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Chemical Tankers

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1 Description

Modern chemical tankers are arguably the most technologically advanced vessels of all the major commercial ship types. The complexity of this vessels results from wide range of cargo that they are designed to carry and the diverse nature and characteristics of these cargoes. Many of the cargoes carried on the modern chemical tankers are considered hazardous materials that require careful handling.

The chemical tanker's mission is to transport liquid chemicals in bulk via the world's waterways while protecting life, property, the environment, and the quality of the cargoes being carried. Chemical tankers, as commercial vessels operating in a competitive global market, must carry out their mission while providing their shipowner/operators with measures of economic benefit.

The design of a chemical tanker may allow the vessel to carry hundreds of different liquid cargoes ranging from petroleum products, to inorganic acids, to fish oil, to specialty chemicals. The cargoes transported by chemical tankers can be categorized in several different ways. The cargoes may be divided into groups based on their chemical composition, such as inorganic and organic chemicals. The chemical cargoes may be divided into following groups based on their origin and a specific heavy group;

- Petro-chemical products;
- Coal tar products;
- Carbohydrate derivatives;
- Animal and vegetable oil;
- Heavy chemicals.

Petro-chemical products are those oil products and chemicals that are derived from the refining of crude oil and natural gas. Coal tar products are derived from the carbonization of coal. The coal tar that results from this process is a source of hydrocarbons used for industrial purposes. Carbohydrate derivatives include molasses and various forms of alcohols.

2 Types of Chemical Tankers

Chemical tankers can be categorized in a number of different ways. Unlike oil and product tankers there is no universally accepted size categorization of chemical tankers, however modern vessels typically fall into one of the following three categories:

- Inland Chemical Tankers - 500 to 4000 tonne DWT.
Typically in the form of self-propelled barges. Commonly used in the river systems of northwestern Europe to load cargo from larger tankers or coastal terminals and transport the material to inland industrial facilities;
- Coastal Chemical Tankers - 3000 to 10000 tonne DWT.
These small tankers, also referred to as short sea tankers, are used to transport chemicals coastwise and to trans-ship cargoes into ports and terminals where larger tankers are unable to call because of any number of restrictions. These tankers may load or discharge cargo from a shore terminal or directly from a larger vessel. These vessels are

commonly used in the intra-Europe, intra-southeast Asia, and the north, central and south American markets;

- Deep Sea Tankers - 10000 to 50000 tonne DWT.
These ocean going vessels typically have a large number of segregations and have either stainless steel and coated tanks. These vessels operate on the major trade routes between North and South America, Europe, the Middle East and Asia.

Alternatively, chemical tankers can be grouped by the level of cargo containment designed into the vessel, known as Ship Type (ST). The IBC code defines three specific ship types, with ST 1 providing the greatest level of containment for the transportation of the most hazardous cargoes. Conversely, ST 3 provides minimal containment for carriage of the least hazardous cargoes by the IBC code. Chemical tanker designs typically fall in one of three ship type arrangements:

- ST 1/2;
- ST 2;
- ST 2/3.

Commercially, the lining of the cargo tanks can be used to categorize chemical tankers. The tanks may be mild steel in construction and covered with a specifically formulated tank coating, or they may be constructed or lined with corrosion resistant stainless steel. Some vessels have a combination of both coated and stainless steel tanks. The cargo tank lining partially determines which cargoes a vessel can carry. Certain cargoes because of their inherent properties or aggressive nature, cannot be stowed in tanks lined with certain tank coatings. Similarly many characters demand stainless steel cargo tanks out of a concern for cargo quality when it would otherwise not be required.

3 System Design

3.1 Hull form and Principal Particulars

The service speed of chemical tankers typically falls between 12 and 16 knots. This speed range, which is a function of the markets governing economics, allows for the use of full hull forms similar to product tankers. Concern for ballast condition speed is minimal as chemical tankers rarely sail in ballast condition for long distances. Block coefficients for chemical tankers range from 0.80 to 0.85 with some smaller ocean-going vessels having finer hull forms with block coefficients below 0.80. Chemical tankers typically employ bulbous bows and trapezoidal sterns. Model tests and CFD analysis are employed when developing new chemical tanker hull forms.

3.2 Propulsion

The most common propulsion system for chemical tankers has been a slow-speed diesel engine driving a fixed pitch propeller. This arrangement often includes a shaft-driven generator to provide electrical power during the sea passage and three or more auxiliary diesel generators to provide power for the in-port electrical loads.

3.3 Maneuverability

On a given port call a chemical tanker will often call at more than one berth. On a given voyage a chemical tanker will typically call at a number load and discharge ports. These two factors result in chemical tankers spending up to 40% of a total voyage's time in port. These factors make it crucial that the vessels have good maneuverability. A maneuverable vessel will be more efficient in port as docking and undocking can be completed more rapidly and require less assistance from tugs. Furthermore, good maneuverability provides an additional level of safety in the congested waters of the largest chemical handling ports. The maneuverability of chemical tankers is enhanced through the use of large bow thrusters and high efficiency rudders.

3.4 Cargo Systems

The cargo systems of chemical tankers are what truly differentiate them from product and crude tankers. A vessel's cargo system, together with its cargo tank arrangement and safety systems determines the cargoes that the vessel can or cannot carry. A chemical tanker's cargo system includes tanks, pumping systems, piping, venting systems, cargo monitoring systems, environmental control systems and tank cleaning systems.

3.4.1 Cargo Tanks

The IBC code provides for four types of cargo tanks: independent, integral, gravity and pressure tanks. The boundaries of an independent tank are not part of the hull structure and therefore do not contribute to the structural strength of the vessel. Independent tanks are designed to eliminate the transfer of stress from the vessels structure to the tank structure. On chemical tankers, independent tanks typically taking the form of deck tanks. On the other hand, the boundaries of an integral tank are formed by the hull structure and the sub dividing of the hull in the cargo area creates the individual integral tanks. Integral tanks are the most common type of tank used on chemical tankers. Gravity tanks are designed for a maximum pressure of 0.7 bar gauge at the top of the tank and may be of the integral or independent type. Pressure tanks are designed for pressure greater than 0.7 bar gauge and are not typically used in chemical tankers. The boundaries of both integral and independent cargo tanks can be stainless steel or coated mild steel. The cargo tank coatings that are used on chemical tankers are primarily of the epoxy or zinc silicate type. There are certain cargoes that are incompatible with stainless steel and cannot be stowed in stainless steel tanks but can be stored in coated tanks. Stainless steel tanks are also easier to clean after cargo discharge than coated tanks.

3.4.2 Cargo Pumping and Piping Systems

The cargo pumping and piping systems are the principal systems in determining a vessel's operational flexibility. Although the IBC code allows for a cargo pump room and shared piping systems, these features are no longer used in modern chemical tankers. The modern chemical tanker is based on the concept of the complete segregation of cargoes. Each cargo tank and its associated systems are independent from the vessel's other cargo tanks. At the heart of the complete segregation approach is the deepwell cargo pump. As its name suggests a deepwell pump is submerged in the fluid that it is pumping with its impeller placed in a well in the cargo tank tank top. Deepwell cargo pumps are of the centrifugal type and are driven



Figure 1: Integral cargo tanks.

by either a hydraulic motor located in the tank with the impeller or by an electric motor that drives a shaft that runs from the deck down to the impeller in the tank.

Hydraulic driven pumps of this type are more popular on chemical tankers than the electrically driven pumps because the electric motors can be eliminated from the cargo area, and because variable speed control makes them attractive. Since centrifugal pumps do not pump high viscosity cargoes well, ships that have centrifugal deepwell cargo pumps and that frequently carry high viscosity cargoes, such as molasses are typically outfitted with a deck mounted booster pump to assist in the discharge process. These booster pumps are of the positive displacement type, with screw pumps being used most often.



Figure 2: Deepwell cargo pumps.

3.4.3 Cargo Monitoring and Control Systems

Proper cargo monitoring is a key component of cargo care, operational safety and environmental protection. The type of cargo monitoring system that is required on a particular chemical tanker is based on the cargoes that it will carry. The monitoring systems must be more advanced if the cargoes the vessel will carry are more hazardous. The IBC code provides requirements for tank gauging, high-level alarms, overflow control systems, temperature measurement and pressure measurement. Chemical tankers that are designed to carry hazardous cargoes are required to be fitted with a closed gauging device such as float-type systems and tank radar. Closed devices can be used without the contents of the tank being released.

4 Tank Cleaning

Chemical tankers transport an enormous variety of chemical and oil products in global and short sea trade. Due to this variety the next cargo is almost never identical with the previous cargo. Thus tank cleaning is essential on chemical and product tankers. The products that need to be cleaned vary widely in their properties and characteristics. In addition, the chemical industry and their customers have continuously increasing quality requirements.

The success of a tank-cleaning job depends on many factors such as thorough planning of the cleaning job, the design of tanks, cleaning machines and their operation, design of piping, heating capabilities, etc. It is generally recognized that tank cleaning is the most hazardous period of tanker operation. Although not officially defined in chemical shipping, two major cleanliness standards should be distinguished:

- Water White Standard: means visually clean, dry and odour-free. Wall wash not required.
- High Purity Standard: is required for very sensitive cargoes to be loaded such as products applied in food processing (Food Grade) or in pharma production (USP), where any contamination is a potentially high risk for the application. Another category of product that typically requires high purity standard are all active solvents, such as chlorinated hydrocarbons, glycol ethers, light alcohols (e.g. methanol), ketones (e.g. acetone) and many hydrocarbons (e.g. hexene). These chemicals tend to dissolve all remaining impurities resulting in potential contamination of the substance.

4.1 Cargo Properties

4.1.1 Physical Properties

Water-soluble substances and water-miscible substances are easy to clean with water, and the solubility of the substances might increase at higher temperatures. The use of a cleaning agent is only advisable for reduction of the cleaning time. For a product with limited or no solubility in water the specific gravity indicates whether the product will float on water or sink.

Products with a high melting point should be washed at a temperature of 15 – 20°C above the melting point. During washing there should be no ballast water or cold cargoes adjacent to the tank to be cleaned. During cleaning, special attention must be given to liquid and vapor line systems to avoid freezing/solidification at cold line segments. Washing as soon as possible after discharge is recommended.

Products with a high viscosity should be washed at higher temperatures. In general, the viscosity is closely related to the temperature and will decrease at higher temperatures. During washing there should be no ballast water or cold cargoes adjacent to the tank to be cleaned. Washing as soon as possible after discharge is recommended.

Products with a high vapour pressure (higher than 50 mbar at 20°C) can be removed from the tank by evaporation. As always during ventilation, special care must be taken to prevent the risk of explosion of flammable products and emission of toxic vapours. All safety and environmental precautions must be taken. The flashpoint is the lowest temperature at which a product gives off sufficient gas to form a flammable gas mixture that can be ignited. The pre-cleaning temperature must be well below the flashpoint. If this is not possible, avoid any ignition source.

4.1.2 Cargo Characteristics

The initial wash of products that tend to polymerise should be carried out with cold (ambient) water. Washing with hot water may result in polymeric residues being left in tanks and lines, which are very difficult to remove.

Cargoes consisting of mixtures with different vapour pressures should neither be cleaned by evaporation, nor pre-washed hot. The evaporation of the light substances from a mixture could result in non-volatile residues, which are very difficult to remove.

Isocyanate's must never come into contact with water, not even the residues, because the reaction product and insoluble urethane (plus CO₂) are very difficult to remove. Such products must be washed with a suitable solvent, that does not contain any water.

Drying and semi-drying vegetable and animal oils react with oxygen to form a varnish-like polymeric film. This is very difficult to remove from the bulkheads etc. Since heat increases the reaction speed the initial washing of these products must be done with water at ambient temperature without any delay after unloading the cargo.

Water hardness is formed by the calcium and magnesium content of the water. Sea water has a very high water hardness. Some products like fatty acids and vegetable oils with a high free fatty acid content will form white sticky residues, if they are cleaned with a water of a high water hardness, e.g. sea water.

Minor residues of a smell-producing cargo left in lines, valves and pumps (including pump cofferdams) can contaminate a sensitive cargo. To neutralise the smell of some chemicals (e.g. Acrylate, Nitrobenzene or Pygas) the use of a smell killer may be recommended.

4.1.3 Ambient Conditions

The temperature during the cleaning steps is one of the most important operating parameters. It must be remembered that the temperature in the cargo tank can be significantly influenced by the surrounding conditions. The following should be taken into consideration: Outside temperature, sea water temperature, ballast conditions and adjacent cargo temperature. A deviation from the desired operating temperature could be caused in the entire tank or just locally on bulkheads, tank bottoms or tank walls. This could have a negative impact on the desired result, such as freezing due to lower than allowed temperature or polymerisation/drying due to higher than allowed temperature. Good operating practice is to avoid problems resulting from adjacent cargoes or from ballast water by respective stowage planning. The effects of the surrounding temperatures should be compensated and thoroughly controlled during the operation.

4.1.4 Tank Surface Conditions

Stainless steel can corrode in service if there is contamination of the surface. Both pickling and passivation are chemical treatments applied to the surface of stainless steel to remove contaminants and assist the formation of a continuous passive chromium oxide, film. Pickling and passivation are both acid treatments and neither will remove grease or oil. If the steel is dirty, it may be necessary to use a detergent or alkaline cleaning before pickling or passivation.

Zinc silicate coating is an anti-corrosive paint system that is based on zinc dust (86% wt) with some additives and a binder. The high levels of zinc dust giving zinc-zinc metal contact resulting in cathodic protection similar to those obtained from galvanising. Zinc coatings are

inherently porous, which is resulting in a variety of cleaning problems. It is believed that the cargo migrates into the pores and capillaries, similar to a fluid adsorption processes. Zinc coatings have a good resistance against solvents, but are not resistant against strong acids and bases.

Epoxy coatings e.g. pure epoxy, phenolic epoxy and isocyanate epoxy form cross linkages to different degrees resulting in relatively good resistance to a greater range of cargoes. Epoxy systems are usually resistant to some weak acids and strong alkalis and do not absorb oil-like substances. Epoxy coatings tend to absorb, however, solvent-like cargoes (resistant with limitations according coating resistance list). This absorption is caused by swelling and subsequent softening of the coating. After transporting aggressive cargoes, the coated tank has to be ventilated until the cargo has been desorbed (released) from the coating film, which results in hardening and decreasing swelling. This can take up to several days, depending on type of cargo, type of coating and film thickness. Water may not be used for cleaning until this ventilation process is finalized. Otherwise the water can lead to blistering and subsequent serious damage of the coating. The more solvency power a cargo has, the more cargo residues could still be present in the coating. This could lead to either contamination of the next or after next cargo or breakdown of the coating film.

4.2 Cleaning Hardware

The tank cleaning machine is the most important equipment and its proper operation is a key success factor for achieving the desired cleaning results. Tank cleaning by means of automated machines is often named "Butterworthing". Arthur Butterworth, in 1920, patented the first *Automated Tank Cleaning Machine* and in 1925 the company was established to produce and market this product. Nowadays, there are several manufacturers of tank cleaning machines.

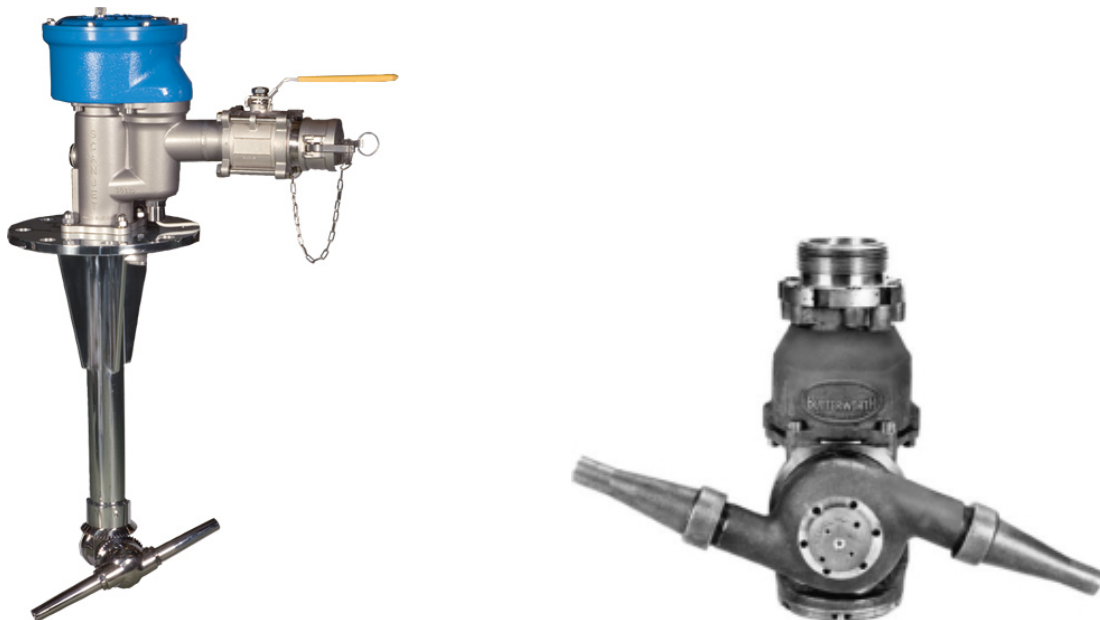


Figure 3: Tank cleaning equipment.

Especially if higher cleaning temperatures are required, heating becomes a critical part of the cleaning operation. It is up to the experience of the operating personal to set up the system in such a way that the recommended temperatures can be achieved. Probably the number of machines operated simultaneously must be reduced to compensate a lack of heating capacity.

4.3 Tank Cleaning Methods

4.3.1 Butterworthing

Spraying of cleaning medium, usually sea or fresh water, onto the tank surface by means of a cleaning machine but without addition of any cleaning agent. At least one full cycle of the cleaning machine should be allowed for sufficient cleaning. Additional cycles might be necessary depending on the degree of difficulty of the cleaning operation.

4.3.2 Injection Tank Cleaning

Injection of the cleaning agent directly into the butterworth line during butterworthing the tank. The quantity to be injected depends on the consumption of the cleaning machines and the concentration, which is usually recommended by the supplier of the cleaner.

4.3.3 Recirculation Tank Cleaning

Prepare a cleaning solution. Butterworth the tank by internal recirculation. The necessary temperature can be achieved/maintained by means of heating coils, cargo heat exchangers or a butterworth heater.

4.3.4 Recirculation Cleaning Via Service Tank

Prepare a cleaning solution in the service tank. Butterworth the tanks to be cleaned with the solution and recirculate the water back into the service tank. Heat the solution with the tank heating coils, cargo heater or butterworth heater.

4.3.5 Rinsing

Spraying of water (usually fresh water) with cleaning machine onto the tank walls in order to rinse chloride containing water and traces of contamination from the tank surface. Typically it is not necessary to run a full circle of the cleaning machine.

4.3.6 Vent - Mop - Dry

Ventilation in order to remove water, moisture and smell. Usually done by forced air circulation. If there are water pools on the tank bottom they should be removed with a mop to reduce drying time. If the next cargo is sensitive to water or moisture, drying must be carried out very carefully.

4.4 Tank Cleaning Recipes

Tank cleaning recipes consist of several tank cleaning steps as in the example of Tab. 1.

Operating parameters are as follows. The common tank cleaning media are:

- Sea water;
- Fresh water;

Step	Method	Time	Temperature	Medium	Cleaner	Remark
1	Butterworth	0,5	Ambient	Sea water		a)
2	Recirculation	1,5	Moderate	Fresh water	0.5% cleaner XYZ	
3	Rinse	0,2	Ambient	Fresh water		

Remark a) Ambient temp due to flammability of cargo.

Table 1: Example of a tank cleaning recipe

- Treated fresh water;
- Demineralised water;
- Chemical products.

Tank cleaning step temperatures can be:

- Ambient (up to 30°C);
- Warm (35 – 40°C);
- Moderate (50 – 65°C);
- Hot (75 – 80°C).

Some cargoes require the use of a cleaning agent for efficient cleaning. Most cleaning agents are additives that are used in combination with water to improve the water solubility of the cargo to be cleaned. A variety of cleaning agents is available for most application problems. Cleaning agents must be IMO approved. Regulation 13.5.2 of the revised MARPOL Annex II - “Control of pollution by noxious liquid substances”, which came into force on January 1, 2007, places restrictions on the cleaning additives permitted for use in tank washing operations, as follows:

- “When small amounts of detergents are added to water in order to facilitate tank washing, no detergents containing pollution category X components should be used except those components that are readily biodegradable and present in a total concentration of less than 10%. No restrictions additional to those applicable to the tank due to the previous cargo should apply.”

A list of approved cleaning additives evaluated through both MEPC/Circ. 363 and MEPC.1/Circ. 590 can be found in annex 10 of MEPC.2/Circ. 15, dated December 17, 2009. This can be downloaded from the IMO website.

4.5 Tank-Cleaning Inspection

To verify the result of the tank-cleaning operation, the tank and all other equipment that was in contact with the cargo must be inspected. This can only be performed by entering the tank. All standards and procedures related to tank entry must be followed strictly.

In the tank, the following items should be inspected because they are known potential problem areas:

- Entire tank surface for visible residues;

- Wall should also be touched and checked for perceptible residues;
- Shadow areas of the cleaning machine;
- Underneath heating coils;
- Heating coil supports;
- Pump suction well;
- Loading line outlet;
- Tank internals, ladder, cleaning machine, thermowells, Level indicators, etc.

Furthermore the entire stainless steel tank surface should be inspected for discolouration and pitting. If the tank is coated, the coating condition must be checked. The entire tank should also be checked for smell and wetness/moisture.

Although the inspection of lines is almost impossible, as a minimum test the opening of manifold blind flanges should be carried out, to check lines as much as possible visually for residues and moisture. Also smell in the lines could indicate insufficient cleaning. The pump cofferdam should be purged to detect any possible contamination or seal leak. If required by the loader a wall wash must be carried out and checked for compliance with the requirements, which are usually defined by the loader. A variety of analytical procedures are available for testing the wall wash sample.

4.6 Tank Cleaning Result Tests

4.6.1 Permanganate Time Test

The permanganate time is used to judge the presence of oxidizable materials that may be associated with contamination during distribution and to access compliance with a specification. The test is based on the ability of potassium permanganate (KMnO_4) to oxidise hydrocarbon impurities that could be present in the wall wash liquid. If there is a reaction in a neutral solution, the potassium permanganate is reduced and changes its colour from pink-orange to yellow-orange. The more impurities the faster a change in colour occurs.

4.6.2 Water Miscibility (hydrocarbon test)

The purpose of this test is the qualitative detection of non-water-soluble contaminants. It works on the basis that many impurities are soluble in the wall wash liquid (Methanol, Acetone) but not in water. Sometimes this test is also called hydrocarbon test.

4.6.3 Chloride Test

The Chloride test is used to judge the presence of chlorides on bulkheads, etc. Chloride levels vary from 0.1 ppm to 5 ppm depending on the requirement of the charterer. Chlorides will react with Silver nitrate/nitric acid solution forming Silver chloride (AgCl) which makes the solution turbid. By comparing the sample solution with the various prepared standard solutions one can establish the ppm chlorides in the wall wash.

4.6.4 Colour Test

Certain impurities result in discolouration of the wall wash sample. The colour of the wall wash liquid is compared with unused wall wash solvent. Mostly the so-called Apha colour is measured.

4.6.5 UV Test

The UV-Test is used to identify certain hydrocarbons and chemicals. Many hydrocarbons and chemicals have the ability to absorb UV-light when they are exposed to such light. Certain molecular electrons will get excited if exposed to light. This excitation results in absorbance of light which can be measured. Absorbance at a specific wavelength is a measure for concentration of specific compounds. In a special apparatus called spectrometer, a sample containing hydrocarbons and a reference sample, containing just a solvent such as methanol, are exposed to a UV light source.

4.6.6 Acid Wash

The Acid Wash Test Method is used to determine the presence of benzene, toluene, xylenes, refined solvent naphthas, and similar industrial aromatic hydrocarbons. This test is also used for detecting of impurities in methanol. Compounds which cause darkening in the presence of concentrated sulphuric acid due to carbonization can be detected with this test. In methanol analysis this is often referred to as carbonizables.

4.6.7 NVM

Test used to determine if there are non-volatile impurities on the tank surface. A defined quantity of the wall wash liquid is evaporated. The weight of the residue, the so-called NVM (Non Volatile Matter), is detected by weighing. This is then divided by the original weight of the sample. The NVM content must not exceed the value specified by the loader.

4.7 Tank Cleaning Safety Hazards

A hazard is a physical situation with a potential for human injury, damage to property, damage to the environment, to capital investment or some combination of these. Hazards can be identified through a review of the physical properties characteristics of the product to be cleaned. Typical hazards that exist during tank cleaning and related activities are:

- Fire and Explosion

Three elements are necessary to create a fire: fuel, an oxidiser (usually air) and a source of ignition (energy). In theory, ignition is not possible, if any one of the 3 is eliminated. Most cleaning operations will be carried out in tanks that are filled with air, thus the oxidiser is present in most cases, unless the tank is inerted. Fuel as far as tank cleaning is concerned could be the product itself, if this product has a low flash point, or a flammable cleaning solvent. Under certain circumstances even substances with a high flash point can be ignited and must thus be considered as a fuel (mist). During many tank cleaning operations the atmosphere in the tank must be considered as flammable because the product to be cleaned is flammable and inertisation is not possible. Under these circumstances the only way to guarantee that an explosion cannot occur during

cleaning is to make certain that there is no source of ignition. A potential source of ignition during tank cleaning is electrostatic discharge. Especially during water spraying electrostatic charges could be induced.

- Undesired reactions:

- Polymerization, depletion of inhibitor or excessively high temperature;
- Saponification, creation of hard soap forming a layer on the tank requiring acid cleaning or even removal by hydro-blasting;
- Drying/hardening, formation of hard debris that is no longer soluble, requiring treatment with a Solvent;
- Reaction with water, violent reaction of an isocyanate after pre-cleaning with water;

- Corrosion

Corrosive substances destroy human tissue on contact, e.g. skin, eyes and mucous membranes in the mouth and respiratory tract. Metal or other material used in ship construction could be corroded at an excessive rate.

- Overexposure to toxic substances

Death of operator after wiping phenol residues by tank entry without wearing a full chemical suit and SCBA (self-contained breathing apparatus)

- Asphyxiation

Oxygen deficiency, entry into a tank with an inert gas atmosphere;

- Emissions:

- To the air:

As always when ventilating, special care must be taken to prevent the risk of explosion (flammable products) or with regard to toxic vapours. All normal safety precautions must be taken. (No smoking, accommodation ventilation on recirculation, etc.) The wind strength and wind direction must also be a decisive parameter for the Master to allow ventilation. To avoid a build-up of explosive or toxic vapours on deck the amount of gas to be escaped from the tanks should be limited. Never open and ventilate several tanks at the same time;

- To the water:

Emissions to the water should be reduced to the absolute minimum. All on-board facilities must be operated carefully according to the P&A Manual to reduce the residues during unloading. All regulations, especially MARPOL, must be followed strictly.