specific procedures should be written or modified to address relevant VOC emissions, such as the following operations:
    - .1 Loading;
    - .2 Carriage of relevant cargo; and
    - .3 Crude oil washing;
  - .2 If the ship is equipped with VOC reduction devices or equipment, the use of these devices or equipment should be incorporated into the above procedures as appropriate.

#### .3 Training

.1 The plan should describe the training programmes to facilitate best management practices for the ship to prevent or minimize VOC emissions.

## Section 1 – The hull and its pressure limitations

### 1.1 Allowable cargo tank ullage pressure

1.1.1 The cargo tank structure is designed to withstand a range of design loads and parts of the tank structure will also contribute to the global longitudinal strength of the ship. The classification societies' specified load conditions and loads are applied in verification of the structural design. One such load is the combined pressure from the liquid cargo and the tank ullage pressure. The tank ullage pressure is to be minimum  $25 \text{ kN/m}^2$  or the opening pressure of the pressure relief device (P/V valve), whichever is greater. Accordingly, the maximum allowable ullage pressure in a standard tanker is typically interpreted as  $25 \text{ kN/m}^2$  (i.e. approximately 2,550 mmWG). It should however be noted that global strength considerations and the impact of other design loads may imply that actual allowable pressure could be higher.

1.1.2 In terms of under pressure, SOLAS regulation II-2/11.6 indicates an allowable under pressure of -700 mmWG. From a structural point of view, the maximum allowable tank under pressure is presumably lower.

1.1.3 Exceeding the maximum allowable pressures could lead to structural failures. If such a structural failure results in opening of the tank structure to atmosphere, uncontrolled VOC emissions will occur together with the possibility of oil pollution to the seas. Further, it could result in loss of inert gas protection with subsequent hazards related to fire and explosion.

### 1.2 **Typical cargo tank venting systems**

The design of cargo tank venting and inert gas systems is governed by SOLAS 1.2.1 regulation II-2/11.6 and 5. Most crude oil tankers have a common cargo tank venting and inert gas main pipeline which is also used for vapour emission control (ref. section 4). Branches to each cargo tank are provided with isolation valves and blanking arrangements. The isolation valves and blanks are typically only used in connection with tank entry. SOLAS chapter II-2 requires that the isolation valves are to be provided with locking arrangements to prevent inadvertent closing/opening of said tanks. The cargo tank venting/inert gas main is connected to a mast riser. The mast riser has a minimum height of 6 metres with an IMO approved flame arrestor at its outlet. An isolation valve is provided between the cargo tank venting/inert gas main and the mast riser. Some designs have a small capacity pressure/vacuum valve fitted in a bypass across the isolation valve. This latter enables thermal breathing from cargo tanks when the isolation valve is closed. A liquid-filled P/V breaker is typically connected to the cargo tank venting/inert gas main. The P/V breaker has a capacity to accommodate the gas flow from cargo tanks during loading (125% of the loading rate and discharge rate). The cargo tank venting/inert gas main is typically used during loading and discharging operations. During loading the mast riser valve is open (unless vapour emission control is performed) and VOC is expelled to air. During discharge the same valve is closed and inert gas used to replace the tank atmosphere. The cargo tank venting/inert gas main is also used during voyage but the mast riser valve will be operated only in the event of increasing ullage pressure.

1.2.2 In addition to the common cargo tank venting/inert gas main, each cargo tank is required to have a pressure/vacuum relief device for thermal breathing in the event the cargo tank is isolated from the common cargo tank venting/inert gas main. Although classification societies accept that these devices have the capacity to accommodate gas volumes resulting from variations in cargo temperature only (i.e. thermal breathing), latest industry practices have led to the installation of devices with the capacity to accommodate the full gas flow from loading of cargo tanks.

# 1.3 Typical settings of pressure/vacuum relief devices

1.3.1 Although the design pressure of cargo tanks is typically +2,500 mmWG and -700 mmWG, the typical setting of pressure/vacuum valves on crude tankers is +1,400 mmWG and -350 mmWG.

1.3.2 The typical settings of the P/V breakers are +1,800 mmWG and -500 mmWG. It should be noted that for liquid filled P/V breakers, the settings have to take into account ship movement (rolling and pitching) as specified by the classification societies.

# Section 2 – Crude Oil Tanker Pressure control/release systems

## 2.1 Introduction

2.1.1 Traditionally, vapour release from crude oil tankers occurs on three discrete occasions, they being: during loading, during the loaded voyage to the discharge port, and during the ballasting of cargo tanks at the discharge port.

2.1.2 Since the introduction of the International Convention for the Prevention of Pollution from Ships together with its Protocol in 1978 (MARPOL), tankers built after 1 June 1982 (regulation 18), termed MARPOL tankers, are all designed with the required totally segregated (designated) ballast tanks. With these regulations in force, cargo tanks are never used for the loading of ballast, except on very rare occasions for bad weather purposes where one of the Crude Oil Washed cargo tanks is dedicated to take in ballast water. Therefore, the displacement of vapour from the relevant crude oil cargo tank at the discharge port has ceased to occur for the MARPOL compliant type tankers. Given this situation then, only two occasions remain where vapour emissions from crude oil tankers generally occur, namely on loading and during the transportation of the cargo.

# 2.2 Load Port Displacement of VOC

2.2.1 Displacement of crude oil cargo vapours at the loading port continues to occur. The reasons for the existence of these volumes of this displaced, but co-mingled<sup>1</sup>, vapour must be subdivided and attributed to two discrete tanker operations; namely existing vapour in the cargo tank system before loading and, the evolved vapour created during the loading programme.

2.2.2 The first portion of the vapour displaced from the cargo tanks to be considered is that from the evolved vapour generated during the previous discharge programme and in particular that vapour generated as a result of the Crude Oil Washing of the cargo tanks. The concentration of this proportion of vapour within the co-mingled gas mixture within a cargo tank can be

<sup>&</sup>lt;sup>1</sup> The vapour emissions on loading are a mixture of hydrocarbon vapours and the inert gas introduced into the cargo tank to achieve a positive pressure within the cargo tank system.

determined prior to commencement of the loading process. The second portion of vapour displaced is that that develops or evolves during the loading programme itself. This vapour evolves as a result of, both, the turbulence generated in the cargo tanks due to the volumetric rate of loading and the pressure differentials within the loading pipeline system creating a degree of "flashing" of the vapour from the incoming crude oil.

2.2.3 To illustrate the extent of these gases within a cargo tank system on a tanker during a loading process, Figure 2.1 below shows the measurements of hydrocarbon vapour concentrations as taken from a tanker during its loading programme. The "X" axis of the graph records the percent status of loading of the tanker whereas the "Y" axis records the percentage of hydrocarbon vapour (VOC) concentration. The graph primarily records the total hydrocarbon gas concentration at the differing percentages of loading of the cargo tanks. However, this total figure is then mathematically proportioned and subdivided, taking into consideration the diminishing size of the vapour volume in the cargo tanks, into the two concentrations of vapours, namely those present at the commencement of loading (in the event approximately 4% of the total tank vapour volume) and the concentration of vapours that evolve as a result of the loading process.

2.2.4 These vapours are displaced by the incoming cargo volumes, throughout the loading period, and released through the ship's vapour pipeline system (inert gas pipeline) to atmosphere via the ship's mast riser. In order to prevent excess pressures within the cargo tank system the isolation/control valve to the mast riser is fully opened at the commencement of loading and remains opened until completion of loading. Once the mast riser valve is shut and loading is completed, the necessary "in tank" positive pressure is achieved to prevent any form of air/oxygen entry into the cargo tank vapour system as is required by the SOLAS regulations.

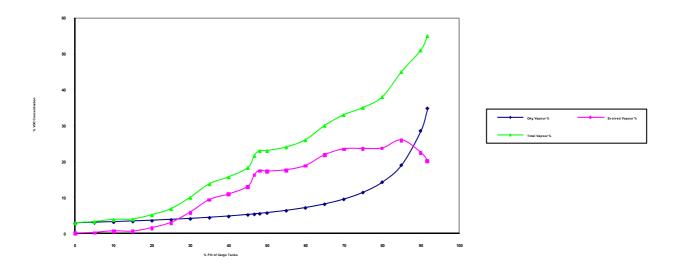


Figure 2.1 – Hydrocarbon vapour concentration in the vapour phase during a loading

2.2.5 In Figure 2.2 below, a photograph shows the deck of a tanker and highlights the relevant pressure control and release mechanisms, namely the vessel's mast riser, the individual tank Pressure/Vacuum (P/V) valves and the secondary safety mechanism of the P/V breaker. These mechanisms will be explained further in this section.



Figure 2.2 – Main Cargo Deck of a Crude Oil Tanker

2.2.6 Typically a normal loading programme will take about 24 hours for a VLCC with a volumetric rate of loading of up to 20,000  $\text{m}^3$ /hour. The mast riser is normally used during loading for tank vapour pressure control. Its exit location, being at least 6 metres above the deck, allows for the free flow of the vapours displaced from the cargo tanks by the incoming liquid crude oil at the rate of loading of the cargo. The rate of displacement of VOC vapours from the cargo tank system will be the same as the loading rate but the concentration of VOC vapours in the displaced stream will be greater dependent upon the extent and rate of evolution of VOC vapour mixture already existent in the cargo tank prior to loading, as shown in Figure 2.1 above.

# 2.3 **VOC release during the voyage**

2.3.1 During the voyage, the temperature of the gases/vapours in the ullage space of the cargo tanks and the liquid cargo varies. The gas phase consists of a mixture of unsaturated gases (Inert Gas – for tank safety and protection) and saturated vapours (evolved hydrocarbon vapours from the cargo). The temperature of the gas phase of the tank varies diurnally with its maximum temperature being achieved by mid afternoon and its coolest temperature in the early hours of the morning. The liquid phase temperature varies very much slower and is dependent upon both the hull design and the temperature of the surrounding seawater.

2.3.2 Figure 2.3 below records, as an example, the vapour pressure and cargo temperature data of a reported voyage for a single hulled (but segregated ballast) tanker. The graph records on the "X" axis the days of the voyage whereas the "Y" axis records both the cargo temperature ( $^{\circ}C$ ) and the pressure (mmWG) within the vapour phase of the cargo tank system. Superimposed upon the graph is both the normal operational release pressure as well as the P/V valve opening

pressure levels. The vapour pressure readings were recorded every four hours whereas the cargo liquid temperature readings (blue) were recorded daily.

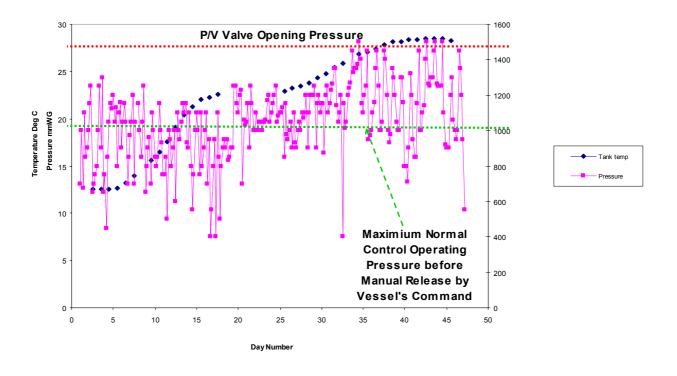


Figure 2.3 – Temperature and Pressure profile for a crude oil voyage

2.3.3 The double hulled construction of a crude oil tanker has a void/ballast space located between the cargo tank and the outer hull, this causes the temperature of the liquid cargo to remain closer to the temperature of the cargo upon loading for a longer period due to the so called "Thermos Effect" or heat loss insulation created by the void or empty ballast space. The cargo temperature profile, as shown in Figure 2.3, reflects the expected changes to temperature for a cargo carried on board a single hulled vessel where the impact of the seawater temperature upon the cargo is more apparent. This aspect can be more clearly seen in Figure 2.3 for the early/interim days of the 47-day voyage from North Sea to the Far East.

## 2.4 A Crude Oil Tanker's vapour pressure control mechanisms

2.4.1 A crude oil tanker is designed and constructed to withstand high vapour pressures up to a certain value. In order to protect the vessel's structure against excessive pressures, two differing levels of safety mechanisms are installed to control and limit the pressures exerted in the vapour phase of the cargo system. The installation of both these systems is a requirement within the International Convention for the Safety of Life at Sea (SOLAS). These mechanisms are:

- .1 the individual tank Pressure/Vacuum (P/V) valve; and
- .2 the common Pressure/Vacuum (P/V) breaker.

2.4.2 The P/V valve is the primary mechanism for the protection from cargo tank over pressure. The design and operational requirements of the P/V valves are set out in the ISO 5364:2000 standard but the opening and closing pressure setting of the individual valves is set in accordance with the designed tolerance of the relevant structure having applied the necessary safety margins.

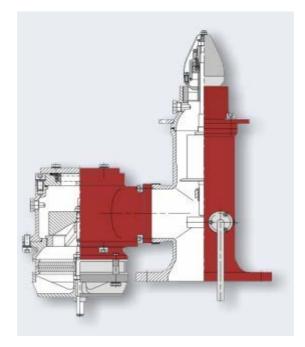


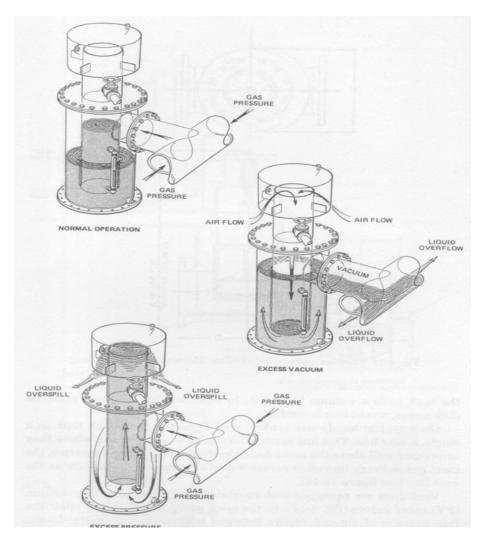
Figure 2.4 – A design and construction of a P/V valve<sup>2</sup>

2.4.3 A design of a P/V valve may be seen in Figure 2.4 above. The valve is fitted to a vertical pipeline connected directly to the vapour space of a cargo tank (see Figure 2.2 above). The valve consists of two sections, namely the vacuum protection section on the left hand side of the valve as shown and the pressure control mechanism of the right hand side. Both mechanisms rely upon a weighted diaphragm that will be lifted when the pre-designed pressures are met. On the pressure side of the valve the exit nozzle is designed such that the exit velocity of the vapours reach the required velocity so as to maintain the deck working area clear of hydrocarbon vapours.

2.4.4 Each cargo tank is normally equipped with its valve so that full protection is available, should the individual cargo tank be isolated from the main common vapour system on board the tanker. The typical pressure setting for a P/V valve is traditionally measured in millimetres of water gauge and would be in the range from 1,400 to 1,800 mmWG. These valves are supported on a connecting pipeline to the tank's atmosphere by a 100 to 150 mm diameter pipeline and located at least 2 metres above the deck. Due to the requirements to prevent mechanical damage to these valves the closing pressure is controlled by a damping mechanism (to prevent hammering of the valve). As a result of the damping mechanism the closing pressure of the valve will vary but will be in the range of 400-800 mmWG.

<sup>&</sup>lt;sup>2</sup> Courtesy Pres-Vac Engineering A/S: www.pres-vac.com.

2.4.5 Supporting the over pressure safety system of the P/V valve is the secondary safety mechanism of the P/V breaker. In the event of a rapid pressure fluctuation within the common vapour system the P/V breaker is available to relieve such an over pressure. The single P/V breaker is located on the common vapour pipeline, serving all the cargo tank branch pipelines, which ends at the vessel's mast riser (see Figure 2.2).



**Figure 2.5** – The design and operation of a P/V breaker<sup>3</sup>

2.4.6 The construction and operation of the P/V breaker may be seen in Figure 2.5 above. The pressure setting in the P/V breaker is achieved by way of the internal water column with an equivalent pressure setting of approximately 2,000 mmWG. The water column also isolates the vapour phase from external air ingress into the system. In the event of an excessive pressure surge within the tank vapour system the water column would either be displaced out of the breaker onto the deck, in the event of excessive pressure, or drawn into the cargo tanks in the event of an under pressure. This will, therefore, open the total vapour system to the external environment and atmospheric pressure and, due to the equipment's dimensions, will relieve the pressure in the system very quickly. Thus, this safety mechanism, due to its pressure setting, will only operate if the vessel tank's P/V valves fail to operate or are not of sufficient capacity to relieve the pressure surge adequately.

<sup>&</sup>lt;sup>3</sup> Reference – G.S. Marton, Tanker Operations – a Handbook for Ship's Officers, page 76.

2.4.7 It should, however, be noted that once the P/V breaker operates then, as stated above, it will reduce the pressure within the tank vapour system to atmospheric pressure, thereby exposing the tank system to ingress of oxygen. Therefore, this system is a "last resort" system to preserve the structure of the tanker from damage.

## Section 3 - VOC generation systems in Crude Oil

3.1 Why limit VOC Emissions to the atmosphere? VOCs are a pollutant to the air and act as a precursor to the formation of Tropospheric Ozone – commonly termed Smog.

Thus, to control this emission, there are four criteria that impact on the extent and rate of evolution of gaseous VOC from crude oils and its subsequent release to atmosphere. These are:

- .1 the volatility or vapour pressure of the crude oil;
- .2 the temperature of the liquid and gas phases of the crude oil tank;
- .3 the pressure setting or control of the vapour phase within the cargo tank; and
- .4 the size or volume of the vapour phase within the cargo tank.

Each of these criteria are defined and briefly explained below together with any interaction between the criteria for general operational circumstances.

## 3.2 The volatility or vapour pressure of the crude oil

3.2.1 Reid Vapour Pressure (RVP) – this is an industrially developed standard test method to determine the Air Saturated absolute Vapour Pressure of volatile, non-viscous hydrocarbon liquids in compliance with the requirements specified in the Institute of Petroleum test procedure IP 69.

3.2.2 The RVP is the vapour pressure obtained within a standardized piece of test equipment for the evolved hydrocarbon vapour at a temperature of 100°F or 37.8°C. The standard test parameters for the determination of this pressure are important to identify and relate to the ratio of a fixed liquid volume to a fixed vapour volume. This ratio is one part liquid to four parts vapour. Thus, the pressure reported for this parameter reflects, in principle, the pressure that would be registered when the cargo tanks are about 20% loaded.

3.2.3 This leads to the importance of two other parameters, namely the Saturated Vapour Pressure and Unsaturated Vapour Pressure. These two parameters, and the physics behind them, give more clear indications and guidance with respect to a crude oil's volatility with respect to vessel operations and VOC control.

3.2.4 Saturated Vapour Pressure  $(SVP)^4$  – is the equilibrium pressure generated by the liquid phase for the vapour volume within a defined system. The Saturated Vapour Pressure is developed only by the evolved hydrocarbon vapours from the crude oil liquid phase. For a Saturated Vapour to be present it must have contact with its own liquid phase. If the liquid phase temperature

<sup>&</sup>lt;sup>4</sup> An empirical equation exists to correlate the Reid Vapour Pressure (psia) to the Saturated Vapour Pressure of a crude oil at the constant temperature of 37.8°C. This equation is:  $P = (6.2106^* \text{ Ln } P_R) + 4.9959$ ; Where P is the Saturated Vapour Pressure (psia) at 37.8°C and P<sub>R</sub> is the Reid Vapour Pressure (psia) at the same temperature.

increases or decreases so will the Saturated Vapour Pressure vary accordingly – an increase the liquid temperature will cause an increase in the Saturated Vapour Pressure.

3.2.5 However, if the vapour volume increases or decreases for a known liquid temperature, the pressure should, in theory, remain constant (for further understanding on this parameter see paragraph 3.5.2 below). These circumstances, respectively, will only cause the vapour to condensate and fall back to the liquid phase or more vapour to evolve from the liquid phase to maintain the Saturated Vapour Pressure. This physical characteristic is indicative of equilibrium pressure – between the liquid and vapour phases within the defined system.

3.2.6 From the foregoing it can be readily recognized that Saturated Vapour Pressure should not vary with the size of the vapour volume and will only vary with the temperature of the liquid phase – not the vapour phase temperature.

3.2.7 Unsaturated Vapour Pressure (UVP) – contrary to the concept of Saturated Vapour Pressure, an Unsaturated Vapour is not in contact with its liquid phase. In this case the vapour is obtained from other sources such as air or, more likely, Inert Gas. Thus, by reference to the standard laws of physics and what is termed the Ideal Gas  $Law^5$ , both variations in volume and/or temperature (this time it is the gas or vapour phase) will vary the pressure within a closed system.

3.2.8 From an operational perspective this type of behaviour is the primary cause of the variation of pressures within a cargo tank system over a 24-hour period and is to be associated with the Inert Gas phase within a cargo tank. However, the pressure generated from this type of gas/vapour is not the total vapour pressure in the cargo system.

3.2.9 Behind the pressure generated from the Unsaturated Vapours (Inert Gas) lies the pressure generated by the Saturated Vapours (the hydrocarbon vapours evolving from the crude oil cargo). As stated above, this pressure will remain as a constant for a given cargo/liquid temperature and, as is well recognized, a cargo temperature will not vary to the same extent as the vapour temperature due to heating or cooling from external sources (sunlight, sea temperature, air temperature, etc.). Thus, the variation for the tank observed Total Vapour Pressure is due to the presence of Inert Gas in the cargo tank.

3.2.10 Total Vapour Pressure – this pressure is the total pressure to be achieved within a defined closed system given the variable parameters of vapour volume and the differing control temperatures. In fact it is the combination or addition of the Saturated and Unsaturated Vapour Pressures (Dalton's Law of Partial Pressure<sup>6</sup>) within a closed and defined system.

3.2.11 Thus, on board a tanker, the pressure measured within Vapour System is the Total Vapour Pressure of the system which is the sum of the two individual pressures generated by the differing types of gases present in the system.

<sup>&</sup>lt;sup>5</sup> The Ideal Gas Law equation is PV = nRT or P = (nRT)/V where: P = Pressure, T = Temperature, V = Volume and nR are gas constants.

<sup>&</sup>lt;sup>6</sup> Dalton's Law of Partial Pressure states that "The pressure of a mixture of gases is the sum of the partial pressures of its constituents".

## 3.3 The temperature of the crude oil in a cargo tank

3.3.1 The measurement and determination of temperature upon the two differing phases in a crude oil cargo tank have differing impacts upon the size and extent of pressure exerted at any one time in the cargo tank. In this regard it is necessary to consider the two phases separately with regard to the impact of temperature.

3.3.2 The temperature of the liquid in a crude oil cargo tank – the temperature of the liquid phase in a crude oil cargo tank will vary little over the period of a voyage unless cargo heating is being undertaken. It is this temperature that determines the Saturated Vapour Pressure that will be exerted by the evolving VOCs from the cargo volume and contribute to the Total Vapour Pressure in the cargo tank at any one time. The cooler the liquid phase temperature the lower will be the Saturated Vapour Pressure of the crude oil but care should be taken not to allow cooling of waxy cargoes too much, such that it promotes wax precipitation.

3.3.3 The temperature of the vapour or gas in a crude oil cargo tank – the temperature of the gas phase in a cargo tank will change more rapidly and vary during the day/night cycle. As this phase in the cargo tank contains a mixture of Saturated (evolved hydrocarbon gases) and Unsaturated (Inert gas) gas species the pressure in this space will vary with temperature due to the reaction of the Unsaturated Gas component to temperature (Ideal Gas Law<sup>5</sup>). Thus, during the day when the gas phase warms, the pressure in the tank will increase so long as there is an Inert Gas component in the gas phase. The obverse will occur at night as the gas phase cools.

## 3.4 The pressure setting or control of the vapour phase within the cargo tank

3.4.1 The technologies available on board crude oil tankers for the control of pressure within the cargo tank vapour system are discussed in section 2. However, it is important to identify the significance of pressure with respect to the evolution of hydrocarbon vapours from a crude oil liquid phase.

3.4.2 Control of the extent of the pressure within a crude oil cargo tank vapour system will determine the extent of further vapour evolution from a crude oil cargo. If the pressure within the system is controlled at the Saturated Vapour Pressure of the cargo, then equilibrium pressure between the liquid and vapour phase is obtained and no further VOC will evolve from the cargo. However, if the vapour pressure in the crude oil tank vapour system is reduced to a pressure below the Saturated Vapour Pressure of the cargo, then VOC will evolve to restore the equilibrium balance in the system.

## 3.5 The size or volume of the vapour phase within the cargo tank system

3.5.1 The size or volume of the gas or vapour phase in the cargo tank system (usually a common system on a crude oil tanker due to the interconnection through the Inert Gas pipeline system) is an important criterion to establish the pressure within the system. Again separate consideration should be given to the two differing types of gases to be found in the vapour phase and how volume may impact these component gases.

3.5.2 Saturated vapours from the crude oil liquid phase, as described above in paragraph 3.2.2, under theoretical conditions the pressure generated by saturated vapours will not be affected by a change in the volume space occupied by the vapours. However, due to the numerous species of hydrocarbon types to be found in evolved vapour from a crude oil it has been found that a volumetric change of the vapour phase from a 2% volume (V:L ratio of 0.02) to a 20% volume

(V:L ratio 0.2) will impact the saturated vapour pressure of a crude oil at a constant temperature. For vapour volumes greater than 20% of the total volume the pressure behaves similar to that expected of a Saturated Vapour; namely nearly isobaric. These circumstances can be seen in Figure 3.1 below for a selection of crude oil types.

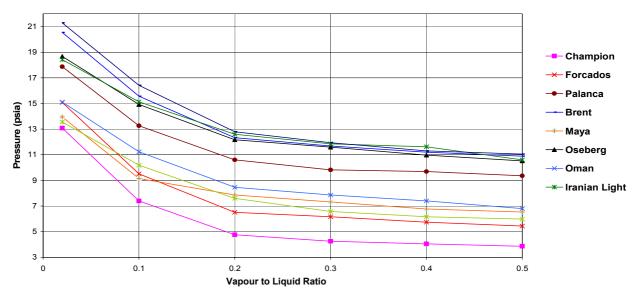


Figure 3.1

3.5.3 The change in pressure with respect to volume, for a vapour percent volume from 2% to 20%, for complexed vapour phases evolved from crude oils, is due to the influence of the individual volatile hydrocarbon types and their varying proportions in both the liquid and vapour phase that separately contribute to the final saturated vapour pressure under equilibrium conditions. The ratio of concentration of the individual hydrocarbon compounds in the vapour phase is due to the *Partition Coefficients* for each hydrocarbon type in relation to another type. This will cause a differing distribution of hydrocarbon species to that in the liquid phase when the vapour phase volume is smaller.

3.5.4 Unsaturated gases (Inert Gas) in the vapour phase system – this type of gas behaves in a manner simulated by the Ideal Gas Law equation<sup>5</sup>. Therefore any reduction in the volume occupied by this gas will cause an increase in the pressure exerted by the gas at a known temperature.

## Section 4 – Methods and systems for the control VOC

In this section, examples of methods and systems for the control of VOC are provided.

# 4.1 Methods and systems for the control of VOC during Loading

## 4.1.1 Best Practices and design

- .1 Manual pressure relief procedures (tank pressure control);
- .2 P/V valve condition and maintenance;
- .3 Condition of gaskets for hatches and piping;

- .4 Inert gas topping up procedures;
- .5 Partially filled tanks;
- .6 Loading sequence and rate; and
- .7 Use of vapour return manifold and pipelines when shore facilities are available.

#### 4.1.2 Vapour Emission Control Systems

The principle behind VECS is that VOC generated in cargo tanks during loading is returned to the shore terminal for processing, as opposed to being emitted to atmosphere through the mast riser.

Vapour Emission Control Systems (VECS) were introduced in 1990 as a requirement for tankers loading oil and noxious liquid substances at terminals in the United States (USCG 46 CFR Part 39). IMO followed up with the introduction of IMO MSC/Circ.585 "Standards for vapour emission control systems" in 1992. International regulation requiring vapour emission control was introduced through regulation 15 of MARPOL Annex VI adopted in 1997, although it is only required for ships loading cargo at terminals where IMO has been informed that VECS is mandatory.

Since 1990, most crude tankers have installed a VECS system in compliance with USCG regulations. The regulations cover both the technical installation (vapour recovery piping and manifold, vapour pressure sensors and alarms, level gauging, high level and independent overflow alarms) as well as operational restrictions and training. The operational restrictions are found in a mandatory VECS manual which also includes maximum allowable loading rates. The maximum allowable loading rate is limited by one of the following:

- .1 the pressure drop in the VECS system from cargo tank to vapour manifold (not to exceed 80% of the P/V valve setting);
- .2 the maximum pressure relief flow capacity of the P/V valve for each cargo tank;
- .3 the maximum vacuum relief flow capacity of the P/V valve for each cargo tank (assuming loading stopped while terminal vacuum fans are still running); and
- .4 the time between activation of overfill alarm to relevant cargo tank being full (min. 1 minute).

The calculations are to be based on maximum cargo vapour/air densities as well as maximum cargo vapour growth rates, which again may limit the cargoes that can be loaded with VECS.

Further, the calculations are to be carried out both for single tank and multiple tank loading scenarios.

The USCG regulations also contain additional requirements to vapour balancing, i.e. for tankers involved in lightering operations. These include operational requirements as well as technical requirements for an in-line detonation arrestor, oxygen sensors with alarms and possibly means to prevent hazards from electrostatic charges.

For ships provided with a VECS system as per IMO or USCG regulations, the control of VOC emissions will be through returning VOC to the shore terminal in accordance with the procedures found in the onboard VECS manual.

The maximum allowable loading rates and corresponding maximum vapour/air densities and vapour growth rates should be specified in the VOC management plan.

#### 4.1.3 Vapour Pressure Release Control Valve (VOCON valve)

The VOCON valve operates as a hydraulically controlled valve that controls the closing pressure for the valve and therefore undertakes a similar procedure to the manual VOCON procedure as described in 4.2.2 below. However, for the loading programme, the valve also allows a higher pressure to be maintained throughout the loading process in order to limit the extent of vapour evolution from the crude oil once saturated vapour pressure is achieved within the tank vapour system. This valve is normally a single valve facility and located at the bottom of the mast riser by way of a by-pass pipeline to the mast riser control valve. The relevant closing pressure setting for the valve may be done locally or remotely in the Cargo Control Room depending upon the sophistication of the installed system.



Figure 4.1 – Hydraulically controlled VOCON valve

Similar valves with fixed pressure arrangements are to be found and are currently installed on tankers and located at the same position; namely at the bottom of the mast riser by way of a by-pass pipeline to the mast riser control valve. These valves operate as a form of "tank breather" valve but release vapour through the mast riser.

## 4.1.4 Cargo Pipeline Partial Pressure control system (KVOC)

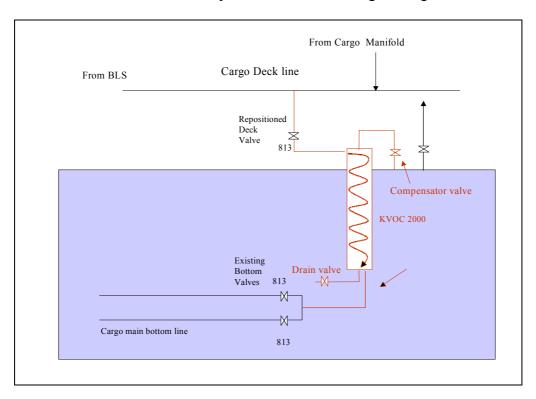
The purpose of the KVOC system installation is to minimize VOC release to the atmosphere by preventing the generation of VOC during loading and transit. The basic principle of KVOC is to install a new drop pipeline column specially designed for each tanker with respect to expected loading rate. The new drop pipeline column will normally have an increased

diameter compared to an ordinary drop line. The increased diameter will reduce the velocity of the oil inside the column and by that means ensure that the pressure adjusts itself to approximately the boiling point of the oil independent of the loading rate. In the initial phase of the loading process some VOC might be generated. The pressure inside the column will adjust itself to the SVP of the oil so that there is a balance between the pressure inside the column and the oil SVP. When this pressure has been obtained in the column the oil will be loaded without any additional VOC generation. This means that KVOC column prevents under pressure to occur in the loading system during loading.

The KVOC system is not designed to remove all VOC, but to minimize generation of VOC. VOC remaining in the tanks from the last cargo and COW operations has to be displaced from the cargo tanks when loading. Also, if the oil boiling point (SVP) is higher than the tank pressure, some crude oil will generate VOC in the tanks and additional VOC be released. Bad weather together with very volatile oil will also increase the VOC emissions due to its SVP also when KVOC is applied.

The KVOC column has an effect on the VOC release during transit, because gas bubbles have been prevented from forming. This means that the amount of gas bubbles in the oil available for release during transit will be minimized. To further reduce the release of VOC, the pressure in the cargo tanks should be held as high as possible. A high pressure, from about 800 to 1,000 mmWG, will reduce possible boiling and diffusion of VOC in the crude oil cargo tanks.

KVOC has also shown a similar effect on  $H_2S$  as on minimizing VOC generation. If the KVOC system has been installed, it should therefore always be used when loading sour crude to minimize  $H_2S$  concentration in the void spaces and release during loading and transit.



#### Pipeline Flow Plan for KVOC

### 4.1.5 Increased pressure relief settings (Applicable also for transit conditions)

As described in sections 2 and 3, as long as the tank pressure is maintained above the Saturated Vapour Pressure of the cargo, then equilibrium is obtained between the liquid and vapour phase of the cargo and no further VOC will evolve from the cargo. This means that if the pressure/vacuum relief settings are increased to, e.g., 2,100 mmWG, VOC will not evolve from a cargo as long as the Saturated Vapour Pressure of said cargo is below the pressure relief setting.

As indicated earlier, the maximum design pressure of a cargo tank is at least 2,500 mmWG and, as such, increasing the settings of the pressure/vacuum devices up to, e.g., 2,100 mmWG, should not require additional strengthening. It will however require adjustment/replacement of P/V valves. Note that for some P/V valves designs, the pressure after initial opening increases, and this has to be taken into account if an owner intends to increase the setting of P/V valves.

Needless to say it will also require replacement/modifications to the P/V breaker, as well as water loops serving the inert gas deck water seal, as well as settings of pressure sensors and alarms in the inert gas and VECS system. It is of course also essential that onboard operational procedures in terms of manual pressure release have to be adjusted.

One additional benefit is that increasing the pressure/vacuum relief settings will increase the acceptable loading rate during VECS.

Although the primary benefit of increasing set pressure will occur during voyage. It will also have an effect related to loading, as the increased set pressure will limit the existing vapour in the cargo tanks, i.e. the vapour generated during the previous discharge and Crude Oil Washing.

For ships that have been provided with increased pressure relief settings, the VOC emissions will be controlled when the saturated vapour pressure of the crude oil is below that of the pressure relief valve settings.

It is important that terminals and cargo surveyors acknowledge that if ships with higher pressure settings are required to de-pressurize prior to cargo handling operations, this will limit the ships' ability to control VOC emissions.

#### 4.1.6 Vapour recovery systems – General

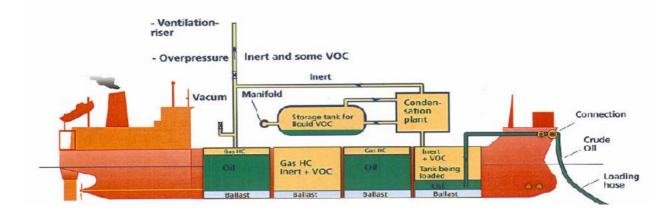
In the late 1990s certain Administrations required offshore installations to reduce their emissions of VOC and this led to the development and installation of vapour recovery systems on board shuttle tankers in the North Sea. Different concepts were developed for the purpose of reducing the emissions of VOC (VOC). The initial efficiency requirement was set to 78% (i.e. 78% less VOC emissions when using vapour recovery systems). The systems can recover VOC in all operational phases.

For ships that have been provided with vapour recovery systems, the VOC emissions will be controlled when the recovery plant is in operation.

The VOC recovery plant efficiency as well as any operational limitations related to, e.g., applicability for different cargo handling modes (loading, transit, COW), maximum allowable loading rates or crude vapour pressures, are to be specified in the VOC management plan.

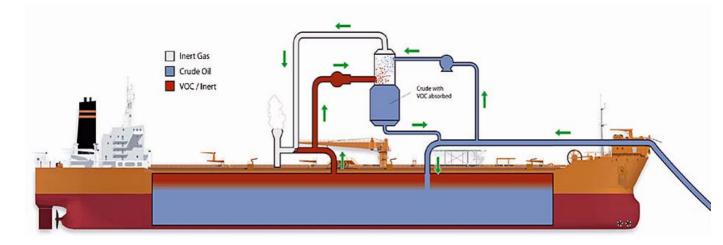
### 4.1.6.1 Vapour Recovery Systems – Condensation Systems

The principle is similar to that of re-liquefaction plants on LPG carriers, i.e. condensation of VOC emitted from cargo tanks. In the process, the VOC passes through a knock out drum before it is pressurized and liquefied in a two stage process. The resulting liquefied gas is stored in a deck tank under pressure and could either be discharged to shore, or be used as fuel (possibly including methane and ethane) for boilers or engines subject to strict safety requirements. It is also conceivable that the stored gas could be used as an alternative to inert gas subject to the Administration's acceptance.



#### 4.1.6.2 Vapour Recovery Systems – Absorption Systems

The technology is based on the absorption of VOCs in a counter-current flow of crude oil in an absorber column. The vapour is fed into the bottom of the column, with the side stream of crude oil acting as the absorption medium. The oil containing the absorbed VOC is then routed from the bottom of the column back to the loading line where it is mixed with the main crude oil loading stream. Oil pumps and compressors are used to pressurize the oil and gas. Unabsorbed gases are relieved to the riser to increase the recovery efficiency. Similar concepts have been developed using swirl absorbers instead of an absorption column.

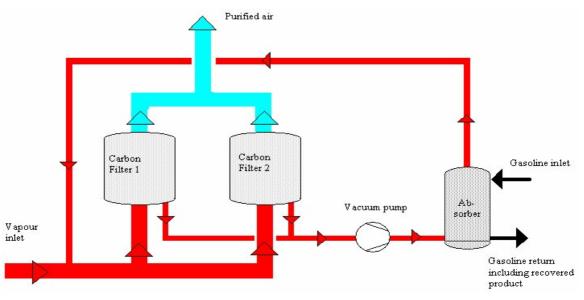


#### 4.1.6.3 Vapour Recovery Systems – Absorption Carbon Vacuum-Regenerated Adsorption

In the CVA process, the crude oil vapours are filtered through active carbon, which adsorbs the hydrocarbons. Then the carbon is regenerated in order to restore its adsorbing capacity and adsorb hydrocarbons in the next cycle. The pressure in the carbon bed is lowered by a vacuum pump until it reaches the level where the hydrocarbons are desorbed from the carbon. The extracted, very highly concentrated vapours then pass into the absorber, where the gas is absorbed in a stream of crude oil taken from and returned to the cargo tanks.

As carbon bed adsorption systems are normally sensitive to high concentrations of hydrocarbons in the VOC inlet stream, the VOC feed stream first passes through an inlet absorber where some hydrocarbons are removed by absorption. The recovered VOC stream may be reabsorbed in the originating crude oil in the same inlet absorber.





## 4.2 Methods and systems for the control of VOC during Transit

### 4.2.1 Best Practices/Design

- .1 Manual pressure relief procedures (tank pressure control);
- .2 P/V valve condition and maintenance;
- .3 Condition of gaskets for hatches and piping;
- .4 Inert gas topping up procedures;
- .5 Partially filled tanks;
- .6 Loading sequence and rate; and
- .7 COW procedures (closed cycle<sup>7</sup>).

## 4.2.2 **VOCON procedure**

By reference to Figure 4.2 below, this procedure requires the monitoring and the recording of the pressure drop during a release of gas from the cargo tank vapour system. This can be undertaken with the use of the Inert Gas pressure gauge in the cargo control room or, as available, located on the Inert Gas pipeline on deck. Figure 4.2 shows a pressure drop profile using the mast riser and the inflection in the pressure drop where the mast riser valve should be shut.

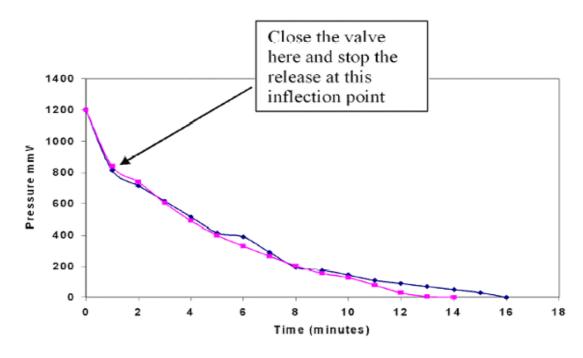


Figure 4.2 – A mast riser release

<sup>&</sup>lt;sup>7</sup> "Closed Cycle" crude oil washing means that the tanker's slop tank is used as the reservoir for the crude oil wash stock and this wash stock is stripped or cycled back to the slop tank for reuse. Thus, using a defined volume of crude oil for washing of the specified cargo tanks will limit the amount of VOC associated with the wash stock volume as distinct from using fresh crude oil throughout the washing programme.

#### The VOCON operational procedure

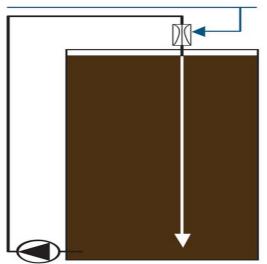
- (1) Before opening the mast riser, note the pressure in the Inert Gas pipeline system.
- (2) Open the pressure release valve and record/monitor the pressure within the Inert Gas pipeline at regular short intervals (every 30 seconds for a mast riser release).
- (3) Plot the pressure drop profile. This can be achieved either manually or by use of the Inert Gas Oxygen and Pressure Recorder in the Cargo Control Room but an increase in the Recorder paper feed rate will be required to achieve definition of the plot.
- (4) When the rate of pressure drop becomes constant (after the initial rapid pressure drop) then the gas release should be stopped and the valve closed.
- (5) Monitor the Tank Gas Pressure after completion of the controlled release in order to check the final pressure obtained within the Vapour/Inert Gas system.

#### Advice Notes

- (A) A review of Figure 4.2 shows a clear change in the rate of pressure drop during the release period. If the gas release continues after this point then the pressure in the Inert Gas system will be quickly restored to the pressure associated with the point where the rate of pressure drop changes.
- (B) If there is a straight line drop of pressure observed and no inflection observed by 800 mmWG, then close the release valve anyway.
- (C) By reference to the ISGOTT Publication, all safety measures should be taken to minimize the hazards associated with vented gases from the vessel's cargo tank system.

#### 4.2.3 Recovery of excess VOC and tank absorption (Venturi system)

The Venturi system involves a process where evolved VOC is reabsorbed back into the cargo. The system typically consists of a pressure controlled pump, feeding oil to a unit with Venturi(s). The Venturi draws VOC,  $H_2S$  and inert gases (IG) from the common cargo tank venting/inert gas main line. The Venturi unit is designed to generate a bubble size optimal for their collapse in the crude oil cargo and rapid absorption. Released near the tank bottom, the soluble compounds are kept dissolved by the pressure head there. Inert gas will eventually surface.



Oil is pumped from a cargo tank through the Venturi unit. Gas is sucked in from the main inert gas line and injected at the bottom of the tank.

For ships that have been provided with a Venturi type system, the VOC emissions will be controlled when the system is in operation.

The VOC control system efficiency as well as any operational limitations related to, e.g., applicability for different cargo handling modes (loading, transit, COW), maximum allowable loading rates or crude vapour pressures, are to be specified in the VOC management plan.

#### 4.3 Methods and systems for the control of VOC during Discharging/Ballasting

Emissions of VOC during ballasting had relevance when tankers took ballast into cargo tanks for stability and longitudinal strength reasons and thus displaced VOC from cargo tanks being ballasted. After the implementation of requirements to segregated ballast tanks and, of course, double hull, VOC releases during discharge and ballasting are no longer an issue.

During discharging of cargo tanks, it is important that pressure monitoring is exercised in order to avoid excessive supply of inert gas to cargo tanks.

## Section 5 – The Monitoring and Control of VOC Releases

5.1 Record keeping is necessary in order to document compliance with the requirements of the management plan and, potentially, the extent of release of gases from the crude oil cargo tanks. The form of record keeping is dependent upon the specific form of method used to minimize the emission of VOC from the crude oil cargo. It will also be dependent upon the operation being performed by the ship necessitating the release of VOC, namely loading during the carriage or as a result of a crude oil washing (COW) operation.

5.2 As a general example of the type and scope of record keeping to be undertaken on board the crude oil tanker, the methodology of the manual VOCON procedure is used. The appropriate record keeping is as follows:

- .1 The target or minimum pressure within the tank gas/vapour system for the specific voyage
  - .1.1 A record of the time and pressure within the tank gas/vapour system before the release takes place.
  - .1.2 A record of the time and pressure within the gas/vapour system after the release has been completed.

5.3 The foregoing data and information may be compiled by the ship's management company or operators in order to assess or quantify the extent or degree of VOC release. As an outline to such assessment the following can be taken into consideration:

.1 For those ships operating with manual VOC control by the VOCON procedure, the released volume of gas/vapour can be estimated by use of the pressure change (opening to closing pressures) relationship to the total gas/vapour volume in the cargo tank vapour system (Ideal Gas Laws – reference to section 3).

## **Section 6 – Training Programme**

6.1 A training programme is to be developed for the persons intended to assume overall charge of the VOC management on board each ship. The programme is to include the following:

- .1 An introduction to the purpose of VOC emission control:
  - .1.1 Volatile organic compounds (VOCs) may be toxic, and when they evaporate into the air they can react with Nitrogen Oxides  $(NO_x)$  in sunlight and split apart oxygen molecules in air and thereby form ground-level ozone, commonly referred to as smog. The layer of brown haze it produces is not just an eyesore, but also is a source of serious illnesses. Ozone is extremely irritating to the airways and the lungs, causing serious damage to the delicate cells lining the airways. It contributes to decreased lung function, increased respiratory symptoms and illnesses.
  - .1.2 Regulation 15 of MARPOL Annex VI
- .2 An introduction to the principles of VOC emission control:
  - .2.1 VOC generation systems in crude oil (ref. section 3)
  - .2.2 Crude oil tanker pressure control/release systems (ref. section 2)
- .3 General VOC emission control options:
  - .3.1 Methods and systems for the control of VOC emissions (ref. section 4)
- .4 Ship specific VOC emission control options:
  - .4.1 Ship specific methods and systems for the control of VOC emissions (ref. section 4)

- .5 Monitoring and recording of VOC release:
  - .5.1 Methods for monitoring and recording of VOC emissions (ref. section 5)
- .6 Hazards and Safety related to VOC emission control:
  - .6.1 The hull and its pressure limitations (ref. section 1)
  - .6.2 Personnel safety hazards related to exposure to crude oil vapour.

## Section 7 – Designated Person

7.1 A person should be designated to assume overall charge of the VOC management on board the ship.

The designated person should preferably have:

- .1 At least one year's experience on crude oil tankers where his or her duties have included all cargo handling operations relevant to VOC management. In the absence of experience with VOC management, he or she should have completed a training programme in VOC management as specified in the VOC management plan;
- .2 participated at least twice in cargo loading operations, Crude Oil Washing Operations and transit where VOC management procedures have been applied, one of which should be on the particular ship or a similar ship in all relevant aspects, for which he or she is to undertake the responsibility of VOC management; and
- .3 full knowledge of the contents of the VOC management plan.

## Section 8 – List of drawings

8.1 The following drawings are recommended included as appendices to the management plan:

- .1 General Arrangement drawing;
- .2 Tank plan;
- .3 Schematic drawing(s) of the Cargo tank venting system;
- .4 Schematic drawing of the inert gas system;
- .5 Schematic drawing of the vapour emission control systems (if applicable);
- .6 Schematic drawing(s) Vapour Recovery System or other VOC control systems; and
- .7 Details of pressure vacuum relief devices including settings and capacities.

## References:

- .1 Vapour Emission Control System manual (if applicable);
- .2 Vapour Recovery System manual (if applicable);
- .3 Other VOC control system manual (if applicable);
- .4 Inert Gas manual; and
- .5 COW manual.