World Maritime University Dissertations   Dissertations

1992

Control of tank atmospheres on oil tankers

Abdou Gning
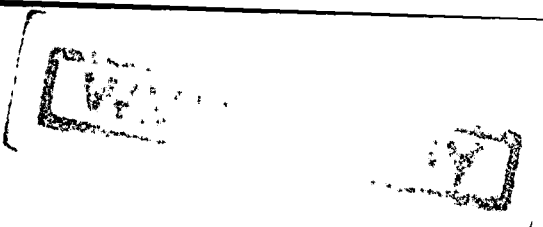*World Maritime University*

Recommended Citation

WORLD MARITIME UNIVERSITY
Malmo, Sweden

CONTROL OF TANK ATMOSPHERES ON OIL TANKERS

by

Abdou GNING

Senegal

A dissertation submitted to the World Maritime University in partial fulfilment of the requirements for the award of the

Degree of Master of Science

in
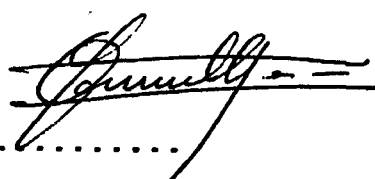
Maritime Education and Training (Nautical)

Year of graduation

1982

I certify that all material in this dissertation which is not my own work has been identified and that no material is included for which a degree has been previously conferred upon me.

The contents of this dissertation reflect my personal views and are not necessarily endorsed by the University.

(Signature)...................

(Date) 26.Oct.1992

Supervised by:

G. ZADE
Vice-Rector, and Academic Dean
World Maritime University

Assessed by:

T. D. HAZARI
Principal
Maritime Training Institute
Bombay, India

Co-assessed by:

H. KAPS
Professor
Hochschule Fur Nautik
Bremen, Germany

T O

S A F E T Y

And

To my parents, wife and children

C O N T E N T S

iv

A C K N O W L E D G E M E N T S

----- o -----

I wish to express my appreciation for the cooperation of various individuals and organizations which have contributed either directly or indirectly to the realization of this thesis.

First of all, I would like to thank the Government of SENEGAL and the International Maritime Organisation for giving me the opportunity to study at World Maritime University.

I would like to express my profound gratitude to Dr Gunther Zade, vice rector of WMU and my course professor in MET(N); to Capt. Tarasingh D. Hazari, Principal of Training Institute in Bombay; to Capt. Hermann Kaps, Professor at Hochschule Fur Nautik in Bremen, who have undertaken the supervision, assessment and co-assessment respectively, of this dissertation. Their assistance and guidance have contributed greatly towards successful completion of this project.

In addition, I wish to acknowledge deeply Mr Jeph H. Mulders my course-professor during my first academic year in WMU.

I am also extremely grateful to Mr David Mottram Professor at WMU and Bob Simpson, Principal Consultant of BP Shipping in London, for their help during the preparation of this thesis.

Finally, I would like to thank all the visiting Professors, Lecturers and English Language Progamme Lecturers who fully involved themselves in transmitting their knowledge and experience.

----- o -----

v

A B S T R A C T

This dissertation is a study and analysis of the control of tank atmospheres in oil tankers. It reveals the various aspects of hazards and points out the required prevention for each possible problem related to them.

In the introduction, the dissertation outlines its aim, scope, reasons and basic concepts.

A study is made on static electricity within cargo tanks, examining how the electrostatic charges are generated and what are the necessary precautions to be taken for safe operations.

The origin of mineral oil, its chemical structure and physical properties are described. Then, the different types of tank atmospheres, control of same and safe tanker operations for each situation, including tank-cleaning, gas-freeing and ventilation, are also covered.

Flammability hazards, inert gas operations and the control of environmental pollution are also described.

Finally, some suggestions on the control of vapour emissions and ventilation of double hull spaces have been given.

It is hoped that this dissertation will be of benefit to practising ship officers of oil tankers and lecturers on oil tanker courses in MET institutions, as it explains in a simplified way the problems, hazards and control of tank atmospheres on oil tankers.

vi

ABBREVIATIONS

Ar	Argon
CO_2	dioxide de carbon
EDL	Electric Double Layer
HC	Hydrocarbon
He	Helium
IGS	Inert gas system
IMO	International Maritime Organization
ISGOTT	International safety guide for oil tankers and terminals
LEL	Lower explosive limit
LFL	Lower flammable limit
MARPOL	Iternational convention for the safety of life at sea 1973/1978
MET(N)	Maritime education and training (nautical)
N_2	Nitrogen
O_2	oxygen
SOLAS	International convention on safety of life at sea
STCW	International convention on standards of training, certification and watchkeeping,1978
UEL	Upper explosive limit
UFL	Upper flammable limit
VLCC	Very large crude carrier
WMU	World Maritime University

CHAPTER 1

INTRODUCTION

When I was in career on an oil tanker, I often felt the need for a simple and straightforward written manual on the principles of tank atmospheres. Hence, I took this opportunity during my stay at World Maritime University to write this dissertation on the "Control of Tank Atmospheres on Oil Tankers".

A tank atmosphere can be defined as the composition and amount of gases contained in the ullage space of a tank. These gases include hydrocarbon gases, water vapour, inert gas, air and hence oxygen, etc. The term oil has been used as a general word to describe crude oil and the products derived from it such as gasoline, kerosine, lubricating oil and so on.

The aim of the dissertation is to provide, for ship's officers, lecturers and others, a large view of the subject and a good understanding of how to prevent or to eliminate hazards in a cargo tank of an oil tankar.

Tank atmosphere control can be considered in terms of safety and operational concerns:

- the safety concerns include the risk of fire, explosion and air pollution associated with the handling of the tank atmospheres; and,

- the operational concerns deal with all aspects of tanker operations, namely loading, discharging,

deballasting, tank-cleaning, gas-freeing, inert-gas operations etc. In order to carry out the afore-mentioned operations in a safe and pollution-free manner, the training of operating personnel plays a very important role. In fact the best way of preserving safety is training.

Experience of injuries, dangerous occurrences, fires, explosions and other such events in many fields including tanker safety problems, shows that human causes are much more common than equipment failures. I have written this paper with this in mind and therefore more emphasis has been placed on what an operator should do than on the functioning of equipment. Further, the dissertation has been restricted to the area of tank atmosphere control related to the various aspects of tank operations.

CHAPTER 2

STATIC ELECTRICTY WITHIN

CARGO TANKS

2.1 : GENERAL

2.1.1 :CHARGE GENERATION

When two dissimilar bodies are in contact with each other, there will be an imbalance of electrical charge at the interface. If subsequently the two bodies were separated by some mechanical action, one of them will carry an excess of positive charge or protons and the other one an excess of negative charge or electrons. If also the separated charges are nearby, they attempt to recombine the charges by what we call conduction. However, if one of them is a poor conductor of electricity, the recombination will be limited and a difference in electrical charge and hence a difference in potential, will exist between them. This electrical charge due to the separation of the two bodies is called Static Electricity. This explanation shows how liquid pumped through a pipeline can be electrically charged when it enters into the cargo tank.

2.1.2 : CHARGE ACCUMULATION

The ability of a liquid to retain an electrostatic charge is function of its conductivity. This characteristic may be expressed in terms of

conductivity (1 conductivity unit = 1 picoho per metre, ps/m = 10^{-14} OHM^{-1} CM^{-1}) or in the inverse form as resistivity (1 resistivity unit = 10^{14} OHM.CM). The lower the conductivity of a liquid is, the more it accumulates a static charge of electricity and vice versa. For example, crude oil which has a relatively high conductivity accumulates very little static charge.

2.1.3 : ELECTROSTATIC DISCHARGE

The charge accumulated in a liquid, on a solid or in mist establishes an electric field between it and nearby earthed body. If the electric field at any point exceeds approximately 3000 kv/m, then an electrostatic discharge or spark will occur [1]. The type of discharge depends on the conduction and other properties of the charged body. It is more important with material of higher conductivity than with material of lower conductivity.

2.2.: ELECTROSTATIC CHARGING OF OIL

2.2.1 GENERAL CONSIDERATIONS

Oil contains equal quantities of positive and negative ions. Therefore, it is electrically neutral. However, the distribution of ions will be redistributed when the liquid comes into contact with a solid or non-solid body. It will have a new arrangement of ions at the interface in the form of two layers :

- A narrow layer of ions of the same sign lies in

contact with the solid or the other body ;

- Beyond this narrow layer, but still in close proximity to the interface, lies a broader layer of ions of opposite sign to those in the narrow layer.

This layering effect is known as the Electric Double Layer (EDL) [2]. The distribution of ions remains unchanged in the other points of the oil. The oil ions which are in close contact with the solid tend to adhere to the solid so that when the liquid and the solid are separated, part of these ions will stay attached to the solid. Thus, the oil will lose some of its ions through the separation and become electrostatically charged. So will the solid, but in
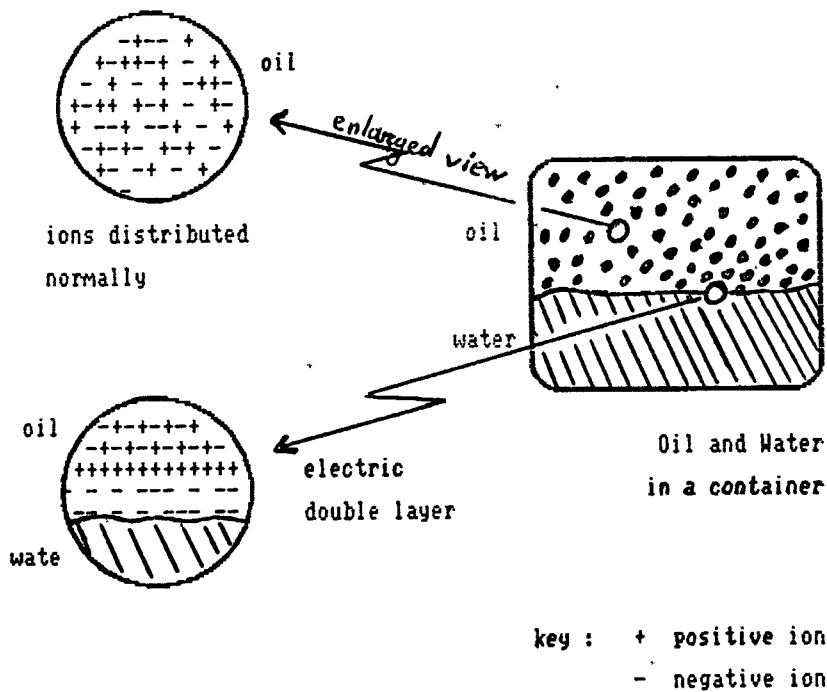
Figure 2.1   ELECTRIC DOUBLE LAYER (EDL)
Case: Liquid against Liquid

the opposite sense. Then, the separate charges will attempt to recombine if they are nearby with more or less success.

The EDL theory applies to any interface between solid and solid, liquid and solid such as oil and ship's structure, liquid and liquid such as oil and water, etc.

2.2.2 :CHARGE SEPARATION DUE TO PIPELINE FLOW:

When oil, liquefied gas or a chemical product moves through a pipeline, some of its ions which are in close proximity to the pipe surface will be left behind upon the pipe. It becomes electrostatically charged as does the pipe in the opposite sense. The separated ions will try to rejoin the oil. Sometimes they are able to do so, but sometimes they are not. The ability of these ions to recombine depends on the conductivity of the concerned liquid. The recombination will be easy for high conductivity oils which are also named black oils, because the impurities in these oils make them highly conductive (see table 2.1). For the so-called white oils, which are essentially pure but contain trace impurities which can be ionized, conductivity is low and both separation and recombination are poor. There are probably no white oils which contain no trace of impurities; hence they are not likely to have nil conductivity.

Liquids are said to be non-conductors when their conductivities are less than 50 pS/m, giving a relaxation time greater than 0.34 seconds.[3]. They are known as static accumulators and can be statically charged. White oils (distillates) are frequently in

6

this category. In practice it is common that shore operators come on board and add an antistatic additive to a petroleum distillate in order to raise its conductivity above 50 pS/m. The conductivity of

CONDUCTIVITY	RESULT	EXAMPLES
HIGH	easy separation, but easy re-combination. = no charge	i) crude oil, fuel oil, bitumen (asphalt) and other 'black' oils. (It is the impurities in these oils which make them conductive). ii) water, alcohol and other water soluble products.
LOW	poor separation but poorer re-combination. = charge	gasoline, kerosine, naphtha. jet fuel, diesel oil, gas oil, benzene, lubricating oil and other 'white' oils. (such oils are essentially 'pure', but contain trace impurities which can be ionised).
NIL	no separation	'white' oils which contain no trace impurities; there are probably no practical examples.

Table 2.1   TENDENCY OF A LIQUID TO BECOME CHARGED
BY PIPELINE FLOW

petroleum liquid can be summarized as follows [4]:

Highly Purified Hydrocarbons : 0.001   pS/m
Light Distillates :   0.01 to 10   pS/m
Black Oils :   1,000   to 100,000 pS/m

Oils which have a conductivity of more than 50 pS/m are
conductive. They are not statically dangerous because
their charges recombine as fast as they are generated.

The effect of an electrostatic charge is affected
by the rate at which a liquid flows through a pipeline.
The faster the flow , the faster charge separation will
occur and the greater will be the build-up of static
charge.
        The presence of filters in cargo lines is another
factor which contributes to electrostatic generation
caused by pipeline flow. Charge separation may be
considerable as liquid passes through a filter.
However, with the use of a coarse filter, which is very
common, the increase in charge is almost insignificant.

2.2.3 : CHARGE SEPARATION DUE TO OIL MIXING WITH WATER:
        During the loading period, if there is water lying
in the bottom of a tank or in the pipeline, it will be
carried inside the tank and cause turbulence by the
flow of the oil. Charge separation will therefore occur
as water droplets pass through the oil in accordance
with the theory of EDL (Electric Double Layers) . After
loading is completed, the water droplets will lose
their charge to the tank structure after they have
settled on the bottom and the oil will get two

additional charges: one being left behind by the droplets of water and the other caused by the pipeline flow. The oil will stay in an electrically charged state if it is a white oil. However, if it is a black oil, the ions will recombine and the charge will dissipate.

2.2.4: CHARGE SEPARATION DUE TO LIQUID SPLASHING WITHIN A TANK

The liquid (water or crude oil) used to wash tanks causes generation of electrostatic charges. The droplets of oil will knock against the structure of the tank. Through the shock, they will leave behind some of their ions on the surface of the metal. Then, both the droplets and the metal become charged. Furthermore, the accumulation of charge on the oily mist or spray in the tank is very important. Experience has shown that the voltage of the electrostatic charge within the tank is more critical in the center of the tank than near the internal structures. See fig 2.2.

The electrostatic charge of the oil mist or spray is not dependent on the conductivity of the oil. Thus, both white and black oils may become charged by splashing or spraying because the charge recombination in this case is not easy. For this reason precautions must be taken to control the tank atmosphere during or after washing. Examples of this hazardous situation can be illustrated by the three supertanker explosions, namely "MARPESSA", "MACTRA" and "KONG HAAKON VII" which occured in December 1969. All these tankers were new and all were cleaning tanks at the time of the explosions, on a ballast passage. This particular

Figure 2.2

source : Reference [15]
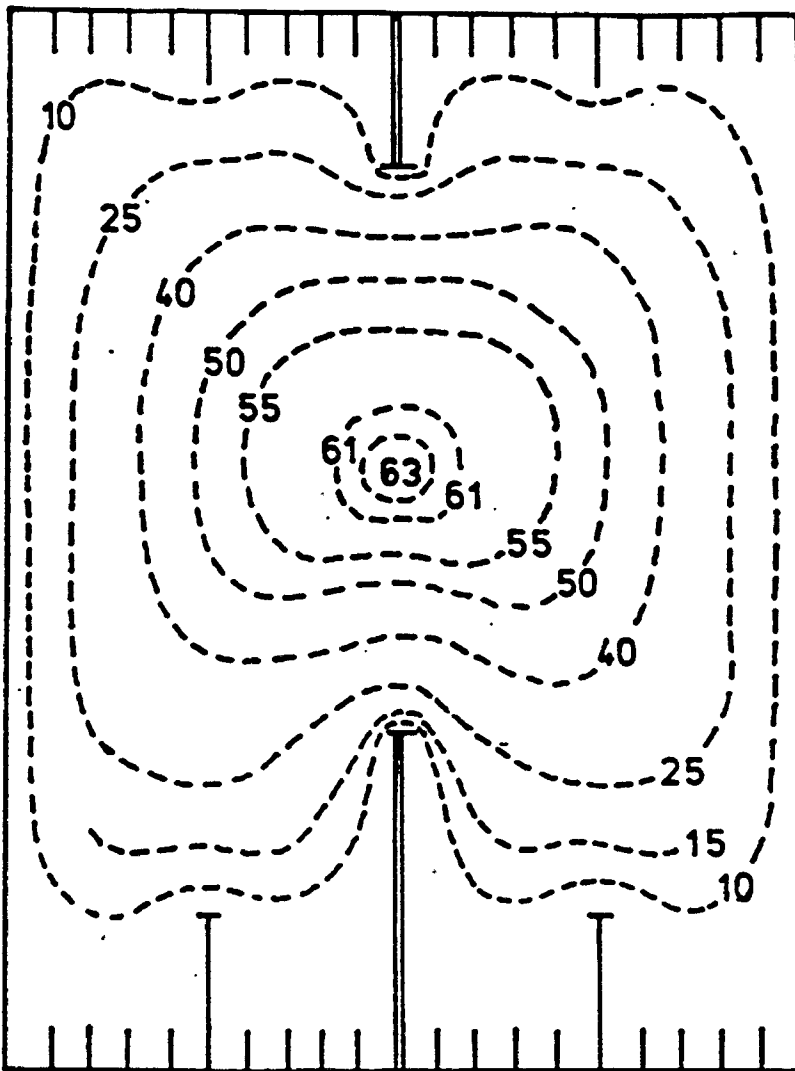
a) Voltage distribution over a vertical section of a VLCC centre tank

figures show percentage of voltages to be expected without internal structures
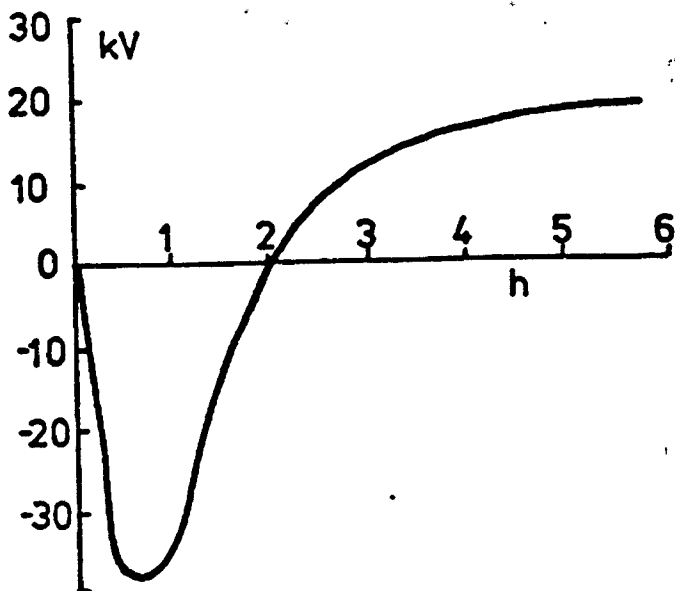
b) Voltage measurement during cold water washing a 27 000 m³ centre tank with one internal bulkhead

measurement taken 4 m away from bulkhead whilst washing with 4 guns in closed cycle

example shows how static electricity can occur in such situations and needs great attention.

2.3 : CONTROL OF ELECTROSTATIC HAZARDS ON TANKERS.

Ignition hazards from static sparks can be eliminated by controlling the generation of electrostatic charge, or the discharge of static charges, or by controlling of vapour-air mixtures. These three elements are considered in the paragraphs below.

2.3.1 : CONTROL OF STATIC GENERATION BY CARGO FLOW VELOCITY.

In order to reduce the generation of charge and minimize the hazard, the flow rate of static liquid accumulators such as oils should be restricted during loading. In the beginning of the loading operations, when oils and particularly white oils are being loaded into each individual tank, the flow rate in its branch line should not exceed a linear velocity of 1 metre/second. Thereafter, the linear velocity can be increased progressively, to the maximum loading rate. Let us illustrate the importance of this restriction by the following example :

On July 31,1986, the U.S tank barge TTT 103 exploded and finally sank while loading gasoline at the Chevron Oil Refinery in Pascagoula, Mississipi. In the accident report the U.S. National Transportation Safety Board (NTSB)determined that the probable cause of the

explosion was the initial high loading rate of the highly volatile low conductivity gasoline which resulted in the generation and discharge of an electrostatic charge in the flammable tank atmosphere.

2.3.2.: CONTROL OF ELECTRICAL DISCHARGE:

2.3.2.1 Ship/shore insulating, bonding and earthing:

The purpose of bonding and earthing is to eliminate electrical sparks on board the ship and on the shore during operation or work on the deck. These sparks can have their source in the following currents:

. Static electricity built up on board the ship by the entrance of the liquid cargo.

. Galvanic current which exists between the ship and the jetty due to the fact that the ship which is partly immerged in the sea acts as a cathode in an electrolyte, because she is an entity of metal and the sea water is a solution containing salt.

. Leakage effects from board or shore electrical power sources.

To provide protection against arcing, all metal and conducting objects on board the ship should be bonded (connected). On the shore side all metal should also be connected and earthed.

12

However there should be an electrical discontinuity between the ship and the shore. Shore metal arms or cargo hoses, if not totally non-conductible, should be fitted with an insulating flange before connection to the ship. Therefore, a ship/shore bonding cable should not be used. It is not effective as a safety device. The reason for this is that the galvanic current which need this bonding cable has low voltage so that the appropriate and necessary low resistance wire for such bonding wire is difficult to find. Thus, IMO "Recommendations for the Safe Transport, Handling, and Storage of Dangerous Substances in Port Areas" urges port authorities to establish a total insulating system between the shore and the ship.

2.3.2.2 : Increasing static dissipation:

Static dissipation, that is the recombination of ions, is slow for white oils because these oils have poor conductivity. Therefore, when static charges are high, we can reduce them by using antistatic additives which increase the conductivity of the liquid and therefore increase static dissipation.

2.3.2.3 : Precautions when sampling or ullaging

There is risk of producing sparks during sampling or ullaging a charged petroleum liquid in a cargo tank. The apparatus we use for these operations should be appropriate, as given below:

a) conducting apparatus:
If the apparatus used for sampling or ullaging is

a conducting object, it becomes charged as follows:

i. By contact with the ullage pipe or the worker if he is barefoot on the wet deck: sparks are possible on the point where the apparatus touches the surface of the liquid as it can be seen in the figure 2.3. This is due to a difference in charge between the liquid and the tank structure which has the same charge as the worker and the apparatus.

ii. By the petroleum liquid : a spark is also possible while the apparatus is in contact with the ullage pipe. This is due to the fact that, being first in contact with the liquid and remaining so, the apparatus has the same charge as the liquid, and a contrary charge to the ullage pipe.

Conducting apparatus, if ever used, should be bonded or earthed.

*NB The polarity need not necessarily be as indicated. However, the charge in the oil will be opposite to that on the ullage tape..

tape becomes charged by contact with the ullage pipe.

steel ullage tape

KEY

+ positive ion*

● negative ion*

SPARKS PRODUCED BY A STEEL ULLAGE TAPE NEAR A CHARGED OIL SURFACE.
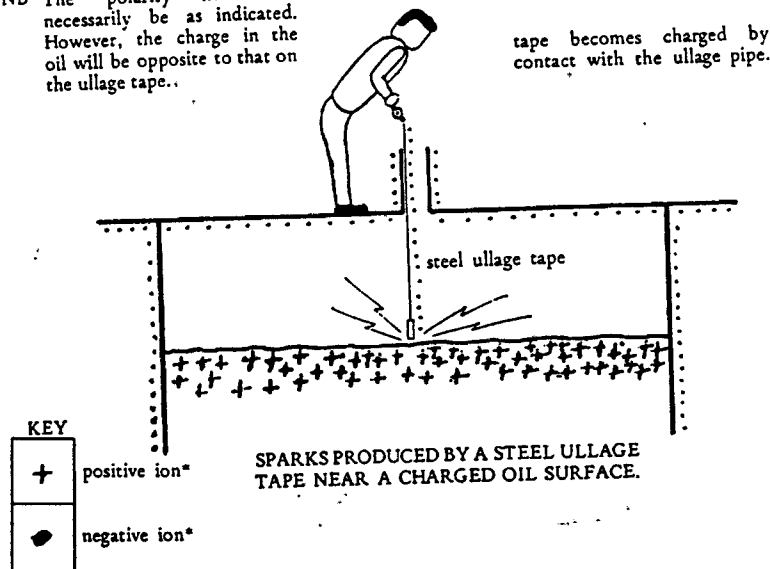
Figure 2.3

source : Reference [2]

14

b) Non-conducting apparatus:

It is safer, when ullaging or sampling, to use a non-conducting apparatus. However, it should not be wettable because a wet material is considered as a conductor.

If the tank is well inerted, for tankers which use an inert gas system, then precautions regarding static electricity hazards are not necessary (see table 2.2).

Requirements for static electricity precautions when loading, discharging, ullaging, dipping and sampling

Electrostatic Classification	Volatility Classification	Whether static precautions necessary			Examples
		Tank Atmosphere			
		Inerted	Gas Free	Non-Gas Free	
Non-Accumulator	Non-Volatile (Flashpoint 60°C or above)	No	No	No	Hard asphalts (bitumens) Black diesel oils Residual fuels
	Volatile (Flashpoint below 60°C)	No	No	No	Crude oils Cut back asphalts (bitumens)
Accumulator	Non-Volatile (Flashpoint 60°C or above) Oil temperature $<FP-10°C$	No	No	Yes	Heavy gas oils Clean diesel
	Non-Volatile (Flashpoint 60°C or above) Oil temperature $>FP-10°C$	No	Yes	Yes	High flash jet fuels Lubricating oils
	Volatile (Flashpoint below 60°C)	No	Yes	Yes	Kerosenes Heating oils Jet fuels Naphthas White spirits Motor gasolines Aviation gasolines Natural gasolines

Table 2.2   **source : ISGOTT (Reference [3])**

CHAPTER 3

OIL AND TANK ATMOSPHERES

3.1 : PROPERTIES OF OIL

3.1.1 : CHEMICAL STRUCTURE

Chemical knowledge of tanker cargoes is vital for efficiency and safety. For this reason, a certain amount of chemical analysis must engage the attention of ship's cargo operators so that if remedial action is required, it will be carried out with precision.

Petroleum is derived from the Latin words "petra" (rock) and "oleum" (oil). It is a mineral oil consisting essentially of hydrocarbons with a very small amount of sulphur, nitrogen, oxygen and some other organo-metallic elements such as vanadium, nickel and iron.

A hydrocarbon molecule is formed with atoms of hydrogen and carbon. A hydrogen atom has one bond and a carbon atom has four. These bonds allow each carbon atom to be able to combine with four hydrogen atoms or other carbon atoms. By this means combinations of carbon and hydrogen atoms can occur and many kinds of hydrocarbon molecules can be formed. The general formulas of hydrocarbons are as follows:

a) - **Paraffin or alkane:** $C_nH_{2n} + 2$; with n = number of carbon atoms. Examples of hydrocarbons belonging to the Paraffin series are: methane (CH_4) which is a gas at normal atmospheric temperature and

pressure; ethane gas (C_2H_6), propane gas (C_3H_8); butane gas(C_4H_{10}). Compounds with four or more carbon atoms can have a structure in the form of a straight chain arranged as follows :

```
      H   H   H   H
  H - C - C - C - C - H
      H   H   H   H
```
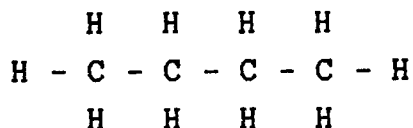
gas butane C_4H_{10}

or a branched chain :

```
          H   H   H
      H - C - C - C - H
          H   I   H
              I
          H - C - H
              H
```
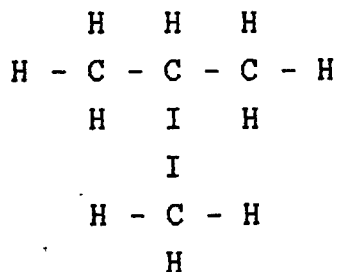
gas butane C_4H_{10}

These hydrocarbon molecules called the paraffin or alkane series have the following factors in common :
i).   they do not react easily with other chemicals,
ii). their vapour can be made to burn when mixed with
      air,
iii). their vapour is usually toxic.

b) - **Cyclo-Paraffins** : Cn H2n
An example of a hydrocarbon in the cyclo-paraffin series is cyclo-pentane, C_5H_{10}. This type of hydrocarbon

is found in crude oil and usually contains five, six
or seven carbon atoms arranged in the form of circle.
Cyclo-paraffins take their names from paraffin because
they have the same number of carbon atoms. Both have
the same general factors.

c) - Olefins : CnH2n

The olefins and the cyclo-paraffins have the same
formulas but the structure and physique of the
molecule, is not the same. Olefin atoms are not
attached in the form of a circle; and also they are
linked in double bonds. An example of olefin is
Ethylene (C_2H_4), which is shown below :

```
      H     H
      C  ==  C
      H     H
```
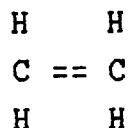
Olefins are found in very small amounts in crude oil
but they are produced in large quantities in the
refinery. The double bonds give them the ability to
react rapidly with other atoms or chemical groups. The
paraffins have their name ending by the suffix "ane"
wile the olefins take the same name but ended by
"ylene" or "ene". For example: propane C3H8 (paraffin);
propylene or propene C_3H_6 (olefin).

d) Acetylene : CnH2n-2

These hydrocarbons have triple bonds joining the carbon
atoms. They are very reactive. Example: acetylene
C2H2:

```
      H - C ≡ C - H
```

18
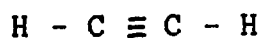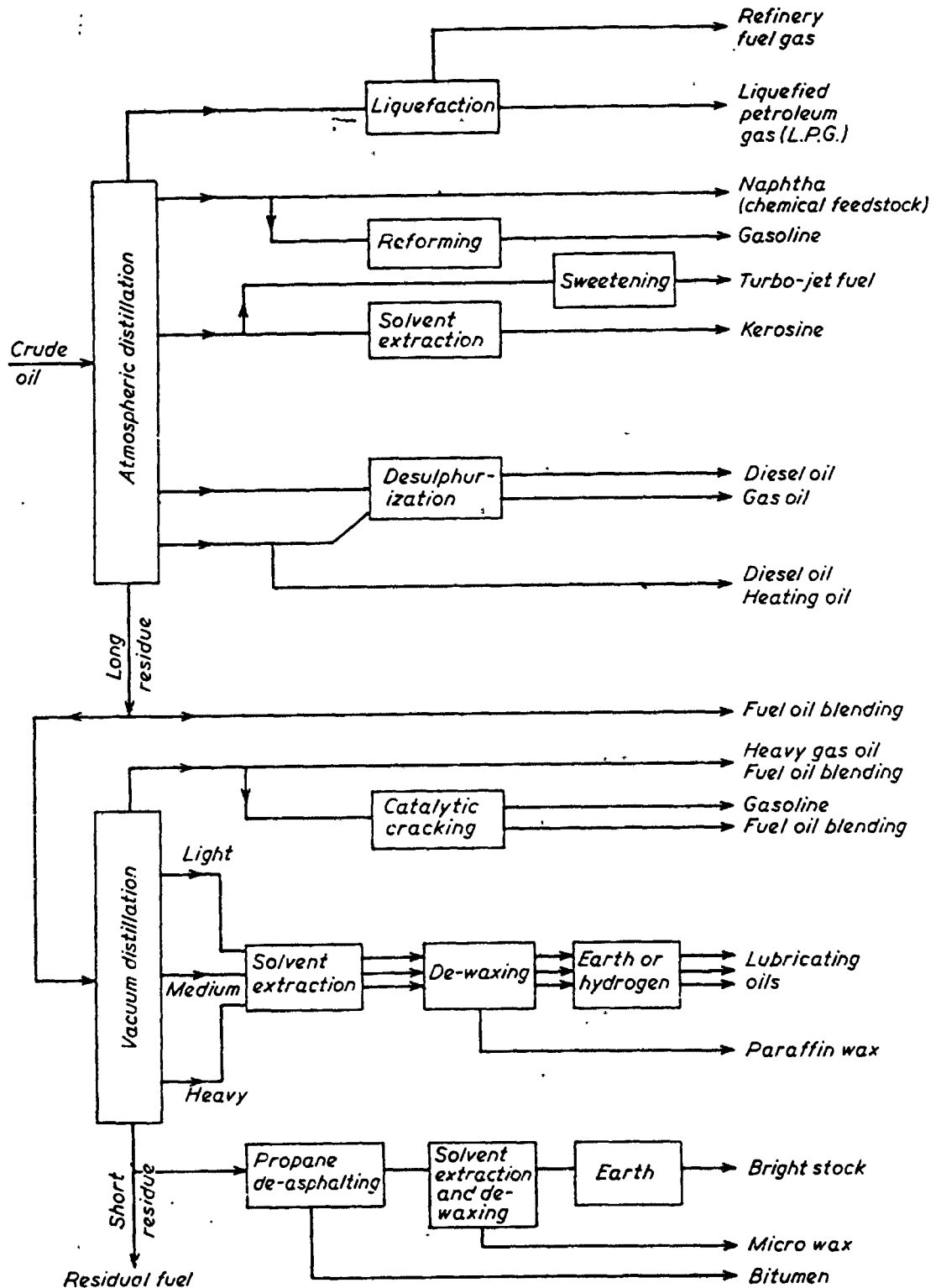
Diagrammatic sketch of crude oil refining.

Figure 3.1   source [18]

19

e) **Aromatic hydrocarbons** : CnHn

One of this series is benzene: C_6H_6. These hydrocarbons have this particular name because many of them have a distinct aromatic odour. They are in the same arrangement as benzene which has six carbon atoms disposed in the form of a circle (benzene rings) in which the carbon atoms are linked alternately by single and double bonds.

When Crude Oil is brought up from beneath the ground, it contains mainly paraffin, cyclo-paraffin, and aromatic series in a mixture. After refining we get various oil products as shown in Figure 3.1. on the previous page.

3.1.2. VAPOUR PRESSURE

When oil is loaded into a gas-free tank, it commences to evaporate gas in the space above it. There is also a tendency for the gas to re-condense in the liquid. An equilibrium is ultimately reached with a certain amount of gas evenly distributed throughout the space. The pressure exerted by this gas is called the Equilibrium Vapour Pressure (E.V.P) or simply saturated vapour pressure.

The Reid Vapour pressure (RVP) is the vapour pressure of the liquid measured at 37.8 degrees C when the volume of the liquid is equal to one fifth of the internal volume of the container. The RVP is used to evaluate the volatility and the flammability of the liquid.

3.1.3 : FLAMMABLE LIMITS:

3.1.3.1 : General:

When there is combustion, hydrocarbon gas will react with the oxygen in the air and this produces carbon dioxide and water. The temperature of the reaction is so high that it forms a visible flame. The heat vaporises hydrocarbon liquid into gas and ignition may continue.

3.1.3.2: Flammable limits and gas distribution:

Oil and sediments remaining in cargo tanks give off hydrocarbon gases (HC-gases) which will diffuse upwards into the ullage space. They will combine with air if the ship does not use inert gas, and form a mixture of air and HC-gases. This mixture can or cannot be ignited depending on the ratio of the hydrocarbon gases content to the oxygen content.The mixture includes three different levels (fig.3.2) which are:

a) Too-rich mixture: When a mixture has such a high concentration of hydrocarbon gas that it cannot be ignited, then it is called a"too-rich" mixture. Although a too-rich mixture contains little or nil quantity of oxygen, this is not a guarantee of safety under all conditions, because air may unfortunately enter the tank and may reduce the gas concentration to a flammable mixture. The resulting flammable atmosphere may then be ignited by any other source of energy.

b) Too-lean mixture: If the the concentration of hydrocarbon gas is lower so that the mixture is unable

to catch fire or to explode, then that mixture is called "too-lean".

c) Flammable area: Between these two above areas, the mixture is explosive or flammable and can result in a fire or explosion if ignited. This is therefore called "flammable area" or "flammable range". This
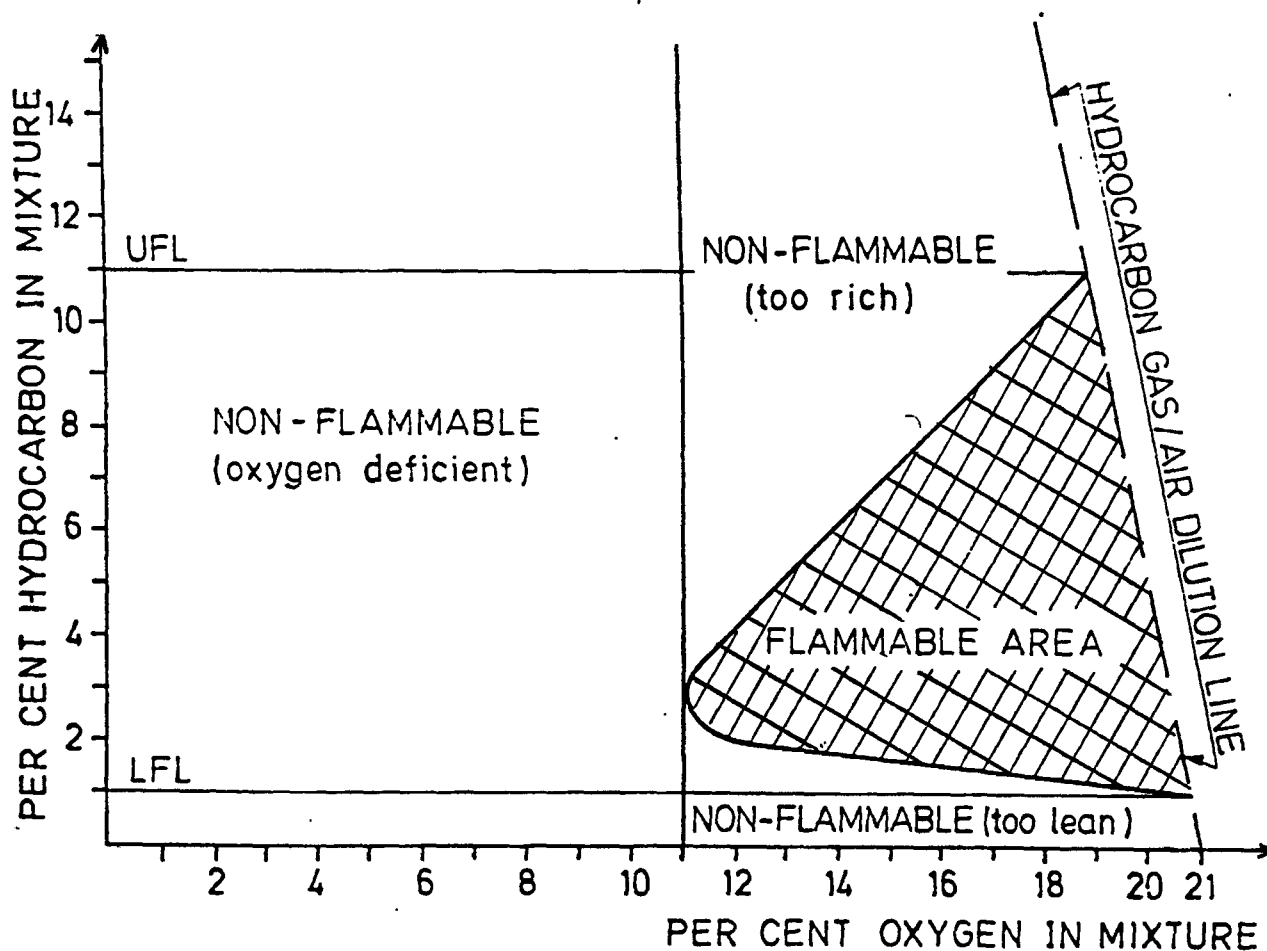
Figure 3.2   **Flammability composition diagram of tank atmosphere**

source : Reference [14]

zone contains sufficient hydrocarbon gases and sufficient oxygen so that it can catch fire or explode in the presence of an ignition source.

The division between an explosive zone and a too-rich mixture, is known as the Upper Explosive Limit (UEL). The division between an explosive zone and a too-lean mixture is called the Lower Explosive Limit (LEL).

For hydrocarbon gases generated from crude oil and sediments it is usually assumed that: the UEL is at about 10 per cent of the volume of the mixture HC-gas/air; and the LEL is at about 1 per cent of the volume. These limits differ from one liquid to another. They also vary with the following parameters:
- temperature of the mixture
- pressure
- oxygen concentration
- volume of the container
- direction of propagation of flame.
- inert gas concentration

The followings are the factors which affect the flammability limits:

Effect of temperature:
The Lower Explosive Limit (LEL) of a mixture in air, at temperature of 25°C and at an atmospheric pressure, decreases approximatly 8 % with a temperature increase of 100°C. In the same conditions, the Upper Explosive Limit (UEL) increase 8 % with a temperature increase of 100°C. Thus, for a temperature t we obtain

23

the corresponding LEL and UEL as follows [5]:

$$LEL_t = LEL_{25°} - (8LEL * 10^{-4})(t - 25°)$$

$$UEL_t = UEL_{25°} + (8LEL * 10^{-4})(t + 25°)$$

For example a mixture of Hexane which has a Lower Flammable Limit of 1.26 % volume/volume at 25° C at atmospheric pressure becomes at a temperature of 200° C and atmospheric pressure the following LEL :

$$LEL = 1.26-(8*1.26*10)(200-25)$$
$$LEL = 1.08 \% v/v .$$

The calculated value has often small differences with the experienced value. For this example the experience gives: LEL experimented = 1.14 % v/v .

Effect of pressure:

Pressure has a very small effect on the LEL. The reason is that Lower Explosive Limit is essentially constant down to about 5 kpa generally, below which the pressure flame does not propagate.

However, elevated pressure greatly increases the Upper Explosive Limit. For several hydrocarbons from 0.1 to 20.7 Mpa, the UEL depends on the logarithm of the pressure as shown in the next formula:

$$UELp = UEL + 20.6 (\log P + 1) , \qquad [5]$$

where UELp is the UEL at given pressure, P is absolute

24

pressure in megapascal and UEL is at atmospheric pressure (note that 1 atmospheric pressure = 0.101 MPa = 1.01 bars).

This formula illustrates how pressure can affect the flammability of a gas or mixture. In normal conditions, the pressure in cargo tanks of oil tankers is maintained close to atmospheric pressure. Pressure/Vacuum valves (P/V valves) are fitted in gas lines to restrict the flow of gas from, and flow of air into, cargo tanks. P/V valves are set to open when pressure in a tank rises to about 0.137 bars above atmospheric pressure and also when it falls to about 0.035 bars below atmospheric pressure.

Effect of oxygen concentration. When the oxygen content of the mixture diminishes, the flammable range becomes narrower. Eventually, at a sufficiently low oxygen concentration, the flammable range will no longer exist and combustion cannot therefore continue or occur. This state is reached at an oxygen level of 10%. This is an approximate value; in practice it varies with different oil vapours and also according to other factors.

Effect of the volume of the container. Due to the quenching effects of walls, flammability limits in tubes of less than 5 cm diameter tend to narrow. Above this value, little effect is noticed.[10].

Effect of direction of propagation. Flammable limits will vary according to the direction of the accompanying convection currents. Convection currents normally being upwards, propagation is easier in this

direction than downwards, and the flammable range will
therefore be slightly wider.

Effect of inert gas. When an inert material is added
continually to flammable gases, it narrows the two
limits of the flammable range until they meet. The
relative effectiveness of inert materials on narrowing
flammable limits follows the series CO_2 > N_2 > He >
Ar, i.e in narrowing the Flammable Limits, carbon
dioxide CO_2 is quicker than nitrogen N_2 and so on.

3.1.3.3: FLASH POINT:
A flash point is described as the minimum
temperature at which sufficient hydrocarbon gas will be
given off to form a flammable mixture and, in the
presence of an ignition source, a flame will occur
(will "flash") over the surface of the liquid. It is
measured in a standard apparatus in which the liquid is
heated. There are mainly two methods of determining
the flash point. In one method, the surface of the
liquid is continuously open to the atmosphere as the
liquid is heated. The result of such a test is known as
an "open-cup" flash point temperature. In the other
method, the space above the liquid is kept closed
except for a brief interval when the source of ignition
is being applied: this is the "closed-cup" flash point
temperature. The open-cup flash point temperature of a
petroleum liquid is always a little higher (about $5^{\circ}C$)
than a closed-cup flash point temperature.

3.1.3.4 : FLAMMABILITY CLASSIFICATION OF PETROLEUM
Petroleum cargo liquids are classed into two

groups according to their flash point and hence their flammability. One group is volatile oils, and the other non-volatile oils. **Volatile oils** are oils which have a closed-cup flash point temperature below 60° C. They have the ability to give off a lot of vapours. If a volatile oil is placed in a gas free tank, the vapour concentration above the oil will reach an equilibrium state of evaporation when the mixture is in the flammable range or generally above the UEL. **Non-volatile oils** have a closed-cup flash point equal to or more than 60° C. They evaporate very slowly and thus give off a small amount of vapour. In an enclosed space, their equilibrium gas concentration will usually be below the LEL. They include fuel oil, heavy gas oil, diesel oil etc..

3.1.4 : DENSITY

Oil accumulated in a cargo tank generates vapour. This oil vapour is heavier than air and has a tendency to remain at the tank bottom. A mixture of hydrocarbon gas and air has also a density almost 1.1 times as heavy as air if the air content is at least 90 % of the volume. This difference of density between hydrocarbon vapour and air may cause variations of readings, whether the measurement of the mixture using an explosimeter is taken at the top or at the bottom of the ullage space. For this reason, gas measurments should be taken at the bottom, and if possible at various points over the tank bottom. Gas-exchange operations between air and oil vapour should be done bearing in mind the effect of the inequality of densities. Note that the difference of densities

27

between air and inert gas is generally low.
Consequently, the mixture between them is nearly
homogeneous. Thus the exchange of air and inert gas
may take a long time.

3.2 : CARGO TANK ATMOSPHERE IN OIL TANKERS:

3.2.1:GENERAL CONSIDERATION

If oil is introduced in a cargo tank, the tank
atmosphere will contain a mixture of hydrocarbon gases
(HC-gases) and/or air, and/or inert gas. The
concentration of the mixture varies according to the
amount of each of these above elements. This
concentration is susceptible to ignite when the oxygen
content is more than about 10 % and when the
hydrocarbon gasses are between the flammable limits.
Figure 3.3 shows how the concentration may or may not
cause a flammable mixture. The essential information
from the figure is:

- The "Hydrocarbon gas/air dilution line"
which covers tank atmospheres containing only a mixture
of hydrocarbon gas and air. It ranges from the point of
100 per cent hydrocarbon gas (not seen in the figure)
and point F representing 21 per cent of oxygen, i.e.
100 % air.
        - Point A corresponds to a situation of tank with
inert gas protection containing 11.5 per cent of HC-
gases by volume and 3.7 % of oxygen by volume. The
mixture has so low oxygen content that it is not
flammable. However, if it is diluted by air the oxygen

28

Dilutions lines in the HC-gas/air/inert gas mixture
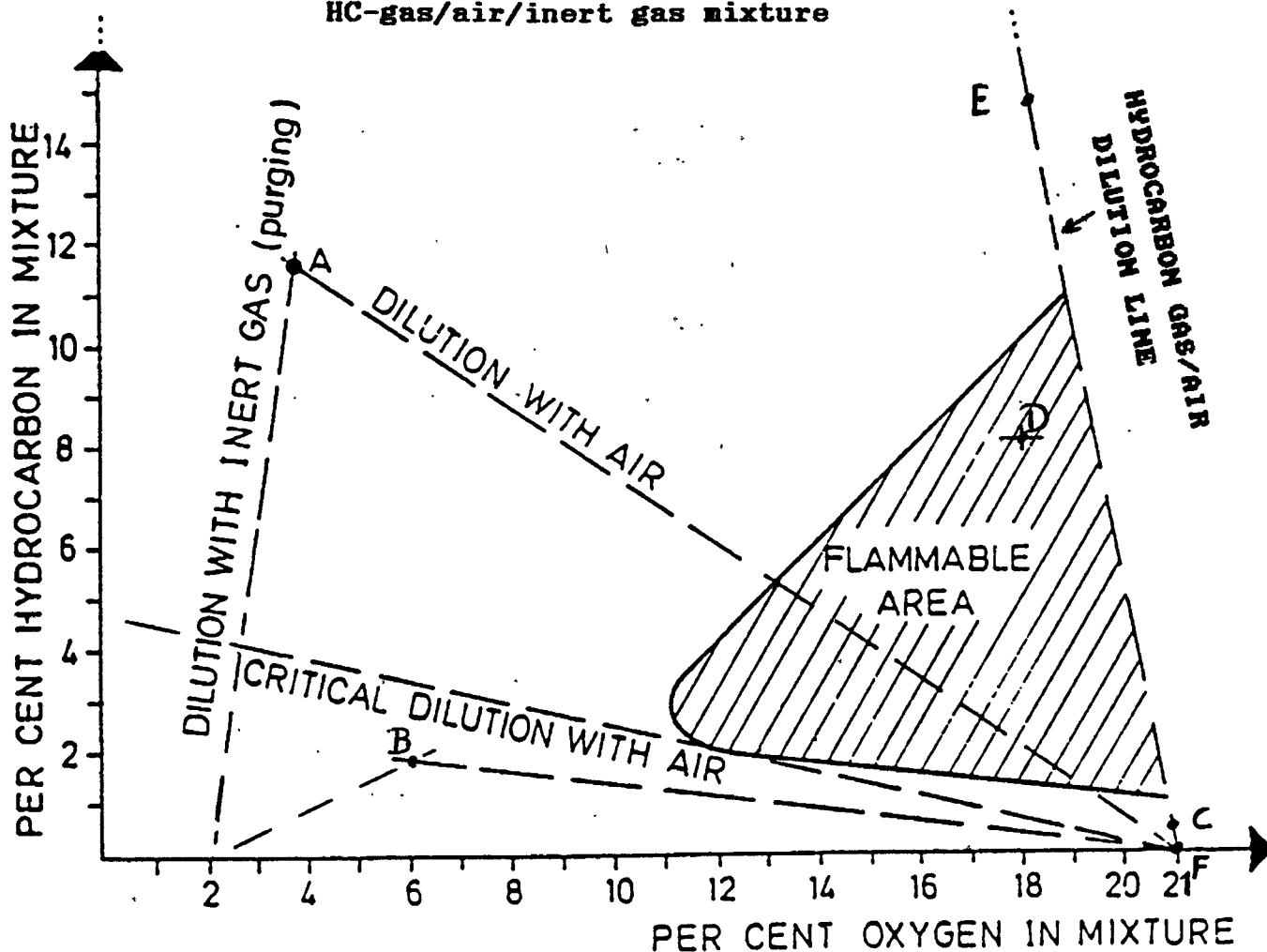
Figure 3.4   **source : Reference [2]**

content will increase and then the behaviour of the
tank atmosphere will follow the "Dilution with air
line" heading towards 21 % of oxygen content. Further,
the tank atmosphere will fall in the "Flammable Area"
where it will be able to support combustion. If, from
the point A we introduce inert gas, the behaviour of
the concentration will follow the "Dilution with inert
gas" line which leads to an oxygen level of about 2 per
cent. The reason for this is that the inert gas

referred, which is boiler flue gases, includes about 2 to 4 % of oxygen (see paragraph 4.1.2).

- **Point B** corresponds to a tank with inert gas containing 1.5 % of HC-gases by volume and 6 % of oxygen by volume. A mixture having these parameters cannot be ignited because of the oxygen deficiencie, and it will not be a flammable area if added with air because B is below the "Critical Dilution With Air" line.

- **Point C** is a case where the tank contains 0.5 % HC-gases and about 21 % (20.9%) of oxygen by volume. The mixture is too-lean to be flammable. With an explosimeter the reading will normally show 50 % of the LEL.

-**Point D** gives a situation where the hydrocarbon gas is 8 % of the volume, and the oxygen 18 % of the volume. The tank is in an Explosive Zone or Flammable Area. It can be easily ignited.

3.2..2: ATMOSPHERE IN CARGO TANK WHILE LOADING

a) In a gas free tank: Volatile oils such as gasoline or crude oils give off oil vapour into the ullage space as soon as loading commences. Because oil vapour is heavier than air, it will be greater immediately above the surface of the oil than in the upper part of the tank. The resulting distribution of gas concentration in terms of flammability is shown as an example in Figure 3.4. It may be mentioned that in practice the configuration and the division between layers are not so distinct. At the completion of loading, the ullage space generally remains in the flammable and the too-

rich vapour layers.

If the oil is non-volatile such as diesel oil, fuel oil, lubricating oil etc, or if the ballast is loaded, then the too-rich layer may not be present.

N.B. The tank was gas-free before loading commenced.

air

too-lean vapour

flammable vapour

too-rich vapour

volatile oil

GAS CONCENTRATION IN A TYPICAL CARGO TANK WHILST LOADING A VOLATILE OIL.
TANK A QUARTER FULL
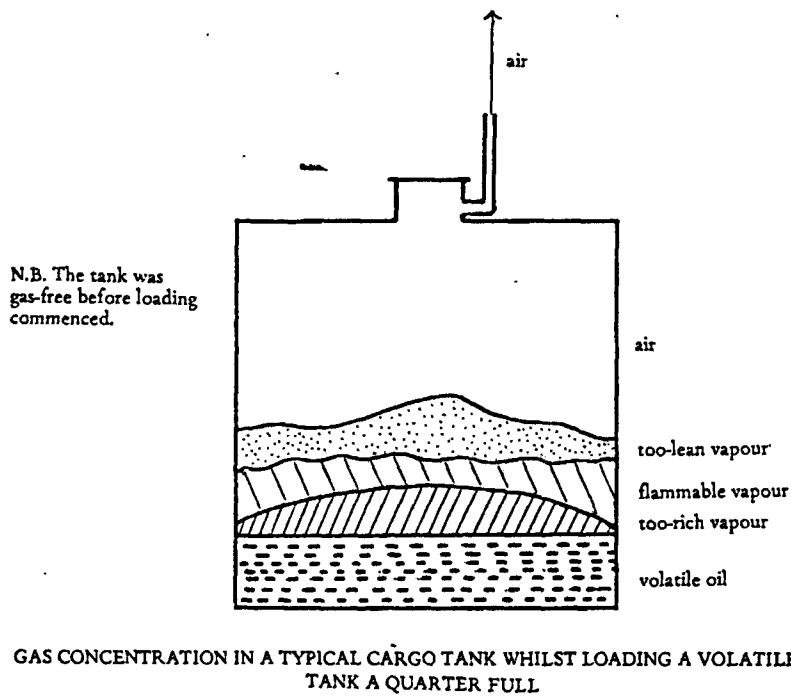
Figure 3.4   , **source : Reference [2]**

b) In an inert tank: If the cargo tank is inerted, then the flammable layers will be replaced by inert gas. The oil vapour which has a heavier density will be under the inert gas layer. At the final stage of loading, it may have only too rich vapour in the ullage space depending both on the level and the type of the liquid - oil or ballast - loaded.

3.2.3: ATMOSPHERE IN CARGO TANK DURING LOADED PASSAGE

Some hours after completion of loading, the atmosphere within the tank generally attains: a homogeneous concentration of too-rich vapour if the oil is volatile. During the voyage, the vapour concentration will vary directly with the temperature. When the temperature decreases, the tank will breathe and air will enter into the tank. If the temperature increases, it results in the escape of gas when the ullage space vapour pressure rises above the atmospheric pressure.

3.2.4: ATMOSPHERE IN CARGO TANK DURING DISCHARGING

a) : For non-inerted tank:

When discharging commences, oil leaving the tank will be replaced by air entering normally through the gas venting system or possibly through ullage openings protected by suitable flame screens. Tank lids should be kept closed. The inlet air velocity will depend on the discharging rate. If the discharging rate is slow, the stratification of gas will be shown in Figure 3.4. The advantage of this is that only part of the tank is explosive. If the emptying process is rapid in association with free access of air to the tank, the gas concentration can readily be rendered explosive. However, there will not be an electrostatic hazard on board while discharging. The reason is that charge separation will not occur until the cargo enters the ship's pumping system and even then the charge will not accumulate on cargo lines or cargo pumps of the system

due to the fact that they are not insulated from the
ship. It is shore tanks which will be electrostatically
charged by the pipe-line flow and/or diverse other
causes.

b) For inerted tank:

If the ship uses on a inert gas system, then the
inert gas will replace the oil leaving the tank. At low
rates of discharging there will be two layers of gas,
consisting of the too-rich vapour layer at the lower
part and the inert gas layer at the upper part. When
the pumping is at a high rate, the inlet of inert gas
should follow the demand. Then, it will result in a
turbulence of gas in the tank and the layers will
disappear. In this case there is a risk of entrance of
air through the Pressure-Vacuum valves or risk of an
under-pressure if the pressure relief valves are set on
the low side or are malfunctioning. Both these hazards
can occur if the oil is being discharged more rapidly
than the inert gas entering the cargo tank. The result
of this can be cargo tank warping and/or rupture of the
pumping system which may lead to fire or explosion.

3.2.5 : ATMOSPHERE IN EMPTY, NON-GAS FREE AND NON-INERTED CARGO TANK

When the discharging is complete, there will be
additional gas generated from the sludge at the bottom
of the tank. If the oil discharged was volatile, the
mixture may be in the form of stratification with too
rich, explosive and too lean layers. Figure 3.5 shows
the type of gas concentration which can be obtained in

Figure 3.5

MAIN DECK

```
D   0 —      ┌─────────────────────────────────┐
E            │          0.3 X LEL              │
P            │                                 │
T            │                                 │
H  10 —    — │          0.4 X LEL           — │
             │                                 │
I            │    TOO LEAN                     │
N            │                                 │
             │                                 │
F  20 —    — │          0.5 X LEL           — │
E            │                                 │
E            │                                 │
T            │                                 │
   30 —    — │          0.6 X LEL         ·  — │
             │                                 │
             │          0.7 X LEL              │
             │  L E L ─────────────────────────│
   40 —      │:::::::::::::::::::::::::::::::::::│
             │::::::::::: E X P L O S I V E ::::│
             │:::::::::::::::::::::::::::::::::::│
             │  U E L ─────────────────────────│
   50 —    — │              OVER-RICH       — │
   55 —      │      48 X LEL                   │
             └─────────────────────────────────┘
```

SHELL AT BOTTOM
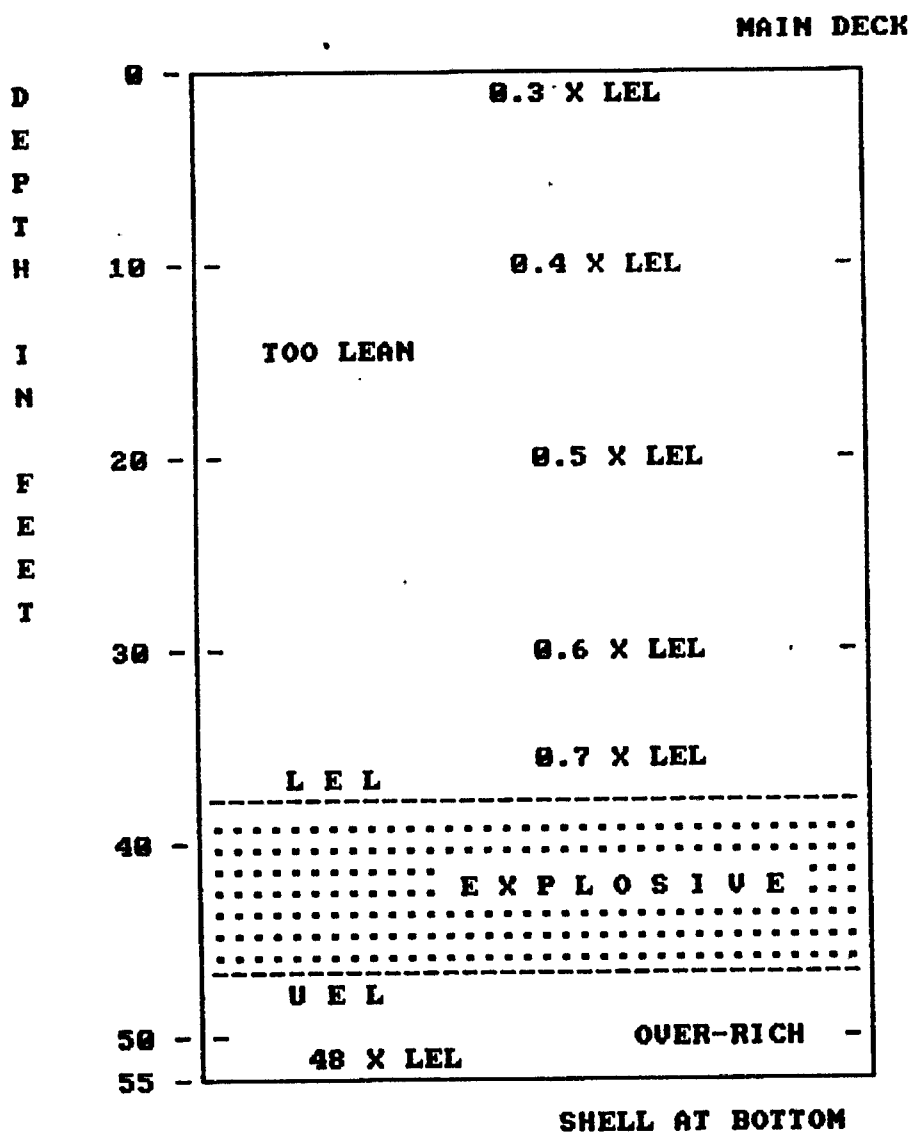
NOTE: UEL = Upper Explosive Limit

LEL = Lower Explosive Limit

GAS STRATIFICATION IN A CARGO TANK
AFTER A CARGO OF CRUDE IS DISCHARGED

(SOURCE [4])

a cargo tank after crude oil is discharged. The stratification shown in the figure will vary depending on the crude handled, the climatic conditions etc... Concerning volatile refined oil, a rapid evaporation would be expected from the remaining oil in the tank. The vapour concentration will increase and diminish the too lean layer until either the tank is saturated or the residual oil has completely evaporated. This can take about a week.

CHAPTER 4

TANK ATMOSPHERE CONTROLS

4.1 INERT GAS SYSTEMS

4.1.1 GENERAL

Inert gas can be defined as "a gas or a mixture of gases containing insufficient oxygen to support combustion of hydrocarbons".

An inert gas system (IGS) is a requirement under SOLAS Protocol (1978) for all new crude and product tankers (constructed from 1 September 1984) over 20,000 dwt and existing crude and products tankers with the exception of tankers below 40,000 dwt which are not using high-capacity tank washing machines.

The purpose of IGS is to eliminate the danger of explosion by reducing the oxygen level in the tank atmosphere. We know that petroleum gives off flammable vapours which are only flammable when air/vapour mixtures are within the flammable range (see parag.3.1.3.2 c). The oxygen content in the atmosphere is 20.9 % , say 21 %, and is capable of supporting combustion. However, if this oxygen level is reduced to below 11 % then there will be insufficient oxygen for a flammable mixture. IGS, under IMO requirements, must reduce the level of oxygen in the tanks to a maximum of 8 % by volume. This is achieved by introducing inert gas containing about 5 % by volume of oxygen. Moreover, some tankers reduce the tank oxygen

content to 5 % by volume to minimize the effect of corrosion.

4.1.2 INERT GAS PRODUCTION

The most common method of producing inert gas on board oil tankers is to use the flue gases produced when fuel oil is burnt during normal operation in the ship's boiler. Figure 4.1 below shows how fuel oil vapour and air combine in a ship's boiler. When good combustion between fuel oil and air has been achieved, the components of boiler flue gases emitted are as follows: oxygen 3 -4 %; carbon dioxide 13 %; sulphur oxides 0.3 %; water vapour 5%; nitrogen 77%; other gases 0.7-1.7 % (see Figure 4.1).

At the end of the process, the resulting mixture known as **inert gas** contains about 3 % oxygen, about 13 % carbon dioxide and about 77 % nitrogen by volume. It can be seen that the oxygen content is well below what is required to sustain combustion and if we can put this gas mixture into the tanks, their atmospheres would be rendered inert and incapable of supporting a fire or explosion.

However, the boiler flue gases are hot and contain sulphur dioxide which is corrosive. Therefore, they must be cooled and cleaned to remove or reduce as much as possible the corrosive impurities before they can be used. This is done by a scrubber, through which the gas is passed.

37
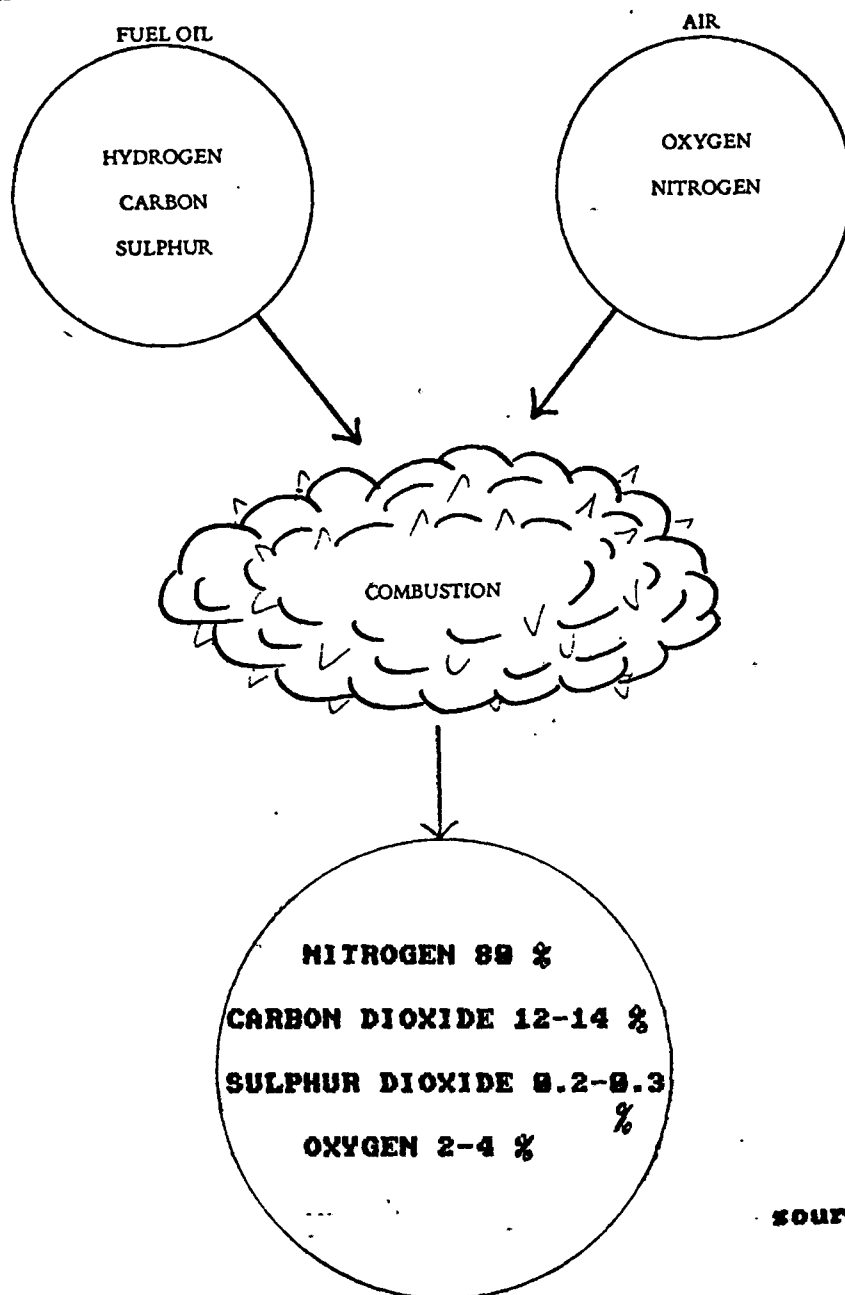
Figure 4.1 :   Inert gas production

sources [2] and [16]

4.1.3: INERT GAS OPERATIONS

For a better understanding,   let   us follow the successive stages of a voyage of a   tanker as it leaves the repair port after a routine drydocking.

1 : Once the ship is at sea the inert gas plant is put in operation and checked until a satisfactory inert

gas quality of less than 5 % oxygen content is obtained. Then the operation of introducing the inert gas into tanks (inerting) and displacing the existing tank atmosphere of air is begun (see Fig.4.2). This inerting operation is carried out by sampling the tank atmosphere by means of an oxygen analyzer. When the oxygen content within one tank is equal to or less than 8 % by volume, then the tank is considered to be inerted and can be shut down. This process continues until all tanks are inert, and the plant can then be shut down.

Figure 4.2 Inerting of tanks filled with air
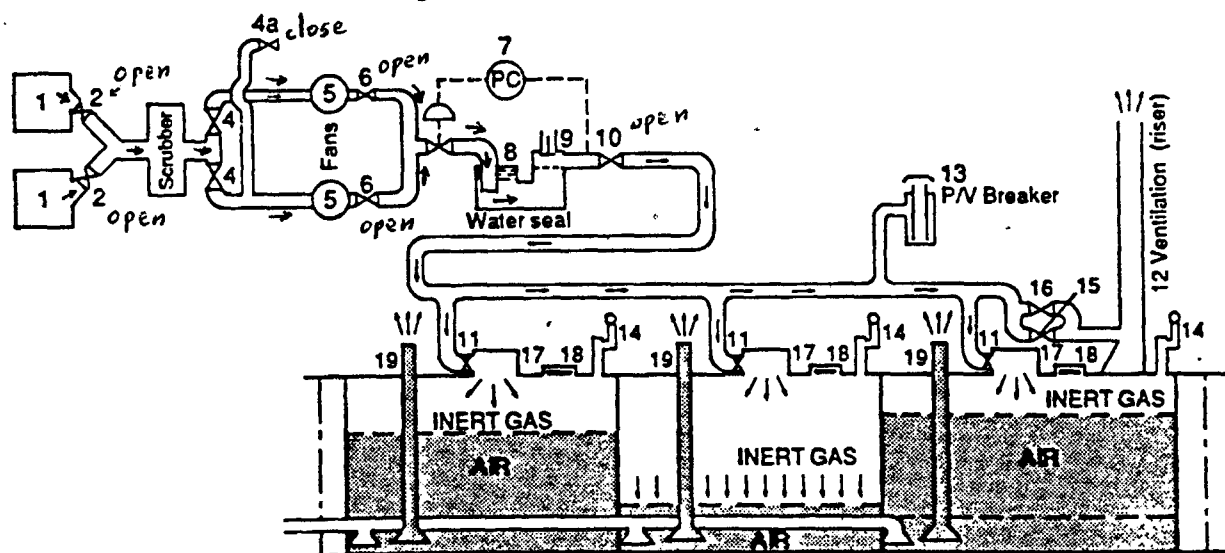
|		
1. Boiler gas uptake or inert gas generator	6. Fan isolating valves pressure side	13. Pressure/vacuum breaker (common)
2. Gas uptake valves	7. Pressure control valve	14. P/V valves (individual)
3. Scrubber	8. Deck water seal	15. P/V valve in ventilation line
4. Fan isolating valves suction side	9. Non return valve	16. By-pass valve
	10. Deck line isolating valve	17. Tank hatch
4a. Fresh air intake valve	11. Tank isolating valves	18. Level indicator
5. Fans	12. Ventilation mast (riser)	19. Purge pipe

source IMO course 1.01

2 : On arrival at the loading port the inert gas plant should be restarted so that inert gas can be used to replace the ballast being discharged in preparation for loading. If this were not done air would be drawn into the tanks as the ballast was pumped out and the oxygen content of the tank atmosphere would increase. When the ballast is completely discharged the inert gas plant is stopped, the mast riser bypass valves are opened and loading can be started.

During the loading operation the inert gas is displaced and, by means of the high-velocity vent and/or the mast riser, the tank atmosphere is vented to the atmosphere or it is recovered for other purposes avoiding air pollution, as the oil enters the tank. On completion of cargo loading, the IGS may be restarted to maintain a positive pressure on the system. This can also be done during the voyage to the discharge port. However, if the cargo has a high vapour pressure it is possible that sufficient vapour will be given off by the cargo to maintain the pressure in the system.

3 : On arrival at the discharging port, the inert gas plant is started up and inert gas is introduced to the tank while the cargo is being discharged. Care must be taken to ensure that a positive pressure is maintained in the system during this phase. If a vacuum occurs, air will be drawn into the cargo tank. Sometimes difficulty is encountered in maintaining positive pressure due to malfunction of the plant. In this case the discharge rate should be slowed down or stopped until normal operating conditions are once again obtained. When the discharge of the cargo is

40

Figure 4.3   Source [15]

Inerted operation area in
in the HC/O diagram
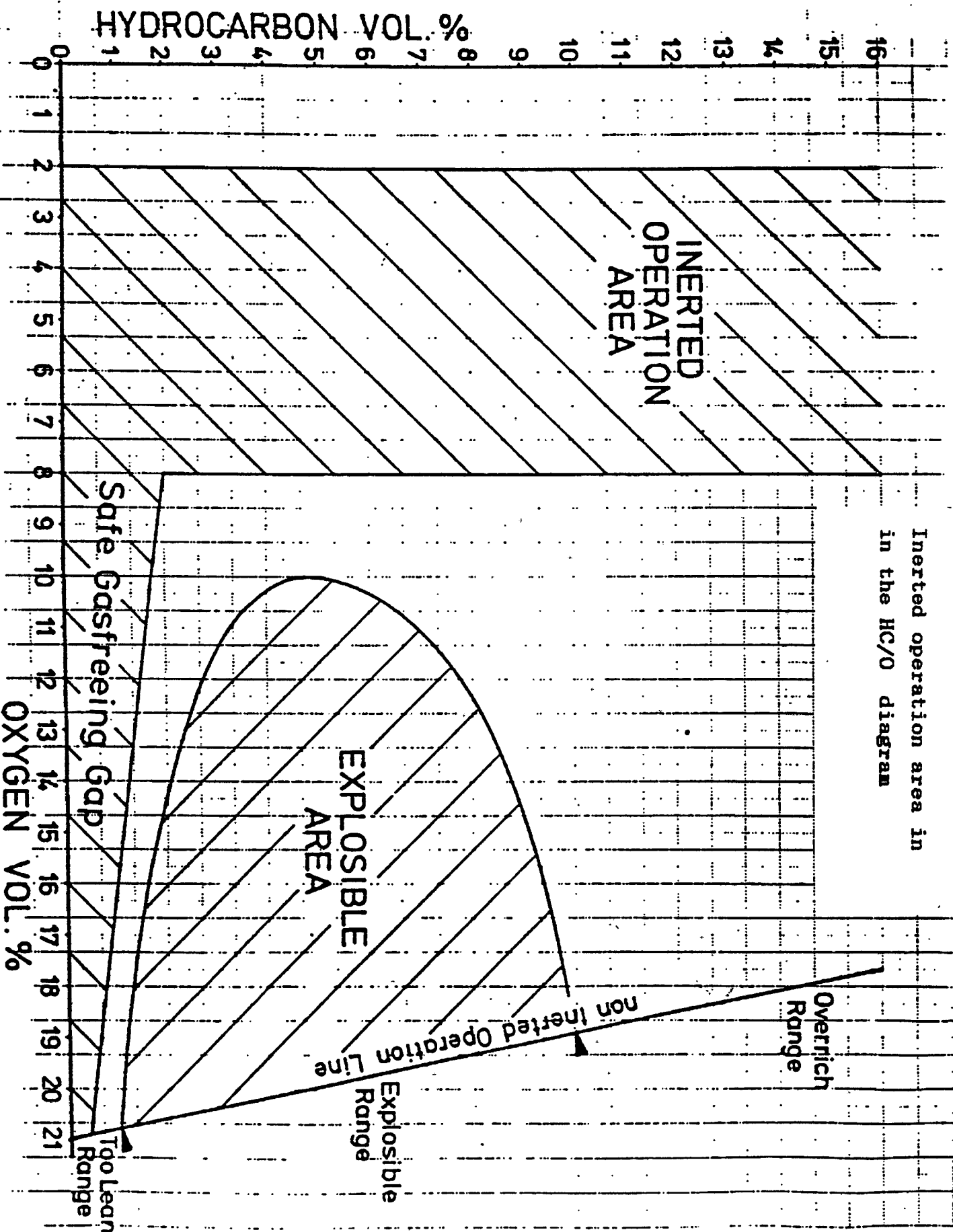
completed, the tank atmosphere will consist of a mixture of inert gas and HC-gas which is not flammable. In this situation the system can be momentarily switched off and departure ballast taken on board. The following steps concerning tank atmosphere exchange can be seen in sections 4.1.4 below.

At the end of the ballasting operation, the tanker is ready for sailing.

4 : After leaving port, it is usual to restart the inert gas system and utilize it for purging the tanks of hydrocarbon vapour coming from the residues of oil from the tank bottom. This is safer and can avoid explosion if ever there is a collision . The system is also maintained in operation while tank cleaning is carried out. When tank cleaning is completed, it is necessary to purge the tanks, once more, to ensure that the oxygen content of the tank atmosphere is below 8 %. Cargo tank atmospheres should be maintained in the "inerted operation area" as shown in Figure 4.3.

4.1.4.: PURGING OF TANK ATMOSPHERE

4.1.4.1: GENERAL

For safety reasons, the atmosphere within a cargo tank is often changed from one gas or air to another. The exchange procedures include gas freeing, inerting and purging. The two main methods for exchange of tank atmosphere are the displacement method and the mixing or dilution method.

a: The displacement method

In this method, the existing tank atmosphere is displaced by the incoming gas or air without any mixing, or with a minimum of mixing (See figure 4.4). Gas or air is led into the tank at deck level and displaces the atmosphere through the purge pipe. the incoming gas or air acts as a << piston >> over the existing tank atmosphere. However, for good results it is required that:

- the tank atmosphere has a higher density than the incoming gas or air in order to obtain stratification , and

- the inlet vertical velocity is low to avoid mechanical mixing.

The first requirement is normally complied with for gasfreeing of tanks, and inert gas purging of hydrocarbon gas/inert gas filled tanks. The principle will be less efficient for inerting a gasfree tank because the density of the inert gas is higher than that of the air.

The second condition requires the inlet arrangement to be so well designed that the vertical velocity is minimized.

Theoretically, the displacement method should require one tank volume of air only, to change the tank atmosphere. But, in practice we have to supply from 1.5 to 2 tank volumes to inert or gasfree a tank.
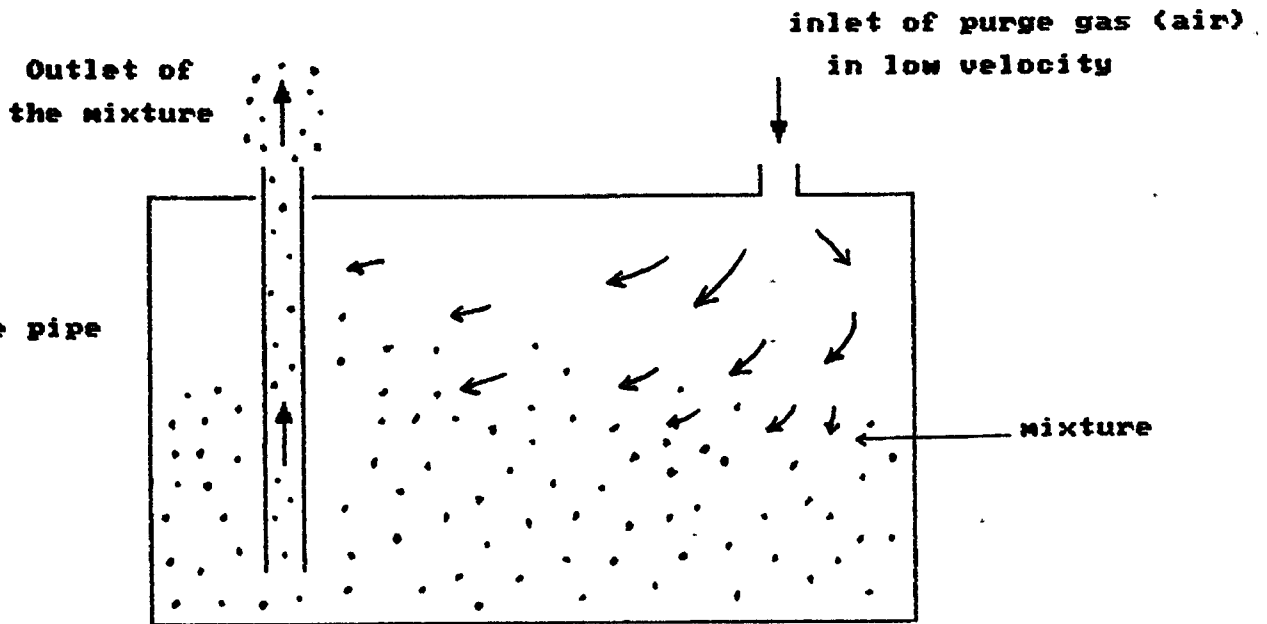
EXCHANGE OF TANK ATMOSPHERE BY THE DISPLACEMENT METHOD

Figure 4.4
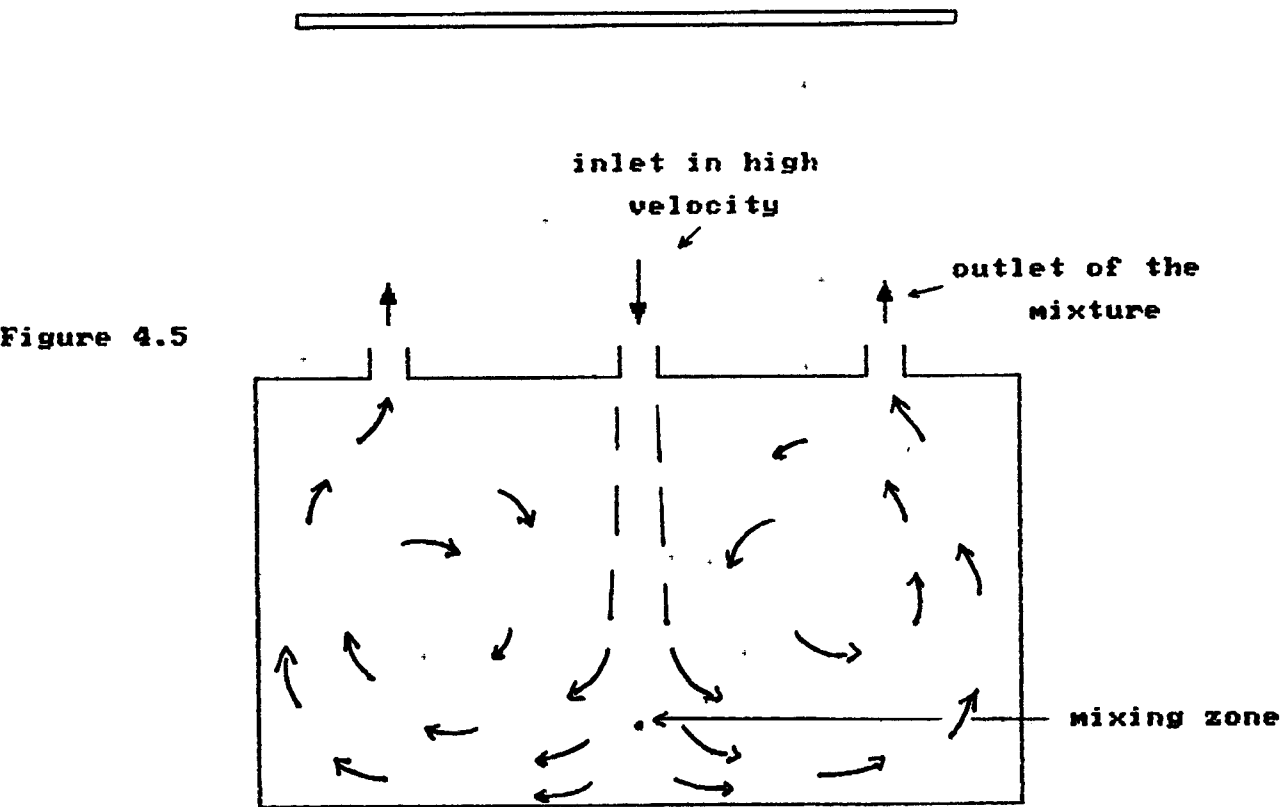
EXCHANGE OF TANK ATMOSPHERE BY THE MIXING METHOD

b: The dilution method

This method means that the incoming gas or air mixes completely with the existing atmosphere in the tank. In this case the gas being exhausted is a mixture of the existing tank atmosphere and the incoming gas or air (See figure 4.5). For achieving an efficient atmosphere exchange by this method, it is necessary that :

- The inlet velocity is high enough so that the jet can reach the bottom,

- The arrangement is established with an inlet in the centre of the tank area in order to provide an easy way out for expelled gases.

In practice, we need about 4 tank volumes of inlet gas or air to supply the existing tank atmosphere while the theoretical need is one and half tank volumes. The Figure 4.6 helps to understand this dilution or mixing method.

Figure 4.7 gives the required minimum volume flow for an inlet if its diameter and the depth of the tank are known. Example :

The depth of a tank is 10 m and the inlet diameter is 400 mm. What is the necessary flow rate for the dilution method ?

- Answer : The flow rate should be at least 5 000 m^3/h (go from the horizontal axis at 10 m , then vertically upwards to curve 400 mm, and finally horizontally to the vertical axis where you will reach the value 5000 m^3/h).

45

$$K = K_o \cdot e^{-z}$$

$$z = \frac{\text{inlet flow rate} \times \text{time}}{\text{tank volume}}$$

$$z = \left(\frac{m^3/h \cdot h}{m^3}\right) = \text{Number of tank volumes}$$
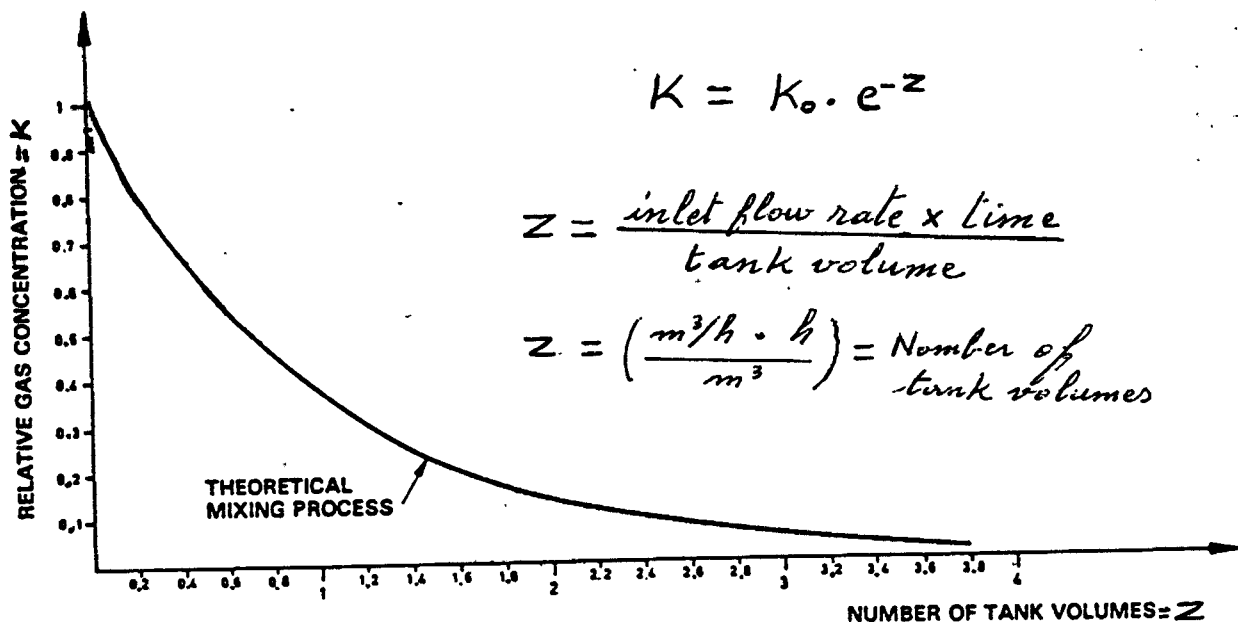
ATMOSPHERE EXCHANGE BY THE MIXING METHOD — SUFFICIENT INLET VELOCITY

Figure 4.6

RELATION BETWEEN FLOWRATE AND PENETRATION DEPTH FOR SELECTED INLET DIAMETERS

Figure 4.7   source [14]

46

4.1.4.2: INERTING OF GAS FREE TANKS

Vessels which are equipped with purge pipes generally use the displacement method. However, as inert gas and air have nearly the same density, the stratification necessar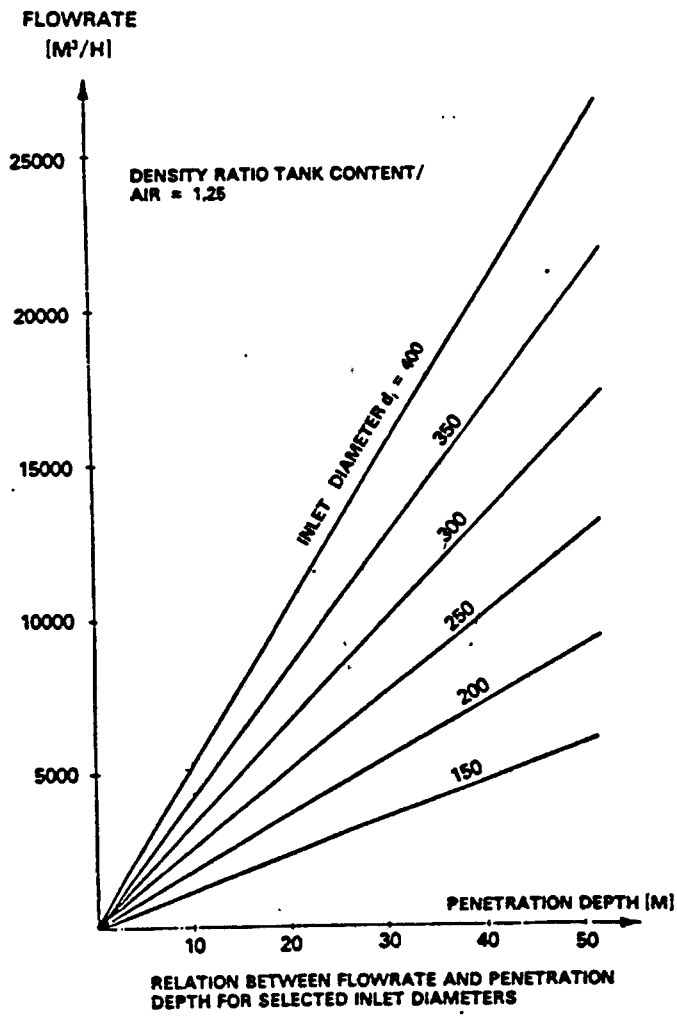y for an efficient displacement process will not occur. This results in rising the mixing process. Therefore, a large amount of inert gas estimated at 1.5-2 times the tank volume will be needed when purge pipes are used in this way.

When the mixing method is practised, the quantity of inert gas necessary to reduce the oxygen concentration below 8 % is estimated to be a minimum of 3 times the tank volume.

4.1.4.3: INERTING OF TANKS WITH AIR/HC-GAS MIXTURE

If the discharging of cargo has been done without the supply of inert gas, then the tank atmosphere will consist of a mixture of air and HC-gas when the unloading is completed. In that case the tank atmosphere is situated on line EC of Figure 3.3 (chapter 3). As soon as possible the tanks must be blown through with inert gas to reduce the oxygen content below 8 per cent. The operation will change the situation of the tank atmosphere from the possible flammable area to the non-flammable area as shown in Fig.3.3 (chapter3). The operator can use the displacement method which is more efficient since stratification will occur due to the relatively higher density of the gas mixture.

4.1.4.4: PURGING OF TANKS WITH INERT GAS /HC-GASES
MIXTURE

When cargo is discharged with a supply of inert
gas, after completion the tanks will contain an
atmosphere of inert gas/HC-gases mixture which is not
flammable, as already seen in parag.4.1.3-3. However,
the HC-gases content will be relatively high. In the
event of air intrusion, from any cause such as
collision, part of the tank atmosphere will become
flammable, and therefore any source of ignition such as
a spark, may cause an explosion. To avoid this
situation, the HC-gases content can be reduced to 2 per
cent by volume, by purging with inert gas so that even
if the intrusion of air takes places, the dilution of
the tank atmosphere will follow a line below the
critical dilution line (see fig.3.3) and thus avoid the
flammable area. This operation should be frequently
repeated particularly for the empty wing tanks because
the remaining oil residues in the tank will constantly
release vapours which increase the HC-gases content.

4.1.4.5: INERT GAS TOPPING-UP OF CARGO TANKS

After purging with inert gas, the tank will have
an over-pressure. If the tanks are normally in a good
condition of gas tightness, the existing non-flammable
atmosphere should be sufficient for the entire ballast
voyage. But leakages can occur through P.V valves or
hatches and then the over-pressure will be gradually
reduced. Moreover, temperature variations of sea water
and air from day to night will cause the tank
atmosphere to expand and contract. In case of leakage,

this will result in breathing so that the gas will be released when the temperature is rising . Inversly, air will enter into the tank when the temperature is falling. Thus, the oxygen content in the tank will increase at the same time. If the ballast voyage is long, then the entire tank atmosphere may become flammable. For this reason, it is necessary to top-up the tanks by filling some inert gas during a long ballast voyage, in order to keep the hydrocarbon gases below 2-3 per cent by volume, at all times. Thus, any dilution with air would not result in a flammable gas mixture because the tank atmosphere will be under the critical dilution line (see Fig 3.3). Topping-up should be started as soon as the pressure in the tank falls close to the atmospheric pressure. Experience has shown that topping-up must be carried out at least once a week. In the same way purging should be done if the oxygen content exceeds 8 per cent by volume.

4.2: OTHER METHODS OF ACHIEVING SAFE TANK ATMOSPHERES

4.2.1: THE SKIMCLEAN METHOD

During tank-washing with high pressure machines a tank which is brought below the Lower Explosive Limit can once again become explosive due to a regeneration of gas from residual oil. To eliminate this danger, a system of skimming oil off the top of the ballast, prior to deballasting, is performed.

This method uses a buoy which floats in the tank on the ballast at such a level that it permits oil on the surface of the ballast to flow over a sill in the

buoy and then to be conducted away through a hose/pipeline system. The outflow from the buoy is taken to a pipeline and conducted to a slop tank. This can be done either by using the existing stripping line or a specially installed skim line on deck. The level surface of the ballast should be clear of under-deck obstructions in order to facilitate the flowing of the oil. Easy movement of the buoy on the surface of the ballast is obtained by means of a specially provided winch. Throughout this method, the tank is ventilated with mechanical blowers.

After skimcleaning a tank, the ballast may be discharged while ventilation continues simultaneously.

With this method, regeneration of gas has been found to be minimal and in some cases non-existent. If a proper operation is done, it should be possible to maintain the tank at below 20 % of the LEL (4), even under adverse conditions. The method provides a safe atmosphere. If it is combined with adequate gas monitoring, it will enable tanks to be cleaned fully and safely with minimum regeneration of hydrocarbon gas.

4.2.2: REPETITIVE BOTTOM FLUSHING

Repetitive Bottom Flushing and associated ballasting and de-ballasting is a method of removing the oil layer. It involves :

a) repeated flushing of the tank bottom with ballast water and draining to slop tanks,

b) de-ballasting with any floating oil being
   transferred to slop tank,

c) reflushing the tank bottoms if necessary.

CHAPTER 5

TANK CLEANING AND GAS-FREEING

5.1 : TANK CLEANING

5.1.1 GENERAL

The purpose of tank cleaning is in general as follows:

- Change of cargo according to the needs of the trade;
- Entry into tank for inspection, for repair work by the ship personnel or for repair in a shipyard;
- Need for preparing a tank for clean ballast;
- To prevent accumulation of sediment on the bottom of the tank.

Tank cleaning is a safe operation if performed correctly, but if the safety rules are not obeyed the consequences can be disastrous. Many risks occur when cleaning tanks such as fire/explosion and the inhalation of toxic concentrations of vapour. However, fire/explosion is the main hazard during tank cleaning due to the electrostatic charge generated by the washing liquid which can ignite hydrocarbon vapours in a flammable zone when it is highly charged (parag.3.3.2.6). The occurence of explosion and fire is serious. They represented 22.52 % and ranked third as the cause of world wide losses of ships in 1989, according to records of Lloyd's Register. Thus extreme care must be taken when washing and cleaning to avoid

this hazard.

In order to have an over view on tank cleaning, reference will be made to the various tank atmosphere conditions called atmospheres A, B, C, and D which refer to the state of the tank atmosphere at the time when tank washing is being carried out. They can be defined as follows (source [7]):

a) Atmosphere A (uncontroled or undefined) : an atmosphere which is not controlled . It can be below, above or within the flammable range.

b) Atmosphere B (Too-lean): an atmosphere made incapable of burning by the deliberate reduction of hydrocarbon content to below the Lower Explosive Limit (LEL). The reading given by a suitable combustible gas indicator should not exceed 50 per cent of the LEL.

c) Atmosphere C (inerted): an atmosphere made incapable of burning due to the deliberate reduction of oxygen content by the introduction of inert gas. The oxygen content of the tank atmosphere should not exceed 8 per cent by volume.

d) Atmosphere D (Over-rich): an atmosphere made incapable of burning by deliberately maintaining the hydrocarbon content of the tank above the upper explosive limit. For crude oil and most liquid petroleum products, a hydrocarbon content of at least 15 per cent by volume should be attained before starting washing and maintained

this hazard.

In order to have an over view on tank cleaning, reference will be made to the various tank atmosphere conditions called atmospheres A, B, C, and D which refer to the state of the tank atmosphere at the time when tank washing is being carried out. They can be defined as follows (source [7]):

a) Atmosphere A (uncontroled or undefined) : an atmosphere which is not controlled . It can be below, above or within the flammable range.

b) Atmosphere B (Too-lean): an atmosphere made incapable of burning by the deliberate reduction of hydrocarbon content to below the Lower Explosive Limit (LEL). The reading given by a suitable combustible gas indicator should not exceed 50 per cent of the LEL.

c) Atmosphere C (inerted): an atmosphere made incapable of burning due to the deliberate reduction of oxygen content by the introduction of inert gas. The oxygen content of the tank atmosphere should not exceed 8 per cent by volume.

d) Atmosphere D (Over-rich): an atmosphere made incapable of burning by deliberately maintaining the hydrocarbon content of the tank above the upper explosive limit. For crude oil and most liquid petroleum products, a hydrocarbon content of at least 15 per cent by volume should be attained before starting washing and maintained

throughout washing.

Each of these atmospheric states requires different methods of cleaning which are explained below:

5.1.2: WASHING IN ATMOSPHERE A, (UNCONTROLLED OR UNDEFINED)

This condition is most commonly found on older and smaller ships where the atmosphere is completely uncontrolled. This represents the most dangerous situation that can be encountered.

The major duty is to avoid any ignition sources when washing is being carried out. Hence, the following precautions should be observed (see also table 5.1):

a. Use of portable machines is advised rather than high capacity washing machines. The water throughput of each machine should not be greater than 60 m^3/h, and the total throughput per cargo tank must in no case exceed 180 m^3 /h (source [3]). The washing capacity should be as low as possible. The reason for this restriction is that the higher the water throughput of a machine is, the greater the static electricity generated by the water jets.

b. Use of only clean sea water is permitted. Oil contaminated water coming from the slop tank, on board crude oil tankers or some product tankers, will produce a high build-up of static charge.

c. Before portable machines are introduced into the

54

Electrostatic Hazard	Rubbing together of synthetic polymers	Flow of static accumulator liquids	Water mist droplets	Particulate matter in inert gas
Cargo Tank Operation When hazard can occur:	Lowering of equipment with ropes of synthetic fibres	Loading clean oils	Tank washing	Cargo discharge, re-inerting, and initial inerting of non-gas free tanks
Precautions Necessary For dipping, ullaging and samping with				
(i) metallic equipment not earthed or bonded:	Use of ropes made of synthetic fibres for lowering equipment into cargo tanks not permitted at any time	Not permitted at any time	Not permitted during washing and for 5 hours thereafter	Not permitted during injection of inert gas and for 5 hours thereafter
(ii) metallic equipment which is earthed and bonded from before introduction until after removal:	,,	Not permitted during loading and for 30 minutes thereafter	No restrictions	Not permitted during injection of inert gas and for 30 minutes thereafter
(iii) non-conducting equipment with no metallic parts:	,,	No restrictions	No restrictions	Not permitted during injection of inert gas and for 30 minutes thereafter
Exceptions Permitted If:	—	(a) sounding pipe is used, or (b) cargo is known to contain sufficient anti-static additive	(a) sounding pipe is used, or (b) tank is continuously mechanically ventilated, when 5 hours can be reduced to 1 hour	—
Exceptions Also Permitted If tank atmosphere non-flammable, i.e. when:	—	(i) tank maintained in inert condition or (ii) tank gas free, and cargo temperature of non-volatile oils does not exceed its flashpoint minus 10°C	(i) tank maintained in inert condition or (ii) tank maintained in over rich condition	(i) tank maintained in inert conditions, i.e. all normal operations

55

Table 5.1   source : ISGOTT (ref [3])

tank, it should be ensured that the water hoses have electrical continuity (resistance shall not exceed 6 ohms/metre lenth); that the machines are properly connected to the hose-end; and that the other end of the hose string is firmly attached to the tank-washing line hydrant. A short preventer strop should also be attached to the hose and machine, to prevent the machine falling to the bottom of the tank.

d. Ropes used for lowering non-metallic equipment into cargo tanks should be natural fibre ropes (manila, sisal, hemp etc.). Synthetic ropes aggravate static generation and hence must not be used.

e. Chemical additives should not be used. If it is deemed essential to use chemicals for any reason, washing should be done under too-lean or inerted atmospheric conditions.

f. Recent tests have proved that the use of hot water results in a significantly higher build-up of static charges. Therefore, it is recommended that the maximum water temperature should not exceed 50° (deg.) C. If water above this temperature is required for any reason, for instance in preparation for dry docking, washing should be undertaken under too lean or inerted atmospheric conditions.

g. Steam must not be introduced into the tank.
      The restriction of using steam can be seen in the following example: On February 1984, the 661 foot-long U.S tank vessel SS AMERICAN EAGLE exploded and sank in

Gulf of Mexico with two losses and two missing lives while she was cleaning and gas-freeing. The probable cause was the ignition of flammable gases in No.3 center cargo tank by steam which induced a strong electrostatic discharge. The use of steam came from the crew's decision to power an air-driven ventilator fitted with a long plastic sleeve without recognizing the hazard created by the introduction of steam into the explosive environment.

h. The tank should be kept drained during washing. Washing should be stopped to clear any build-up of wash water.

i. Sounding and the introduction of other equipment must be done through a sounding pipe if fitted. For tankers which do not have fixed soundings or purge pipes, it is essential that any metallic components of sounding or other equipment are bonded and securely earthed to the ship before introduction into the tank and remain so earthed until removed. This precaution should be observed not only during washing but also during five hours after completion of washing when the water mist diminishes considerably and the generated electrostatic charges are dissipated. However, if the tank is being ventilated after washing, this period can be reduced to one hour (ref.[3]).

5.1.3 : WASHING IN ATMOSPHERE B (TOO-LEAN)
Atmosphere B, which is defined in paragraph 5.1.-

b, has its hydrocarbon gas composition controlled, reduced and maintained at less than 1 % of the tank volume. The control is done after discharge by venting the tank with a deliberate injection of fresh air. The method will vary from ship to ship but typically it will be done by placing gas-freeing fans on the tank washing apertures where the inlet air will be blown, and opening the tank lid and mast-riser to provide a through circulation of the air.

Before washing commences, the tank bottom should be flushed with water and stripped. The piping system, including cargo pumps, crossovers and discharge lines, should also be flushed with water and the liquid drained. When ventilation of the tank commences, the hydrocarbon vapour vented from the tanks may be in the flammable range, and a hazardous condition may exist around the ship for a short period. Strict attention must therefore be paid to control ignition sources in hazardous areas of the ship.

Neither steam nor recirculated water should be used. the tank should also be drained during washing.

The tank atmosphere must be continually monitored during the ventilation process using a combustible gas indicator. The washing should only be commenced when the reading of the hydrocarbon gas on the meter is below 10 % of the Lower Explosive Limit (LEL). During the washing operation, venting of the compartment and checks on the hydrocarbon content of the tank atmosphere should be continued. The readings should be taken in different parts of the tank so that a good average will be obtained. If the gas concentration rises to 50 % of the LEL, then all washing should be

stopped and the ventilation continued until readings of 20 % or less are found. This method can be done safely if the hydrocarbon content is well controlled by the officer in charge of the operation.

Chemical additives may be employed if the temperature of the wash water does not exceed 60°C.

Wash water may be heated. However if the wash water is at 60 C or more, then the gas concentration should not reach 50 % of the LEL.If the wash water temperature is above 60° C , washing should be discontinued if the gas concentration reaches 35 % of the LEL.

5.1.4: WASHING IN ATMOSPHERE C (INERTED)

This method is the one which uses the Inert Gas System. It is much safer than the other methods. It consists of maintaining the oxygen content at less than 8 % of the volume of the tank by introducing inert gas in the cargo tank. It is preferable to lower the oxygen content to five percent by volume.

When portable machines are used, officers should remember that air may enter into the tank through certain places, for example around the washing apertures. To overcome this problem, the pressure within the tank should be slightly higher than atmospheric pressure to ensure that outside air cannot enter. Further, the open area should be reduced by using proper blanks or otherwise sandbags.

5.1.5 WASHING IN ATMOSPHERE D (OVER-RICH)

We can say that this method exists only in theory. It covers enormous difficulties in practice and many risks of failure so that it is not used.

5.1.6. EFFECT OF CRUDE OIL AND WATER WASHING ON TANK ATMOSPHERES.

As we know, water washing has the property to generate a lot of electrostatic charges. Crude oil causes significantly lower charges than water. However, if the crude oil is contaminated with water, the charges are higher than those generated by pure water, depending on the amount of water contained in the crude oil. It is for this reason that oil from the slop tank, which contains retained residues, should not be used for crude oil washing. Figure 5.1 shows the charge densities created by an oil/seawater mixture.

In general, whatever liquid is used for washing, it is essential to control the tank atmosphere to reduce the risk of a fire or explosion. The best tank atmosphere control method is, of course, by the introduction of inert gas into the tank to reduce the oxygen content of the atmosphere to below 8 % of the tank volume. Further, when water-washing by the uncontrolled (undefined) method or by the too-lean method, only clean sea water can be used. When crude oil washing, only "dry" crude (free of water) can be used.

P.10⁻⁸ c/m³ (calculated charge densities)

$P.10^{-8}$ c/m³ (calculated charge densities)

+30

+20

+10

0

−10

−20

−30

```
100      75      50 ·        % Crude Oil
% Water          50     75     100
```
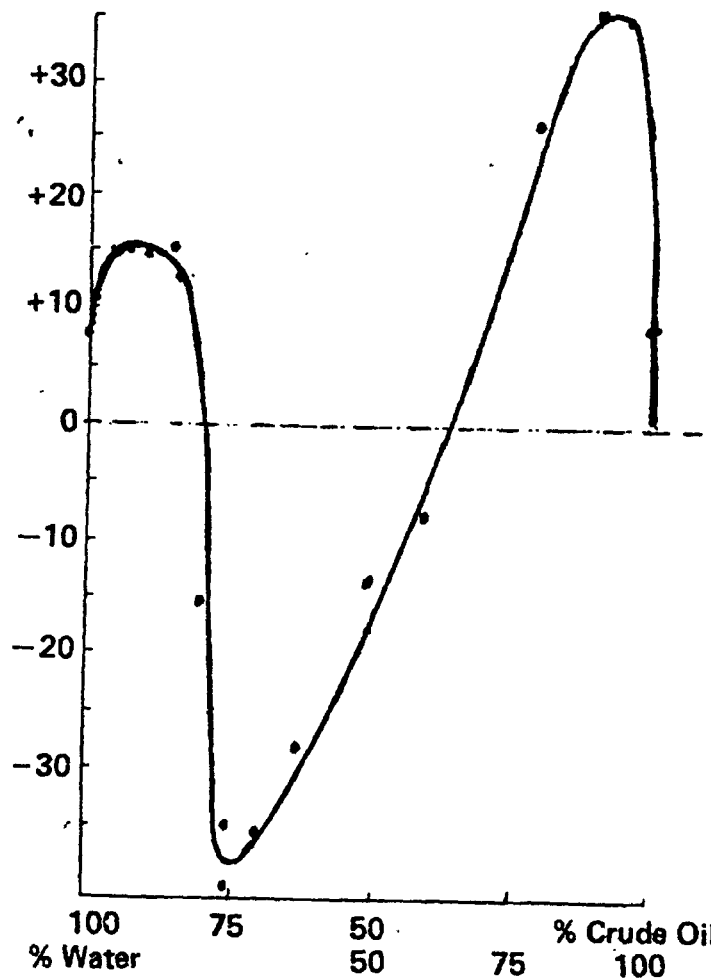
Charge densities created by oil/seawater mixtures

Figure 5.1   source IMO course 1.92

5.2 GAS FREEING

5.2.1: GAS FREEING OF CARGO TANK

A gas free tank is a tank where sufficient fresh air has been introduced to lower the level of any flammable, toxic, or inert gas to that required for specific purposes such as inspections, repairs or docking.

In pratice a tank is safe for entry, whether for

61

inspection, cold work or hot work if: the hydrocarbon gas is not more than 1 % of the LEL ; without toxic hazards or with tolerable toxic hazards such as a Threshold Limit Value (TLV) of 10 parts per million for hydrogen sulphide; and an oxygen content of 21 per cent.

A tank which is required to be gas free for receiving cargo should be ventilated until tests confirm that the hydrocarbon gas concentration throughout that tank does not exceed 40 % of the LEL.

Gas-freeing is normally carried out by one or more of the following three procedures:

a) By portable tank ventilators

b) By permanently installed tank ventilators blowing air to tanks through the cargo oil piping system.

c) By using the inert gas system fans with suction from fresh air instead of the boiler uptake.

Note that there are other methods and type of equipment such as eductors generally operated by steam, water or compressed air. Windsails are also used. They are a cheap and quiet way of maintaining a tank in a gas-free condition. However, this is a slow and time-consuming process.

Whatever procedure is in use for gas-freeing, the following precautions should be taken :

1. The hydrocarbon gas concentration must be measured in each tank to be gas-freed.

2. When gas-freeing an inerted tank, if the HC-gas concentration is above 2 % by volume, then the tank should be purged with inert gas until the HC-gas concentration is reduced to 2 % by volume or less before ventilation with fresh air is commenced.

4. Ventilation should continue until the HC-gas concentration is reduced to less than 1 % of the LEL and the oxygen level is 21 % by volume before the tank is considered gas-free.

5.2.1.1: GAS-FREEING A CARGO TANK WITH PORTABLE FANS

- 1.Portable blowers:

Although permanent, fixed-in-place, tank washing systems are now standard equipment on many tankers, portable machines (see Figure 5.2) are still used on small vessels. Portable blowers are placed over tank openings on the main deck. They are normally driven by steam, compressed air, or water. If the vessel is fitted with standpipes or purge pipes, the displacement method should be the best solution for gas-freeing (See Fig.4.4 in chapt.4).

When the mixing method is used, the inlet air should have a sufficient inlet speed as explained in paragraph 4.1.4.1.b. If this cannot be realized, the

blower should be fitted with canvas hoses or ducts to bring the fresh air inlet to the tank bottom. If the capacity and the outlet diameter of the portable fans are known, the penetration depth of the jet can be obtained from the diagram in figure 4.7. For example if the fan has a capacity of 5 000 m^3/h in an inlet diameter of 250 mm, then the penetration depth would be a maximum of 20 m.
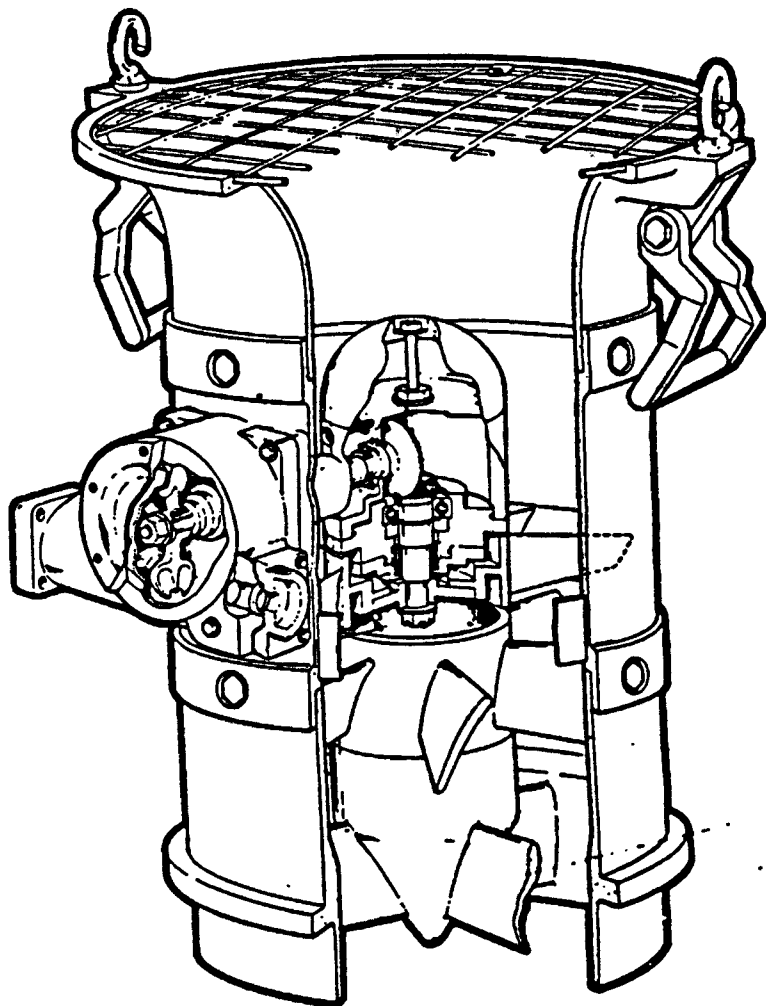
Water driven portable blower Jetfan 125 of DASIC

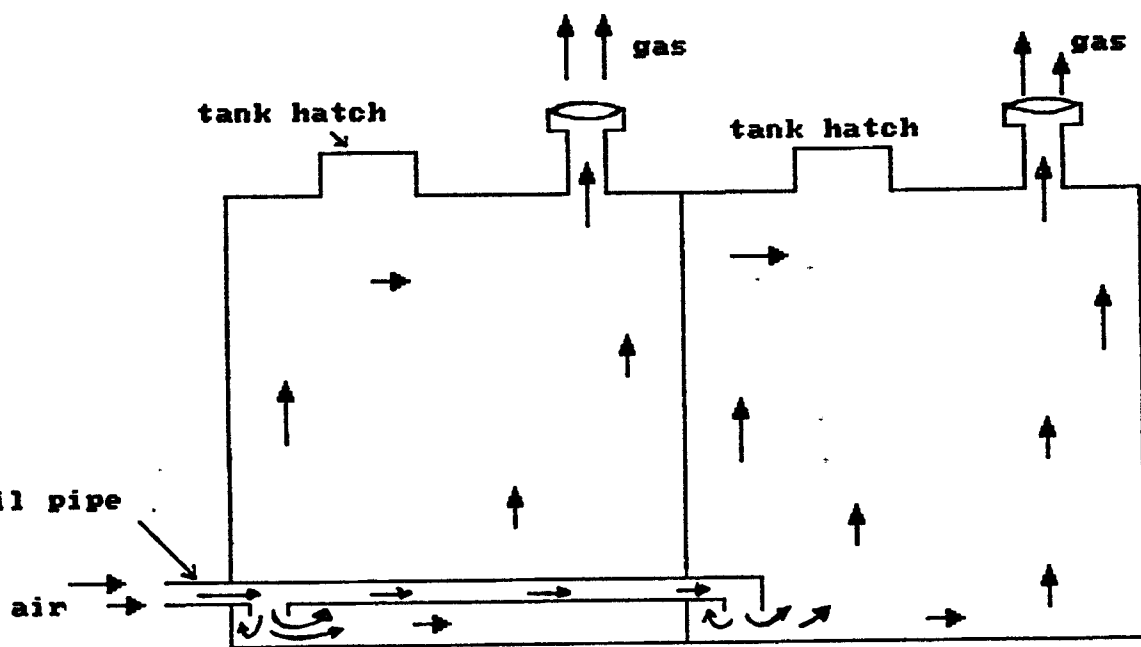Figure 5.2

- 2. Portable extractors

In theory, extractors fitted with an extension pipe will gas-free a tank more efficiently than blowers. With extraction the heavy vapour will be sucked from the bottom of a tank rather like a liquid and will be replaced by air which enters through deck openings. With this method, it requieres theoretically only one air change to gas-free an enclosed space. but in practice it may take two to three air exchanges. An example of an extractor method can be seen in Fig.5.4.

5.2.1.2 GAS-FREEING A CARGO TANK WITH INERT GAS FANS

Most inert gas systems have a connection to draw fresh air and they can gas-free tanks following the inert gas line by passing the scrubber. In this case the openings on deck should be closed and the purge-pipe in the open position. Figure 4.4 shows gas-freeing as well as purging which may use inert gas fans connected to the inlet entrance. The displacement method using inert gas fan is one of the most efficient.

5.2.1.3 : TANK GAS-FREEING USING CARGO OIL LINES

This method uses permanently installed ventilators to provide air through the cargo line (see Fig.5.3). For efficient gas freeing, this arrangement demands good stripping of the tanks to achieve a satisfactory capacity of air supply. Furthermore, it is necessary to sufficiently drain the oil cargo lines in order to avoid a heel of oily water preventing the ventilation.

VENTILATION WITH PERMANENTLY INSTALLED VENTILATORS THROUGH THE VESSEL'S CARGO OIL PIPING SYSTEM

Figure 5.3

The diagram in Fig.4.6 may also be used as a guide for determining the necessary supply of air for this type of arrangement as well. It is important to carry out several measurements of the tank atmosphere, particularly in those parts of the tank where the ventilation is deemed to be poor.

5.2.2 :VENTILATION OF ENCLOSED SPACES OTHER THAN CARGO TANKS

5.2.2.1: GENERAL

Unsafe atmosphere may be present in any enclosed

or confined spaces such as double hull tanks, double bottom tanks, ballast tanks, fresh water tanks, fuel tanks, pumprooms, cofferdams, duct keels and other normally closed spaces. As in a cargo tank, two hazardous factors may be expected in these enclosed spaces:

a: Their atmospheres may not be capable of supporting life, and hence not safe for workers, because they may have insufficient oxygen and/or may contain toxic gases;

b: Their atmospheres may not be safe for hot work because they may contain flammable gases.

For the purpose of safety on board tankers, these enclosed spaces must be periodically gas-freed even totally cleaned to avoid the existence of gas hazards within them. Some interesting cases are described below:

5.2.2.2: VENTILATION OF DOUBLE-HULL SPACES OF OIL
         TANKERS.

The double-hull concept for oil tankers introduces a number of considerations regarding the safety aspect. Two of them are gas-freeing and inerting ballast spaces of the double-bottom or double-hull tankers. Due to the new concept of the double-hull oil tanker, there is , at the moment, no international requirement on ventilating or inerting the double-hull spaces. For

this reason I would like to suggest the following:

Firstly we know that, efficient ventilation allows for safe inspection and ensures the necessary air renewal. Secondly, leakage WILL obviously occur, even in the best maintained vessel. Thus the ability to provide a safe atmosphere will be required. One method of solving this problem is as follows:

1. To fit emergency vent connections to the tanks with suitable flexible ducting to link the inert gas main to the tank. This will provide means to gas-free and/or to inert the spaces when there is a need. However, the designer should foresee an evenly distributed rate of flow both of the inlet air or inert gas, and of the outlet of the existing gas.

2. Due to the geometrical complexity of the double -hull and double-bottom spaces, some form of internal duct is required to ensure that the entire area is adequately ventilated.

3. If the connection is above a clear section of the tank structure, then a relatively short removable purge pipe can be used very effectively. Use of a removable section needs physical work, but reduces the total cost for shipowners, and avoids additional maintenance costs needed to ensure that the duct is always available.

Other solutions than the one presented here may be

envisaged such as:

- use of portable fans: care must be taken in order to have evenly distributed flow rate values in the double-bottom, bearing in mind the uneven disposition and communication of the double-hull and double-bottom spaces.

- ventilating through the ballast piping system: This solution, which of course requires suitable draining of the pipes and provision of a special
fan in the pumproom, may be very cost effective in some practical cases.

5.2.2.3: VENTILATION OF PUMPROOM

A pumproom is a compartment which is much more different to the other enclosed spaces. It is the most hazardous space due to fact that, first, it is at the cross-roads of all cargo and water lines, and second, it includes pumps which are in operation during discharging, ballasting or deballasting.

Ventilation in pumprooms, guidelines for which are given by SOLAS, can be described as follows:

1. It must have fixed exhaust fans (see fig.5.4) leading to a safe place on the open deck. Due to the numerous lines and platforms which can entrain the gas vapour, the ventilation of the pumproom shall have sufficient capacity to minimize the possibility of accumulation of flammable vapour.

2. For safety reasons, the number of changes of air by the fans shall be at least 20 volume changes of the
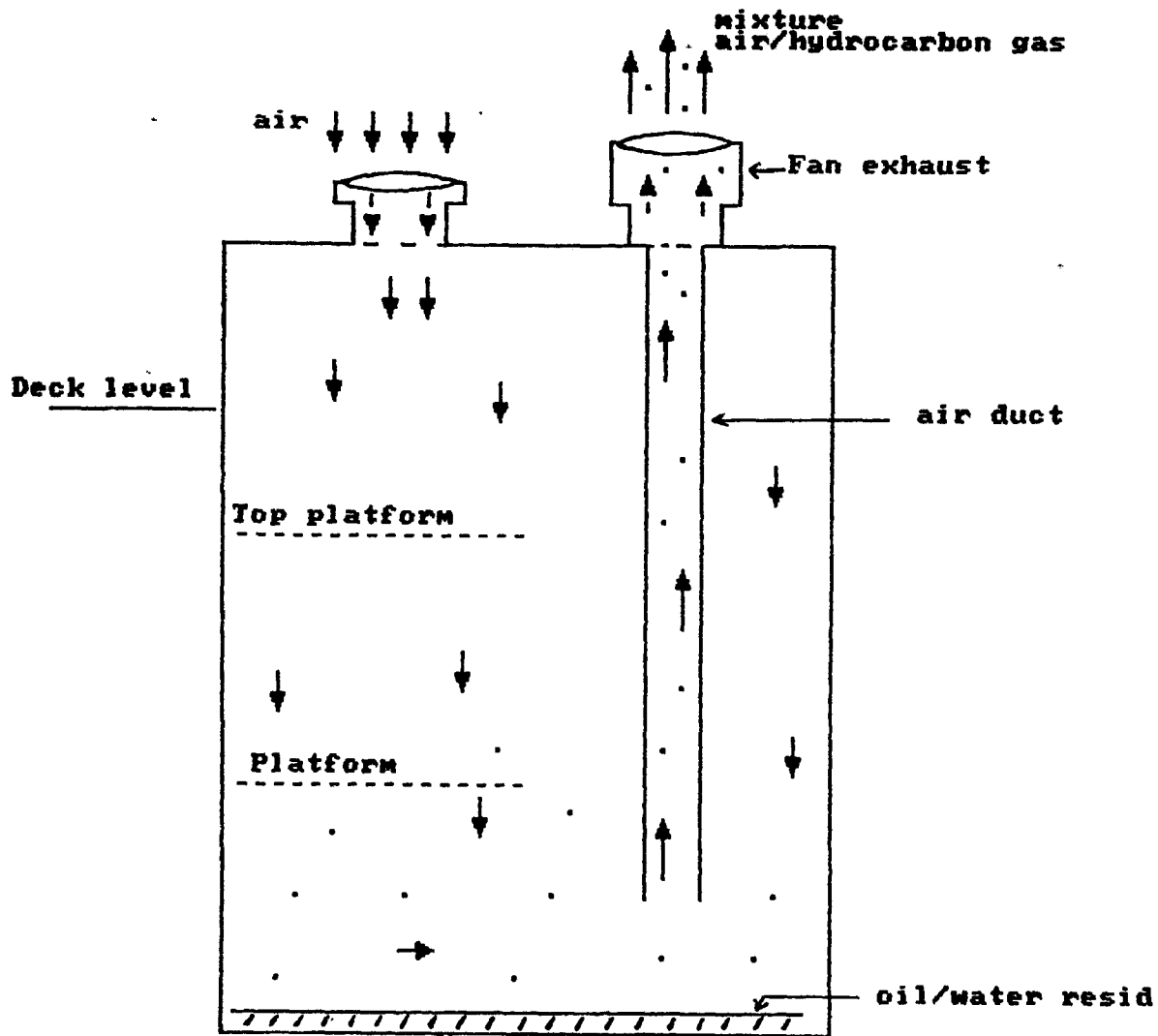
VENTILATION IN PUMPROOM OF OIL TANKER

Figure 5.4

pumproom per hour. This will permit a rapid and
efficacious intervention in a very short time,to
maintain the pumproom in a gas-free condition.

3. The extractor shall have a pipe duct extension to be
more effective in the extraction (see paragraph
2.2.1.1-2) of the hydrocarbon gas which is heavier than
air.

4. To avoid possible sources of ignition by spark from
the extractors, the ventilation shall be of the suction
type using fans of the non-sparking type.

CHAPTER 6

FIRE, EXPLOSION, AND POLLUTION

FROM TANK ATMOSPHERES

6.1 OIL FIRE

Oil itself, like any liquid, does not burn. However, the vapour which it gives off by evaporation can be made to burn when mixed with air in certain proportions. Oil fire is the result of a chemical reaction of oil vapour and oxygen. When molecules of hydrocarbon gas and oxygen come in contact with a source of ignition, they combine to form carbon dioxide and water, and they give off heat. For example ,methane (CH_4), which is a hydrocarbon gas, reacts with oxygen to produce carbon dioxide (CO_2) and water (H_2O) in the form of vapour due to the high temperature.

$$CH_4 + 2O_2 ==> CO_2 + 2H_2O$$
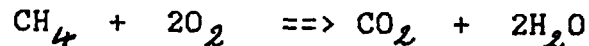
Every fire owes its existence to four indispensable elements which are: fuel; heat; oxygen; and a chain reaction. Therefore, to extinguish a fire at least one of these elements must be removed as follows:

1. **Fuel.** This is the vapour from petroleum or other combustibles which combines with the oxygen to produce a flammable mixture. In theory, removal of fuel is an excellent method of fire fighting, but on tankers carrying thousands of tons of petroleum it is usually

72

impracticable. Nevertheless, certain situations demand that this method be used. For example, if a fire on deck is fed by an overflowing tank, then it calls for an immediate cessation of loading.

2. Heat. Hydrocarbon molecules must be heated substantially by the ignition source before they will combine with oxygen. Heat can transfer through a steel bulkhead and ignite a tank of fuel oil without the aid of an open flame. This process is known as conduction. Heat can also expand and move from one location to another, known as convection. It can finally act by direct radiation as the energy from the sun to heat materials. We can remove heat by using water, which is one of the most effective cooling agents, or foam.

3. Oxygen. Fires need oxygen to survive as do people or plants. Likewise, fires perish without oxygen. It follows that a fire can be extinguished by either reducing the oxygen content until it falls below 11 percent, or smothering the surface of the flame so that oxygen cannot enter. The first method uses carbon dioxide, or inert gas; the second, mechanical foam.

4. Chain reaction. Molecules must pass through several steps in the oxidation process, one after another, in a regular progression. So, if we remove one of these steps, then fire ceases to burn. This theory explains the rapid action of dry chemical and halogenated extinguishing agents in fighting fires. These agents interrupt the vital chain reaction in a fire, thus causing the fire to extinguish. Research continues in

this field and non-CFC (Chloro-Fluoro-Carbon) fire-extinguishing agents of this type may assume a major role in the future.

6.2: FIRE PREVENTION

a. The crew members. The first step in fire prevention is to remain fire conscious at all times while on board a tanker. Crew members must be aware of the hazards of oil petroleum and hydrocarbon gases. They must be trained in fire fighting and fire prevention. They should be encouraged to leave their cigarettes in their rooms or other safe areas. This precaution prevents an individual from lighting-up a cigarette in an unsafe area.

b. The pumproom. One of the most dangerous places on a tanker is the pumproom. Pumprooms are probable sources of fire and explosion. Operators must always assume that an explosive atmosphere exists in the pumproom. Gasoline and other volatile products evaporate quickly, especially when spread across the pumproom bilge plating. The resultant vapour is both toxic and explosive. It is therefore imperative to use great care when descending into pumprooms, and to make sure that the ventilation system is brought into operation well before crew members enter pumprooms.

c. Vapour accumulations on deck. When loading in calm weather, petroleum vapour emissions from vent lines may

settle around the main deck. Being heavier than air, petroleum vapour tends to lie close to the deck in a stagnant, invisible pool until dissipated by the wind. It may eventually find its way into living spaces, contact a source of ignition, and flash back to the tanks. The result would be an explosion, fire or both. In order to safeguard against this possibility, several precautions must be taken:

1. Keep ullage covers closed whenever possible.

2. Use a flame screen if ullage covers must be left open for any reason.

3. During cargo or ballasting operations, all doors and accommodation area openings overlooking the cargo deck must be kept closed.

4. Stop loading operations whenever heavy concentrations of vapour accumulate in the cargo-handling area.

5. If your ship is fitted with an inert gas system, make sure that it is used properly to ensure that the tank atmosphere is not in the flammable range.

6.3: THE EXPLOSION

When a flammable mixture is ignited, flame will travel and spread rapidly accompanied with a quick rise of pressure due to the high temperature. In an open
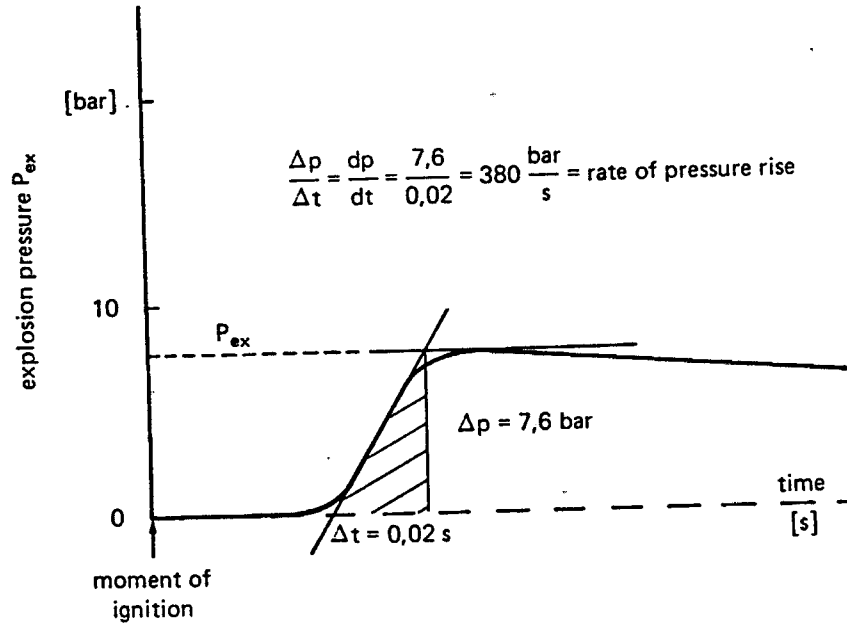
75

space, the gases are able to disperse easily. However, in an enclosed space such as a cargo tank the sudden expanded gas will remain within it and the pressure will continue to increase. Explosion will occur if the pressure rise exceeds the pressure that bulkheads, deck or bottom can support.

The violence of an explosion is evaluated as a function of two factors. The first one is the Explosion Pressure (Pex) which is the pressure in excess of the initial pressure at which the explosive mixture was ignited. The second factor is the rate of pressure rise (dp/dt) which is used as a standard of measurement of the speed of flame propagation and hence of the violence of explosion. A test of an explosive mixture shows that for a pressure of 7.6 bars in a time of 0.02 s gives a rate of pressure rise dp/dt of 380 bars/s (see fig.6.1).

The composition of the flammable gas and the volume of the cargo tanks within which the explosion takes place have a significant influence on the violence of the explosion. The effect of the volume of cargo tanks on the maximum pressure rise for a given flammable vapour is given by the " Cubic Law ":
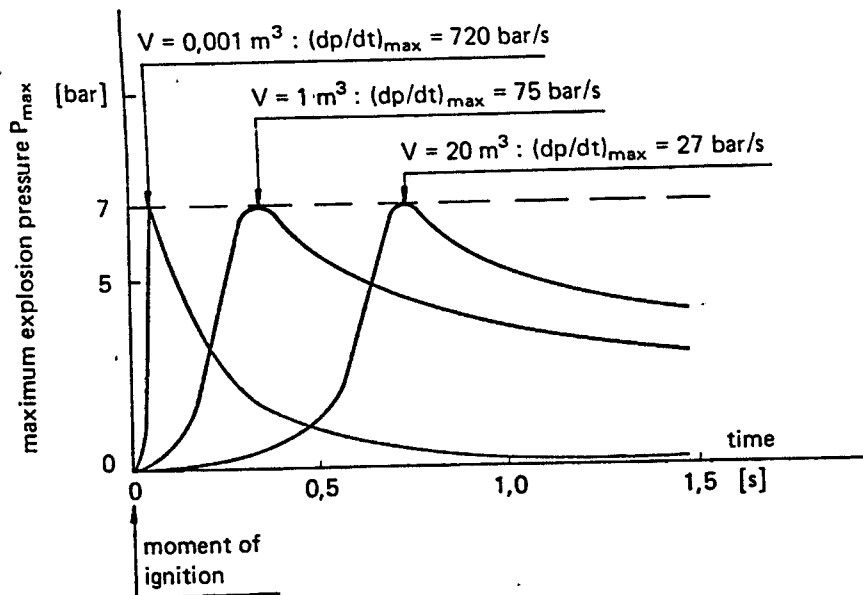
$$ dp/dt \times V = const \; K \qquad ref.[2] \; , $$

where K is a specific material constant of the concerned flammable vapour ; K is calculated as a function of a given energy and pressure. For example, Fig.6.2 shows that propane explosions occuring in closed tanks of different volumes at different times, and hence producing different courses of explosion, but

76

$$\frac{\Delta p}{\Delta t} = \frac{dp}{dt} = \frac{7,6}{0,02} = 380 \frac{bar}{s} = \text{rate of pressure rise}$$

explosion pressure P_{ex}

[bar]

10

P_{ex}

$\Delta p = 7,6$ bar

0

time [s]

$\Delta t = 0,02$ s

moment of
ignition

Determination of the rate of pressure rise dp/dt of a gas explosion

Figure 6.1   source [2]

10

maximum explosion pressure P_{max}

V = 0,001 m^3 : (dp/dt)$_{max}$ = 720 bar/s

V = 1 m^3 : (dp/dt)$_{max}$ = 75 bar/s

V = 20 m^3 : (dp/dt)$_{max}$ = 27 bar/s

[bar]

7

5

2

0

time

0   0,5   1,0   1,5 [s]

moment of
ignition

Influence of vessel volume on the course of propane explosions (stoichiometric mixture)

Figure 6.2   source [2]

reaching the same final pressure of 7 bars. To minimize the initial pressure, some cargo tank gas lines of tankers are fitted with pressure-vacuum valves (PV-valves) which are normally set to open when the pressure in the tank reaches about 0.137 bars above atmospheric pressure. However, if the pressure rises quickly, the gas line will be unable to release the expanding gases. If lids to cargo tanks are left open, expanding gases may issue through them with a velocity which will vary inversely with the size of such openings. But, it is a dangerous practice to leave the lids or any other tank openings open during cargo operations. The reasons are that flammable and toxic vapour will be released, cause pollution of the atmosphere and also affect the health of personnel on board. Also, if a source of ignition can get in, an explosion may occur.

After a tank has exploded, the heat energy given from it may act as a source of ignition for adjacent tanks and compartments. Therefore, there is a possibility of an explosion or fire in a nearby compartment.

6.4 : IGNITION SOURCES FOR FLAMMABLE MIXTURE

6.4.1 : PRELIMINARY REMARKS

A source of ignition will provide combustion in a flammable mixture, only if it is both sufficiently hot and has sufficient energy. The values of energy and temperature necessary for successful ignition vary with different flammable gases and sources of ignition from

which fire and explosion may result. A source of ignition may come from direct heat energy, chemical energy, electrical sparks etc.

6.4.2 : IGNITION FROM DIRECT HEAT

1. **Cigarette smoking** is a great potential hazard on board tankers. It is said that a burning cigarette may not always be hot enough to ignite flammable vapour, but the match used to light a cigarette or throwing a lighted cigarette end is a probable ignition source. Therefore, smoking should not be allowed anywhere on board where flammable vapours may be present. This restriction should apply, not only on board, but also on the jetty and on tugs or other craft alongside.

2. **Welding** should not be done in the presence of flammable vapours. Cargo tanks, pumproom and other similar compartments should be gas-free and clean before welding commences. Likewise, heating coils, cargo pumps, cargo lines and other similar items of cargo equipment should be in a properly clean and gas-free condition before welding is done on them or in their vicinity.

3. **Hot soot:** Sometimes, incandescent carbon from the funnel of the tanker itself or of other craft alongside, may be hot enough to ignite flammable vapours. This can happen in calm wind during loading of volatile oil cargoes which give off flammable vapour remaining in the vicinity of the vessel. It is for this reason that funnel uptakes should be blown through

prior to entry into port. Furthermore, during cargo operations, craft alongside, if any, should be so positioned that their funnels are abaft own vessel's funnel taking into account the favorable side of the wind direction.

6.4.3 : IGNITION FROM CHEMICAL ENERGY

1. **Metallic Smears:** Some lighter metals such as magnesium and aluminium give off sparks easily when they are struck with a sharp heavy object. The spark is partly caused mechanically, but also some of the impact heat energy causes a chemical change. For this reason, portable equipment made of aluminium or its alloys should not be used in cargo tanks or other closed space where flammable mixtures may accumulate. The installation of magnesium anodes in cargo tanks and the use of aluminium paint should not be permitted in these areas.

2. **Spontaneous combustion:** It is a slow oxidation process so that it may not be noticed until the material gets sufficiently hot to act as a source of ignition for other flammable material such as paint or flammable vapour. This ignition is mainly caused by storing wet clothes, oily rags, cotton-waste etc. Spontaneous combustion can be prevented by constant vigilance : firstly, by stowing combustible materials and keeping them as dry as possible; secondly, by cleaning and ventilating the area; and thirdly, by carrying out frequent inspections.

3. **Autoignition temperature**: The temperature at which a
material will burn by itself automatically, without the
presence of any other source of ignition is called the
autoignition temperature. For a given material the
autoignition temperature is generally higher than its
flash point. On board tankers, autoignition may occur
due to the cargo being in contact with an overheated
pump or a fire in an adjacent tank. To prevent oils
reaching their autoignition temperatures, it is
necessary to avoid their coming into contact with
metallic surfaces whose temperature is higher than the
respective autoignition temperature.

4. **Pyrophoric oxidation**: Crude oils and some other oil
products such as naphtha, bitumen and gas oil may
contain hydrogen sulphide which has a typical odour of
rotten eggs. With the presence of hydrogen sulphide,
pyrophoric oxidation may occur in the following phases:

Phase 1 : the tank has rust which is iron oxide (Fe_2O_3)
in the tank structure. It is inerted and thus has a
deficiency of oxygen. Its atmosphere has hydrogen
sulphide (H S) which has probably come from the oil
vapour existing in the tank.

Phase 2 : The rust (iron oxide) reacts with hydrogen
sulphide of the oil vapour. Iron sulphide (FeS) is
formed from the reaction plus water (H O) and sulphide
(S) as follows:

$$Fe_2O_3 + 3H_2S ==> 2FeS + 3H_2O + S$$
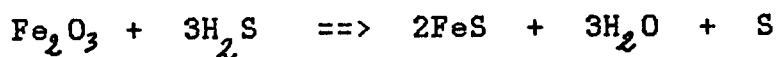
Phase 3 : If air is let into the tank for any reason, the iron sulphide will react with oxygen of the air to return to iron oxide and sulphide.

$$4FeS + 3O_2 ==> 2Fe_2O_3 + 4S$$

This re-oxidation is accompanied by a generation of considerable heat (exothermic reaction). Then, individual particles of the iron may become incandescent and may therefore ignite a flammable mixture of hydrocarbon gas and air.

To avoid this situation, metal surfaces which are impregnated with hydrogen sulphide should be well dampened before any hot work is undertaken around the area. Tanks should, as far as possible, be maintained in an inert or non-flammable condition.

6.4.4 : MECHANICAL SPARKS.

If two objects come into contact, violently, there will be a temperature rise at the point of impact. If one of the objects is sharp, small pieces of hot metal may be dislodged, form a mechanical spark and then become a source of ignition for flammable vapour. For this reason the use of chipping hammers or other mechanically driven tools should be restricted where a flammable mixture may be present. Cigarette lighters are also a great potential danger. The hazard comes from the fact that lighters are often carried in the pocket; and no matter how careful the smoker is , his lighter may one day slip out of the pocket and may drop

into a tank which contains a flammable mixture. As it hits the bottom, the flint may produce a spark which may cause an explosion. Likewise, any metallic object carried in pockets, such as mechanical keys etc is a potential ignition hazard. Hence, nobody on deck should have a metallic object in his pocket which can drop into a tank. That is in order to avoid a possible spark resulting therefrom.

In the same manner, the compression of a gas bubble against a tank structure by a cleaning jet i.e water, can raise the gas temperature sufficiently and may act as a source of ignition.

6.4.5 : ELECTRIC SOURCES

1. Electrical currents

An electrical spark has sufficient energy to act as a source of ignition for petroleum vapour. It is usually the result of a break in a current-carrying cable and arcing in the ionized air. The overloading of a conductor followed by overheating and arcing due to excessive voltage is a further cause of ignition. It is therefore essential that in cargo tanks and other enclosed areas where vapour concentrations are difficult to control, no electrical equipment other than approved equipment should be used. The term "approved equipment" stands for fire or explosion-proof, and intrinsically safe apparatus. Cargo vapour should be prevented from entering accommodation or machinery spaces because much of the electrical equipment therein is neither explosion-proof nor

intrinsically safe.

2. Static Electricity Discharge:

Electrostatic charges are largely developed by high initial loading rates (see Chapt.2.3.1), by loading and mixing of different types of crude oil and petroleum products, and by washing the cargo tank etc. For an electrostatic charge to ignite a flammable gas mixture, three conditions must be satisfied:

i. An electrostatic charge mechanism developed during certain tanker operations.

ii. There must be an accumulation of electrostatic charges on an isolated conductor.

iii. Existance of an incendiary spark caused by a contact of the charged isolated conductor with any part of the tank/ship structure.

The first condition can in certain cases be minimized by for example regulating the flow rate when loading. The second condition can be avoided by bonding and earthing. The third condition is prevented by using, for example, too lean method or inert gas system during the tank operations.

3. Lightning

Ignition of flammable tank atmosphere by lightning strikes may occur by the following mechanisms :

- The rapid changes in a magnetic field, resulting from rapid current pulses of high intensity (up to 200 000 Amperes), are capable of inducing voltages and currents in circuits and structures. Spark-over to earthed points can then occur with sufficient energy to

ignite a flammable mixture.

- A strike on a metal plate could cause local
heating such that the vapour on the other side of the
plate reaches a temperature above the autoignition
temperature.

4. Stray current:

Stray current sparks may occur when pipework is
separated or when there is a connection to the earth.
This generally results .from : - pipeline cathodic
protection;-jetty cathodic protection; - or electric
arc welding equipment. For this reason, shore tanker
terminals must have all pipelines, flange and arms well
bonded as per similar practice on ships. In order to
avoid a possible spark when connecting/disconnecting
ship/shore manifold, an insulated flange is introduced
at the terminal.

5. Radio frequency

During the Second World War, petrol fires occurred
which were alleged to have been ignited by radar
equipment operating at a wavelength of 10 cm (ref. [10]
). After a study on the subject, it was found that
radio waves are a possible source of ignition under
certain circumstances which are:

a. An electromagnetic radiation of sufficient
intensity at the site of the flammable mixture.

b. The presence of a structure capable of behaving as a
receiving aerial to give rise to an induced current.

c. An intermittent contact such that the received energy may be converted into a spark of sufficient intensity.

We are not yet aware of any tank explosion caused by radio frequency, but care should continue to be exretised in order to preserve generally safe conditions on board.

8.5: ALARMS , LIGHTS, AND INDICATORS

1. **Alarms**. In cargo operations, alarms inform the operator that actions need to be taken for preventing a disastrous situation. Audible alarms normally consist of horns, sirens or bells. Different tones or devices are necessary to denote various conditions and thereby avoid confusion as to the alarm being sounded.

2. **Lights**. Lights may be utilized in different colours to inform the tankerman of the status of a tank. In general they are:

    - high level   =>   amber
    - overflow   =>   red
    - other level   =>   owner's choice

3. **Indicators**. They can be mechanical indicators, or digitally displayed. They show level, temperature, pressure etc.

Alarms, lights and indicators are normally located

in a cargo control room from where the tanker officer directs the operations. The most sophisticated control rooms incorporate a computer terminal system through which all important functions are controlled automatically.

6.6: PREVENTION OF POLLUTION FROM TANK ATMOSPHERES

Air pollution may be caused by oil vapours or inert gas finding their way into the atmosphere because of :
- the breathing or venting of loaded tanks,
- purging or gas-freeing operations,
- loading or ballasting cargo tanks,
- release of vapours from tanks.

For the most part, these vapours are hydrocarbon volatile organic compounds (VOCs) which under certain conditions form ozone when mixed with air and sunlight. Some states and local jurisdictions are proposing, or already have regulations prohibiting or limiting air pollution from ships.

The quantity of VOCs emitted depends on the type and the volume of liquid which is in the cargo tank, and whether the vessel is in loading or ballasting.

Emissions of VOCs are calculated by the follwing equations:

- Vessel loading emissions: $E = (c/d) f$

- Ballasting emissions: $E = 0.3 (c/d) f x$

where E = mass of emissions; c = mass of cargo; d = density of cargo (mass per unit volume); f = cargo-specific emission factor (mass per unit volume); x = percentage of tankships without equipment to prevent ballasting emissions.

The emission factor f, expressed in pounds per 1,000 gallons of liquid, is given in the Table 6.1 below:

Emission Factors in Pounds Per 1,000 Gallons of Liquid

Emission Source	Loading Operations		Tanker Ballasting
	Ships	Barges	
Gasoline	1.8	3.4	0.8
Crude oil	0.61	1.0	1.2
JP-4	0.5	1.2	Unknown
Kerosene	0.005	0.013	Unknown
Distillate oil no. 2	0.005	0.012	Unknown
Residual oil no. 6	0.00004	0.00009	Unknown

Source: U.S. Environmental Protection Agency (1985).

Table 6.1   **source [13]**

Studies show that more than 98 per cent of vapour emissions occur at the port of loading (ref.[13]). Therefore preventing emissions of hydrocarbon vapour while operating in a port will resolve the enormous problem of vapour emission.

Measures against air pollution from tanker vapour emissions may be proposed as follows:
- Use of vapour piping lines from ship to shore.

TYPICAL VAPOR CONTROL SYSTEM

VAPOR BALANCE LINE

LIQUID STORAGE TANK

PROCESSING UNIT

FLAME ARRESTER

VAPOR RETURN LINE

LIQUID RETURN LINE

DETONATION ARRESTER

PUMP

CARGO TANK

LIQUID LOAD LINE

BARGE OR TANKSHIP

89
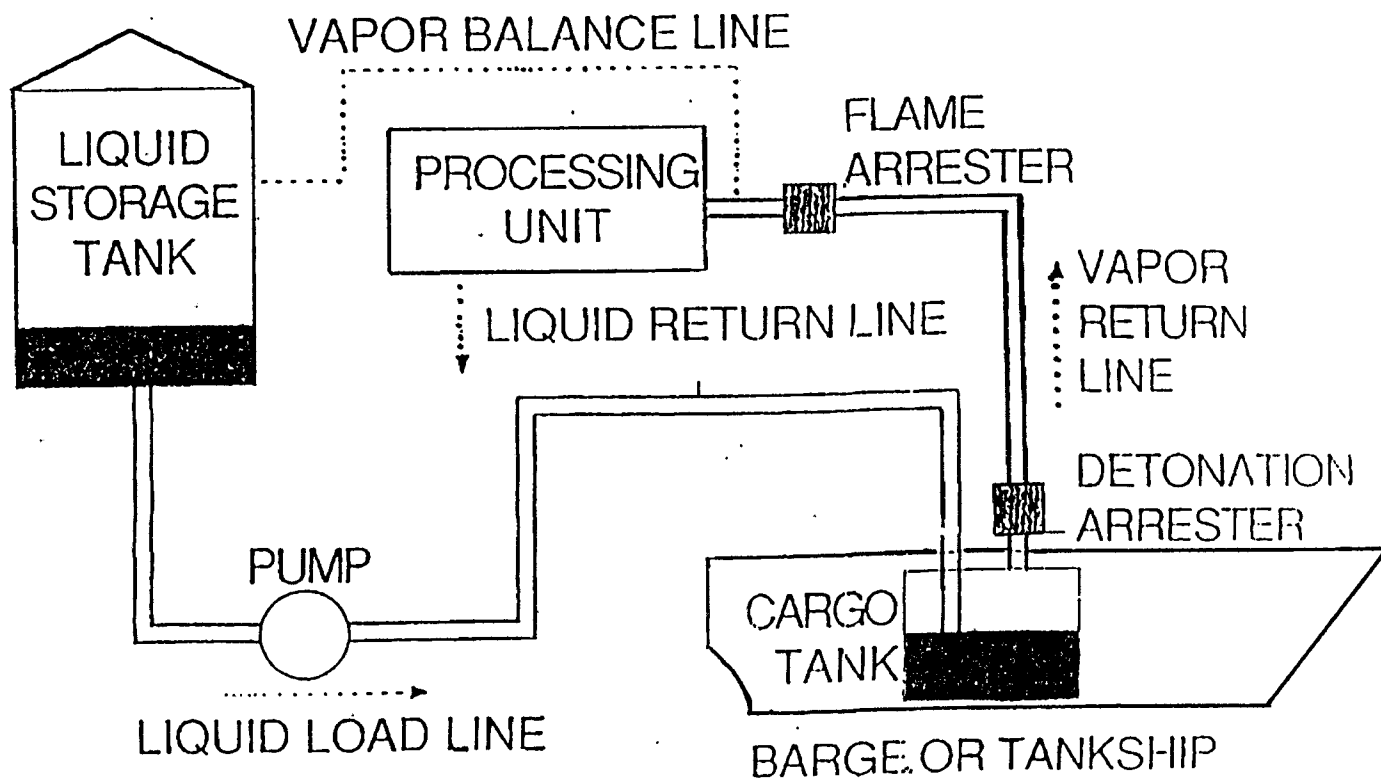
Figure 6.3   source [17]

Vapour will enter the piping lines either through the positive pressure created by the rising oil into the tank or through a vacuum created on shore by mechanical means.Also, gases may be added to the vapour while in the piping lines to increase the control process. Vapour emissions may typically be collected as shown in Figure 6.3.

- On board the ship, a system of collection and storage of vapour emissions may be established for use when the tanker is at sea. This may be connected to the inert gas system with separate storage spaces. The vapour stored may be further used as fuel energy if it does not contain inert gas, or sent to shore reception facilities.

CHAPITRE 7

CONCLUSIONS AND

RECOMMENDATIONS

A variety of matters falling under the umbrella of tank atmospheres have been examined in this dissertation.

We have discussed at great length the various methods of controlling tank atmospheres such as:

- diminishing the oxygen content,
- minimizing the hydrocarbon gas content,
- eliminating sources of ignition,
- use of adequate alarms, etc.

The hazards and the appropriate precautions that should be taken to provide accidents due to tank atmospheres have also been discussed.

Tankers show no compassion for those who challenge their power unprepared. Tremendous tanker explosions have occured primarily due to a lack of knowledge about properties of oil, electrostatic charges and/or operational procedures. This dissertation will help ships' officers to alleviate this situation by gaining a better understanding of the principles of tank atmospheres. It will also be a useful aid for the training of officers, ratings and all persons involved

in tanker operations. Accordingly, this paper can be seen as a modest contribution to the safety and training aspects required respectively by SOLAS and STCW conventions.

Double-hull oil tankers as well as mid-height deck oil tankers, both of which are under discussion in IMO, lead to other problems, such as the efficient ventilation of their double-hull and double-bottom spaces due to the extension and the geometrical complexity of these spaces. This study put forward a proposal for ventilating these confined spaces.

This dissertation reveals the major aspects to be considered regarding vapour emissions, and gives a possible solution for the collection of vapour emissions in order to avoid air pollution from a tank atmosphere.

Finally, we can conclude that, in spite of the hazards, tanker operations and related tank atmosphere control can be carried out safely by taking proper precautions and enlisting the aid of a well-trained crew.

F I G U R E S

TABLES

REFERENCES

[1]   IMO model courses 1.02 : IMO

[2]   Petroleum Tankship Safety : R.C PAGE & A. WARD

[3]   International Safety Guide for Oil tankers and
        Terminal (third edition) : International Chamber
        of Shipping & Oil Companies International Marine
        Forum & International Association of Ports and
        Harbours

[4]   Marine transportation aof LNG and Related
        Products : R.G. WOOLER

[5]   Industrial Explosion Prevention and Protection:
        Frank T. BODURTHA

[6]   Explosion : W. BARTKNECHT

[7]   Second Report on Explosion in Very Large
        Tankers: International Chamber of Shipping (ICS)

[8]   Final Report on Explosion in very large
        Tankers : ICS

[9]   Inert Gas System (1990): IMO

[10]   Sources of Ignition : John Bond

[11]   SOLAS and amendments : IMO

[12]   MARPOL 73/78 and amendments : IMO

[13]   Controlling Hydrocarbon Emissions from Tank
        Vessel Loading : Commettee on Control and
        Recovery of Hydrocarbon Vapors from Ships and
        Barges & Marine Board Commission on Engineering
        and Technical Systems National Research Consil

[14]   A/S course manual on operation of inert gas
        system : Det Norske Veritas classification

[15]   MET(N)-92 course on tankers : Capt H. KAPS

[16]   Tanker Cargo Handling : D. Rutherford

[17]   Marine Vapour Control Training Guidelines :
        American Petroleum Institute

[18]   Chemicals in ships : Kenworthy