Chapter 28

HAZARDS OF GASES

This Chapter mainly concentrates on the quality of the atmosphere to which personnel can be exposed. In addition to the risk to personnel encountering hydrocarbon vapours of a toxic nature, the question of oxygen deficiency is also covered. Methods of checking atmospheres are described.

28.1 Cargo Hazards

All gas carriers are designed so that, in normal operation, personnel should never be exposed to the hazards posed by the products being carried. This assumes, of course, that the tanker and its equipment are maintained properly and that operating instructions are followed.

In the event of accidental leakage, emergency inspections or maintenance tasks, personnel may be exposed to liquid or gaseous product. It is the purpose of this Chapter to review the hazards to health and safety which such circumstances present and to outline means of hazard avoidance.

The overall approach in the avoidance of hazards to personnel should always be, in order of preference:

- Hazard removal,
- Hazard control, and then only
- Reliance on personal protection.

This listing suggests that reliance of personal protection should only be used in cases where hazard removal or hazard control are found impossible to accomplish.

An essential requirement is the thorough training of all personnel. Effective supervision of all tasks where hazards may be present is also vital. Training should go beyond basic instruction on the use of equipment or the execution of procedures, and should include the nature of the hazards, including those which are sometimes not immediately obvious. Broadly, the hazards of liquefied gases or their vapours may be five-fold. These hazards are discussed more fully later in this Chapter. However, the essential components are listed below:-

- Flammability - see Section 28.2.
- Toxicity (poisoning) - see Section 28.3.1.
- Asphyxia (suffocation) - see Section 28.3.2.
- Low temperature (frostbite) - see Section 28.4.
- Chemical burns - see Section 28.5.

In Chapter 27, a description is given of the properties of the liquefied gas cargoes normally carried. In addition, the Cargo Information Data Sheets or MSDS provide detailed health and safety data for products. The risks of flammability, low temperature and asphyxia apply to nearly all liquefied gas cargoes. However, the hazard of toxicity and chemical burns apply to only some of them.

Table 28.1 lists the main liquefied gases together with their flammable and toxic hazards. Where appropriate, asphyxiant hazards are also noted in the column headed 'TLV'. However, this applies only when the gas has asphyxiant hazards and is not recorded as having any toxic effects or where the toxic effects are limited.

The table is subdivided horizontally by a double line. The products above this line are mainly the hydrocarbon liquefied gases and those below the line are mainly chemical gases. It should be noted that the chemical gases tend to have stronger toxic effects.

Cargo vapour in air				Toxic effects of vapour or liquid	
Substance	Flammable	Toxic	Typical TLV – TWA (ppm)	Corrosive/ Irritant	Effects on Nervous Systems
Methane	Yes	-	A	No	-
Ethane	Yes	-	A	No	Yes
Propane	Yes	-	A	No	Yes
Butane	Yes	-	600	No	Yes
Ethylene	Yes	-	A	No	Yes
Propylene	Yes	-	A	No	Yes
Butylene	Yes	-	800	No	Yes
Isoprene	Yes	-	No data	No	Yes
Butadiene	Yes	Yes	10	Yes	yes
Ammonia	Limited	Yes	25	Very	-
Vinyl Chlorine	Yes	Yes	5	Yes	Yes
Ethylene Oxide	Yes	Yes	10	Very	Yes
Propylene Oxide	Yes	Yes	50	Very	Yes
Chlorine	No	Yes	25	Very	Very
Gases shown with an 'A' mark in the 'TLV' column do not have recorded TLVs. These gases are relatively non- toxic in character. They are known as Asphyxiant Gases and will kill when their concentration in air is sufficient to displace the oxygen needed to sustain life (see 28.3.2)					

Table 28.1 - Health data - cargo vapour

The last two columns of the table show how a liquefied gas may affect a person. Broadly, the initial toxic effects on the human body can be corrosive or narcotic (effects on the nervous system). In certain cases, both may apply. In the case of a corrosive compound, depending on exposure and toxicity, its effects may be minor or major. In the case of minor effects, only limited irritation of the skin, eyes or mucous membranes may be felt. An example of a more serious case may be that debilitating effects on the lungs are experienced. In the case of exposure to a narcotic gas, the major initial effect is on the body's nervous system. In such cases, severe disorientation and mental confusion can result. The corrosive and narcotic effects are worthy of note. They are of help in identifying the gas to which a person has been exposed and, additionally, they help in identifying proper medical treatment (see Section 28.3.3).

Cargo Inhibitors				Toxic effects	
Substances	Flammable	Toxic	Typical TLV-TWA (ppm)	Corrosive/ Irritant	Effects on nervoeus system
Hydroquinone	Limited	Yes	1	Very	Yes
Tertial butyl catechol	Limited	Yes	-	Very	-

Table 28.1(a) - Health data - cargo inhibitors

Table 28.1(a) provides similar information to that shown in Table 28.1 but covers the potential hazards of cargo inhibitors. Information on the type of inhibitor used in particular cargoes is given in Section 27.8.

Substance	Frostbite	Chemical burn
Methane	Yes	-
Ethane	Yes	-
Propane	Yes	-
Butane	Yes	-
Ethylene	Yes	-
Propylene	Yes	-
Butylene	Yes	-
Isoprene	Yes	-
Butadiene	Yes	-
Ammonia	Yes	Yes
Vinyl Chlorine	Yes	-
Etylene oxide	Yes	Yes
Propylene oxide	Yes	Yes
Chlorine	Yes	Yes

Table 28.2 - Additional health data - cargo liquid (effects on the human body) Cargo inhibitors

This information is discussed further in Sections 28.4 and 28.5.

28.2 Flammability

28.2.1 Operational Aspects

The single most hazardous aspect of liquefied gases is the flammable nature of their vapours. Much effort is put into tanker design to ensure effective cargo containment to avoid vapours escaping to atmosphere. In addition, tankers and terminals have design specifications for electrical equipment so as to ensure that, within well-defined operating zones, such sources of ignition are eliminated. Furthermore, in the tanker and terminal working environments, operational procedures should apply that limit other possible sources of ignition, such as those described in Section 27.24, to areas outside established safe distances (see also Section 28.2.2).

All liquefied gases transported in bulk by inland waterways with the exception of chlorine and CO_2, are flammable. The vapours of other liquefied gases are easily ignited. The exception to this is ammonia which requires much higher ignition energy than the other flammable vapours. Accordingly, fires following ammonia leakage are less likely than with the other cargoes. However, in practice, it is usual to consider the possibility of ammonia ignition and to act accordingly.

28.2.2 Emergency Aspects

Because of the very rapid vaporisation of spilled liquefied gases, the spread of flammable vapour will be far more extensive than in the case of a similar spillage of oil. The chances of ignition following a spill of liquefied gas is, therefore, much greater. For this reason, many terminals establish ignition-free zones round jetties. The extent of these zones is based on a hazard analysis, taking into account local conditions and involving the dimensions of the gas cloud which could be so formed. To establish the size of such a cloud, it is necessary first to estimate the size of the maximum credible spillage. Such an estimation may be carried out in various ways and numerous methods are available. One simplified method is published in the SIGTTO publication *Guidelines for Hazard Analysis.* Results of such estimations at jetties often show the need for safety distances in the order of several hundred metres.

The hazards to personnel in fighting oil cargo fires are well known and apply generally to liquefied gas fires. There are, however, some points of difference to note (see Sections 27.22, 27.23 and 27.24). Radiation from liquefied gas fires, because of the rapidity of vapour production, can be intense and fire-fighting should only be attempted when personnel are wearing protective clothing suited for purpose.

28.3 Air Deficiency

28.3.1 Toxicity

General

Toxicity is the ability of a substance to cause damage to living tissue, including impairment of the nervous system. Illness or, in extreme cases, death may occur when a dangerous gas or liquid is breathed, taken orally or absorbed through the skin. (In general, the terms 'toxic' and 'poisonous' can be considered synonymous.)

Some liquefied gases present toxic hazards, principally if the vapours are inhaled. Ammonia, chlorine, ethylene oxide and propylene oxide, are also very corrosive to the skin. Vinyl chloride is known to cause cancer and butadiene is suspected as having similar harmful effects.

Incomplete combustion of hydrocarbon vapours may produce the toxic gas carbon monoxide which is found in inert gas in quantities which can vary with the quality of combustion in the generator. Combustion of vinyl chloride may produce toxic carbonyl chloride (also called phosgene).

Many substances can act as poisons and a person can be exposed to their effects by various routes. As a result, toxicology has branched into several specialised areas, one of which is industrial toxicology. In this area, the effects of chemicals in the air or on the body are evaluated.

Toxic substances are often ranked according to a system of toxicity ratings. One such scale is shown below:

Unknown, for products with insufficient toxicity data available;

No toxicity, for products causing no harm (under conditions of normal use) or for those that produce toxic effects only because of overwhelming dosages;

Slight toxicity, for products producing only slight effects on the skin or mucous membranes or other body organs;

Moderate toxicity, for products producing moderate effects on the skin or mucous membranes or other body organs from either acute or chronic exposure; and,

Severe toxicity, for products that threaten life or cause permanent physical impairment or disfigurement from either acute or chronic exposure.

In summary, toxic substances may result in one or more of the following effects:

1. **Permanent damage to the body**: With a few chemicals, such serious ill-effects may occur. Vinyl chloride is a known human carcinogen and butadiene is suspected of having similar effects.
2. **Narcotics:** A patient suffering from exposure to a narcotic product can be oblivious to the dangers around him. Narcosis results in ill-effects to the nervous system. The sensations are blunted, clumsy body movements are noticeable and distorted reasoning occurs. Prolonged exposure to a narcotic may result in loss of consciousness.
3. **Corrosion/Irritation** of the skin, lungs, throat and eyes.

Threshold Limit Values (TLV)

Research into toxicity considers such factors as:-

- The length of exposure.
- Whether contact is by inhalation, ingestion or through the skin.
- The stress of the person, and
- The toxicity of the product.

As a guide to permissible vapour concentrations in air, such as might occur in terminal operation, various government authorities publish systems of Threshold Limit Values (TLVs). These systems cover many of the toxic substances handled by the gas industry. The TLVs, as published, are usually quoted in ppm (parts per million of vapour-in-air by volume) but may be quoted in mg/m^3 (milligrams of substance per cubic metre of air).

TLVs-TWA (see definitions below) for the main liquefied gases are given in Table 28.1. These are provided for purposes of illustration and help to identify the relative toxicity of vapours. However, it must be appreciated that the application of a specific TLV to the workplace is a specialist matter. It is not just the safe level which must be known; it is also the resultant effect on the body which must be understood.

The most widely quoted TLV system is that of the *American Conference of Governmental Industrial Hygienists* (ACGIH). TLV systems promulgated by advisory bodies in other countries are generally similar in structure. The TLVs in most systems are republished annually and updated in light of new knowledge. The latest revision of these values should be made known to operating personnel by their management.

The ACGIH system contains the following three categories of TLVs which describe the concentration in air to which it is believed personnel may be exposed, under certain specific circumstances, without adverse effects:

(1) TLV-TWA. This is known as the Time Weighted Average. It is the concentration of vapour-in-air which may be experienced for an eight-hour day or 40-hour week throughout a person's working life. It is the most commonly quoted TLV. It shows the smallest concentration (in comparison to (2) and (3) below) and is the value reproduced in Table 28.1.

(2) TLV-STEL. This is known as the Short Term Exposure Limit. It is the maximum concentration of vapour-in-air allowable for a period of up to 15 minutes provided there are no more than four exposures per day and at least one hour between each. It is always greater than (1) above but is not given for all vapours.

(3) TLV-C. This is what is known as the Ceiling concentration of the vapour-in-air which should never be exceeded. Only those substances which are predominantly fast-acting are given a TLV-C. Of the main liquefied gases only the more toxic products, such as ammonia and chlorine, have been ascribed such a figure.

As explained earlier in this Section, TLVs should not be regarded as absolute dividing lines between safe and hazardous conditions. It is always good operating practice to keep all vapour concentrations to an absolute minimum so limiting personal exposure. It should be remembered that in some countries local legislation differs and this should not be ignored

28.3.2 Asphyxia (Suffocation)

For survival, the human body requires air having a normal content of about 21 per cent oxygen. However, a gas-free atmosphere with somewhat less oxygen can support life for a period without ill-effects being noticed. The susceptibility of persons to reduced oxygen levels vary but at levels below about 19 per cent, impaired mobility and mental confusion rapidly occur. This mental confusion is particularly dangerous as the victim may be unable to appreciate his predicament. Accordingly, self-assisted escape from a hazardous location may be impossible. At levels below 16 per cent, unconsciousness takes place rapidly and, if the victim is not removed quickly, permanent brain damage and death will result.

In general, such a problem is limited to enclosed spaces. Oxygen deficiency in an enclosed space can occur with any of the following conditions:-

- When large quantities of **cargo vapour** are present.
- When large quantities of **inert gas or nitrogen** are present, and
- Where **rusting** of internal tank surfaces has taken place.

For the above reasons, it is essential to prohibit entry to any space until an oxygen content of 20.9 per cent is established. This can be assured by using an oxygen analyser and sampling the atmosphere from a number of points. These should be at different levels and widely dispersed within the space. As appropriate for the space being entered, tests for hydrocarbon gas and carbon monoxide may also be required (see Section10.3).

With regard to Table 28.1, it will be seen from the footnote that some gases are known as asphyxiant gases. This is because they have limited toxic side effects but can be dangerous if present in sufficient quantities so as to exclude oxygen. Accordingly, a casualty having been exposed to these products is likely to be suffering from suffocation. Immediate action is necessary in such cases as outlined in Section 28.3.3.

If tank entry is absolutely necessary and the above gas-free condition cannot be ensured, personnel entering the space must be protected by breathing apparatus and should follow the advice given in Section 10.7.

28.3.3 Medical Treatment

The symptoms and medical treatment for casualties of asphyxia or from the effects of toxic materials are summarised in this Section.

Medical treatment for exposure to gas first involves the removal of the casualty to a safe area. Where necessary it may also involve artificial respiration, external cardiac massage and the administration of oxygen. Professional medical treatment should always be sought in cases where casualties have been overcome by gas.

Further advice on these issues is available from the material's data sheets and if available, in the *Medical First Aid Guide* (MFAG) published by IMO. The later publication has a number of Chemical Tables associated with it. These tables categorise the main liquefied gases into groups as shown in Table 28.3.

MFAG TABLE	310 Hydrocarbons	340 Chlorinated hydrocarbons	365 Alipatic oxides	620 Liquefied gases	725 Ammonia	740 Chlorine
PRODUCT	Butadiene	Vinyl chlorine	Ethylene oxide	Methane	Ammonia	Chlorine
	Butane		Propylene oxide			
	Butylene					
	Ethane					
	Ethylene					
	Propane					
	Propylene					

Table 28.3 - Liquefied Gas groups - for medicial first aid purposes

In the MFAG, each of the main categorisations (as listed along the top row of Table 28.3) has medical first-aid advice attached to it. This is divided into general advice, signs and symptoms and treatment. If a person is affected by any of the gases listed, it is the tables in the MFAG which should be consulted. With regard to medical treatment, the MFAG has recommended advice for:-

- Inhalation;
- Skin contact;
- Eye contact, and
- Ingestion.

The main points to be remembered in treating patients for gas poisoning or asphyxiation are outlined below (other points are covered later):

Treatment for asphyxia and inhalation of toxic fumes

Remove the casualty at once from the dangerous atmosphere - ensure that rescuers are equipped with self-contained breathing apparatus so that they do not become the next casualty.

To check that the patient is breathing tilt the head firmly backwards as far as it will go to relieve obstructions and listen for breathing with the rescuer's ear over the patient's nose and mouth.

Patient not breathing:

- Give artificial respiration at once
- Give cardiac compression if the pulse is absent

Patient breathing but unconscious:

- Place the patient in the unconscious position
- Check there are no obstructions in the mouth
- Remove any dentures
- Insert an Airway; leave in place until the patient regains consciousness
- Give oxygen. (See the sub-section which follows)
- Keep the patient warm
- Give nothing by mouth
- Give no alcohol, morphine or stimulant

Patient conscious but having breathing difficulty:

- Place the patient in a high sitting-up position and keep warm
- Give oxygen. (See the sub-section which follows)

If breathing does not improve despite these measures, then asphyxia or other lung problems may have occurred. In such circumstances, or if the patient's condition deteriorates rapidly, obtain medical advice.

28.3.4 Oxygen Therapy

Oxygen resuscitators

Oxygen resuscitators are used to provide oxygen-enriched respiration to assist in the recovery of victims overcome by oxygen deficiency or toxic gas. The equipment can be taken into enclosed spaces to give immediate treatment to a casualty. Oxygen resuscitators consist of a face mask, pressurised oxygen cylinder and automatic controls to avoid damage to the victim and give audible warning in the event of airway obstructions. The equipment is provided with a standard eight-metre long extension hose so that the carrying case (with cylinder and controls) may be securely placed and the mask taken to the victim if he is lying in a confined location. Some tankers provide a further 15 metre extension hose. If the equipment is taken into a contaminated atmosphere, it must be remembered that, if adjustable, the instrument must be set to supply only pure oxygen. Caution with its use in a flammable atmosphere is necessary. If the instrument is used when the victim has been removed from the contaminated space, there are means to vary the air/oxygen mix.

It should be noted that the couplings on oxygen resuscitators should not be greased.

Warning: *Smoking, naked light or fires must not be allowed in the same room during the administration of oxygen because of the risk of fire.*

Oxygen must be given with care since it can be dangerous to patients who have had breathing difficulties such as bronchitis.

An accident in which a patient may require oxygen can be divided into two stages:

Stage 1 - During rescue

During rescue the patient should be connected to the portable oxygen resuscitation apparatus and oxygen administered until transferred to safety.

Stage 2 - When the patient is in a safe room

The unconscious patient

1. Ensure there is a clear passage to the lungs and that an *Airway* is in place.
2. Place mask over the nose and mouth and give 35 per cent oxygen.
3. Connect the mask to the flowmeter and set it at 4 litres per minute.

The conscious patient

1. Ask if the patient suffers with breathing difficulty. If the patient has severe bronchitis, then give only 24 per cent oxygen. All others should be given 35 per cent oxygen.
2. The mask is secured over the patient's mouth and nose.
3. The patient should be placed in the *high sitting-up* position.
4. Turn on the oxygen flowmeter to 4 litres per minute.

Oxygen therapy should be continued until the patient no longer has difficulty in breathing and has a healthy colour. If the patient has difficulty in breathing, or if the face, hands and lips remain blue for longer than 20 minutes, seek urgent medical assistance.

Additional measures necessary where exposure to toxic vapours has been experienced include:-

- The removal of affected clothing.
- Eye washing, and
- Skin washing.

28.4 Frostbite

The extreme coldness of some liquefied gases is, in itself, a significant hazard. If the skin is exposed to severe cold, the tissue becomes frozen. This danger is ever-present in gas terminals and on a tanker handling fully refrigerated cargoes. For fully pressurised gases, while containment systems will normally be at or near ambient temperature, liquid leaks will quickly flash to the fully refrigerated temperature. Such areas should never be approached without proper protective clothing.

The symptoms of frostbite are extreme pain in the affected area (after thawing), confusion, agitation and possibly fainting. If the affected area is large, severe shock will develop.

Initial symptoms

- The skin initially becomes red, but then turns white;
- The affected area is usually painless, and
- The affected area is hard to the touch.
- If the area is left untreated, the tissue will die and gangrene may occur.

Treatment

- Warm the area quickly by placing it in water at 42 °C until it has thawed.*
- Keep the patient in a warm room.
- Do not massage the affected area.
- Severe pain may occur on thawing: give pain killer or morphine if serious.
- Blisters should never be cut, nor clothing removed if it is adhering firmly.
- Dress the area with sterile dry gauze.
- If the area does not regain normal colour and sensation, obtain medical advice.

* As immediate action is necessary, and without the warm water close to hand, in the first instance the affected part can be warmed with body heat or woollen material. If the finger or hand has been affected, the casualty should hold his hand under his armpit. Blood circulation should be allowed to re-establish itself naturally. If appropriate, the casualty should be encouraged to exercise the affected part while it is being warmed.

28.5 Chemical Burns

As shown in Table 28.2, chemical burns can be caused by ammonia, chlorine, ethylene oxide and propylene oxide. The symptoms are similar to burns by fire, except that the product may be absorbed through the skin causing toxic side-effects. Chemical burning is particularly damaging to the eyes.

Symptoms

- A burning pain with redness of the skin.
- An irritating rash.
- Blistering or loss of skin.
- Toxic poisoning.

Treatment

- Attend first to the eyes and skin.
- Wash the eyes thoroughly for ten minutes with copious amounts of fresh water.
- Wash the skin thoroughly for ten minutes with copious amounts of fresh water.
- Cover with a sterile dressing.

Otherwise, the treatment is as for burns, details of which are contained in the IMO *Medical First Aid Guide.*

On gas carriers authorised to transport these products, deck showers and eye baths are provided for water dousing; their locations should be clearly indicated.

28.6 Transport to Hospital

It is extremely important to label the patient adequately before removal from the tanker or terminal and a specimen patient-label is shown in Figure 28.1.

For the guidance of Medical Officer

1. Name of Patient .... Age ....
   Home Address ....
   ....
   ....
   Name of Tanker .... Port .... Next Port ....
   Name and Address of Shipowner and Ship's Agent
   ....
   ....

2. Above person was exposed to .... gas
   at (Time) .... on (Date) ....

3. Brief summary of first aid treatment given
   ....
   ....

Figure 28.1 - Patient label

28.7 Hazardous Atmospheres

28.7.1 The Need for Gas Testing

The atmosphere in enclosed spaces must be tested for oxygen, explosive and toxic contents in the following circumstances:

- Prior to entry by personnel (with or without protective equipment).
- During gas-freeing, inerting and gassing-up operations.
- As a quality control before changing cargoes, and
- To establish a gas-free condition prior to drydock or tanker repair yard.

The atmosphere in a cargo tank is rarely, if ever, homogeneous. With the exception of ammonia and methane, most cargo vapours at ambient temperatures are denser than air. This can result in layering within the cargo tank. In addition, internal structures can hold local pockets of gas. Thus, whenever possible, samples should be drawn from several positions within the tank.

Atmospheres which are inert or deficient in oxygen cannot be checked for flammable vapours with a combustible gas indicator. Therefore, oxygen concentrations should be checked first, followed by checks for flammable and then toxic substances. All electrical instruments used should be approved as intrinsically safe.

28.7.2 Oxygen Analysers

Several different types of oxygen analyser are available and reference should be made to Sections 2.4.9 and 2.4.10 for a description of typical analysers that are in use.

28.7.3 Combustible Gas Indicators

Descriptions of various types of combustible gas indicators are provided in Section 2.4 which should be referenced for further information.

28.7.4 Toxicity Detectors

Reference should be made to Section 2.4.7 for a description of toxic gas detectors.