

Titanium Dioxide Manufacturers Association
TDMA
TiCl₄

SAFETY ADVICE FOR STORAGE AND
HANDLING
OF ANHYDROUS TITANIUM
TETRACHLORIDE

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INTRODUCTION

The Guiding Principles of the Responsible Care Programme are central to the European Chemical Industry Council (CEPIC) policy.

Members have signed a commitment to these principles which ensure that they

- operate to the best practices of the industry
- reflect the commitment of continued improvement in their health, safety and environmental policies
- make available to employees, customers and the public, all relevant information about activities that affect health, safety and the environment.

This Safety Advice for the Storage and Handling of Anhydrous Titanium Tetrachloride was developed by the TDMA (Titanium Dioxide Manufacturers Association) in support of the Responsible Care initiative.

The advice was prepared by a working party under the auspices of CEPIC comprising representatives of the titanium tetrachloride sub-group of the TDMA, currently involving the following companies:

- Chemours
- Venator
- Kronos International Inc.
- Cristal
- Tronox Pigments b.v., (Holland)

Since first publication of this document, SCM Chemicals and Thann & Mulhouse have become part of Millennium Inorganic Chemicals which became a part of Lyondell, which transferred to Cristal in 2007. Kerr-McGee Pigments was re-named to Tronox Pigments. Tioxide Europe was re-named to Huntsman Tioxide, then Huntsman Pigments, then Huntsman Pigments and Additives after the acquisition of the Rockwood Business, then Venator. Chemours used to be part of DuPont.

The document should be considered as providing advice only and not as a detailed design code.

Existing installations may not meet all the recommendations and, in some cases, not all the recommendations may be appropriate, as these may be over-ruled by local legislation, or by experience. It is the responsibility of the titanium tetrachloride user, in consultation with the manufacturer (if this is not the user), to assess the needs in any particular case. The final responsibility rests with the operator of the plant to operate safely.

The advice covers four main areas:

- Storage installations

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- Loading and unloading transport containers
- Transport containers
- Basic health and safety measures, emergency procedures and chemical and physical properties.

The document gives examples of storage, loading and unloading installations. Arrangement of plant other than those shown may be equally suitable. Users are recommended to consult with suppliers regarding alternative arrangements and particular aspects of detailed design.

Although great care has been taken in the compilation and preparation of the advice to ensure accuracy, CEFIC or the TDMA cannot in any circumstances accept responsibility for errors, omissions or advice given in this publication.

It is the responsibility of the manufacturer/user to determine the applicability of National Regulations or local planning requirements which may apply to the design, operation and maintenance of the plant. In Europe, particular attention should be paid to the requirements of the Seveso II Directive and the incoming Seveso III Directive.

Only containers complying with the procedure and guidelines described in Section 3 shall be used to distribute $TiCl_4$.

It is the policy to update information periodically, therefore you are advised to check that this document is the latest issue.

Individual sections as shown in the table of contents can be obtained from the European Chemical Industry Council.

It cannot be over-emphasised that the most significant hazardous property of $TiCl_4$ is its violent reaction with water, where hydrolysis takes place to produce hydrochloric acid mist, and finely divided particles of titanium dioxide and oxychloride which create a dense white, highly visible cloud.

This reaction also takes place with moisture in the atmosphere. It is therefore vital to take all necessary precautions to prevent loss of containment of $TiCl_4$. This is particularly important during maintenance activities where joints on pipes or equipment have to be broken.

All such activities should be pre-planned, with risk assessments carried out, and executed by trained personnel wearing appropriate PPE as detailed in Section 4.

SECTION 1 - STORAGE INSTALLATIONS

1.1. General Layout and Siting

1.1.1 Where possible, the installation should be located away from production areas preferably in the open air, but a compromise must be reached here, as pipework between the storage installation and processing plant should be kept to a minimum.

1.1.2 The location of new installations within a site should take into account possible damage caused by failures of neighbouring equipment on the site. The location should be positioned at sufficient distance from the boundary so as not to be subject to damage from off-site incidents e.g. accidents on public roads, etc.

1.1.3 Layout for the area should be planned to provide all facilities necessary for good housekeeping. Ample storage space is required for maintenance and safety equipment which must be readily accessible in the event of an emergency.

1.1.4 TiCl_4 storage tanks should be positioned above ground level on plinths which allow adequate access to the external surface. This is to permit regular inspection of the vessel and its protective coating. Installation in deep pits is not recommended because it increases the difficulties of treatment and disposal of TiCl_4 emissions and of access for maintenance and repairs.

1.1.5 Storage tanks for the export or receipt of TiCl_4 should be installed in a bund which is impervious to liquid TiCl_4 and of a suitable capacity to contain spillage. The design of the foundation and bund walls must take into account the density of the liquid. The bund should have a sloping floor and gullies leading to a collection area. If there are sub-divisions to give separate bunds under each tank in a group, each section should have a sloping floor leading to a collection area which may serve more than one tank. The collection area, which may be a sump, should not be connected to drain. Valves or other entries into the bund wall should be avoided or sealed effectively.

1.1.6 Accumulation of rain water in bunds must be minimised. One way of achieving this is by roofing over the storage area. Other means include regular inspection by plant operators and removal of water over the bund wall, which must be manually controlled by the operator to prevent unintentional pumping of any spilled product.

1.1.7 In considering the capacity and the number of individual storage tanks in a storage facility, the following points should be taken into account: -

1.1.7.1 The minimum size of a tank should be adequate to accommodate the maximum foreseen unit of delivery.

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1.1.7.2 If continuity of supply is essential, at least two tanks will be required to allow time for necessary inspections and to facilitate maintenance. This also provides greater flexibility of operation. Design and operation should also make provision to be able to transfer the contents of a tank in an emergency to other tanks.

1.1.7.3 Increasing the number of storage tanks leads to an increase in the ancillary plant and equipment with a corresponding increase in complexity of operation. The number of storage tanks should be kept to the minimum.

1.1.8 The distance between storage tanks should be adequate to provide good access and egress to the tanks under all circumstances, including those in which bulky protective equipment, such as self-contained breathing apparatus, needs to be used.

1.1.9 All vessels, valves and pipework in the installation should be readily identifiable, e.g. by labelling and/or colour coding.

1.1.10 In the case of installations which are not subject to regular frequent visits by operating personnel, the layout should be such that the storage area is either directly visible from a control room, or is kept under surveillance by the use of TV monitors or other appropriate equipment.

1.1.11: Taking into account the strong hydrolysis reaction of the product, in such case a spillage dependant on the site / plant location could have a large impact on the local neighbourhood. In such instances a confinement of the storage installations, transportation vessel discharging station and the user workshop (processing operation) may be envisaged in order to reduce/mitigate any potential impact on the neighbourhood of the site/plant. Obviously such lay-out requires also the installation of an adequate emergency gas scrubbing system.

1.2 Equipment

1.2.1 Vessel Design

1.2.1.1 Storage tanks for TiCl_4 should be designed to an appropriate national or international standard, for example BS5500, ASME Section VIII Div. 1 or equivalent. The minimum standard of design should be that which compares with ADR (European Agreement Concerning the International Carriage of Dangerous Goods by Road).

New vessels should be designed and manufactured to BS5500 category 1 or equivalent standards. The user should retain copies of all documents and drawings relevant to design and manufacture.

1.2.1.2 The corrosion allowance for storage vessels should be, at a minimum, 2 mm.

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1.2.1.3 The vessel supports should be designed in accordance with the design code to permit thermal expansion and contraction over the design temperature range. Thermal expansion needs to be considered in cases where load cells are used for determining the tank contents.

1.2.1.4 Manhole access should be provided on the top of the vessel. The opening for man entry should preferably be 900 mm and should not normally be less than 600 mm.

1.2.1.5 The dimensions of nozzles should be limited to the minimum required, particularly for the liquid lines. All nozzles should preferably be mounted on a manhole cover to aid replacement / renewal.

1.2.1.6 Connections to the storage tank are: -

1. Liquid $TiCl_4$ inlet
2. Liquid $TiCl_4$ outlet
3. Venting and padding lines (see also 1.2.7).
4. High level interconnection between tanks
5. Connections for instrumentation

1.2.1.7 The number of connections should be kept to a minimum to reduce the potential sources of leakage.

1.2.1.8 The arrangements of valves and pipework should be made as simple as possible to minimise errors in operation. Valves should be fitted directly to nozzles so that pipework can be isolated from the vessel.

1.2.1.9 For guidance on bolted joints, refer to "Guidelines for the management of the integrity of bolted joints for pressurised systems" Published by The Energy Institute (EI), in association with UK Oil and Gas (formerly UKOOA) and ASME PCC-1 "Guidelines for Pressure Boundary Bolted Joints"

1.2.1.10 Gaskets

Asbestos regulations prohibit the use of compressed asbestos fiber (CAF), which has been the universally accepted jointing material up to the year 2000. Present alternative gaskets are based on PTFE bound fiber sheet material such as Novatec Premium and Klingersil C4400. For specific information please seek advice from the $TiCl_4$ supplier.

1.2.2 Pipework

1.2.2.1 Permanent pipework at the loading/unloading station consists of the following lines;

- a) pipework for $TiCl_4$ transfer, articulated arms with swivelled joints on installations with high output, and/or flexible hoses;
- b) pipework for off-gas venting, connected to bulk carrier with flexible hoses;
- c) pipework for services dry nitrogen, dry air.

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1.2.2.2 Lines should be colour-coded and labelled according to national and/or site standards.

1.2.2.3 Routing of pipelines for $TiCl_4$ should normally be above ground and should be such as to maximise protection from mechanical damage. Pipework should be designed, fabricated and tested in accordance with a recognised code. Where practicable, the nominal bore of pipe work should preferably be not less than 50 mm, this is to reduce possibility of choking due to oxychloride deposits present on contact with atmospheric conditions and eliminate any high velocity flows which will result in internal pipework erosion.

It is recommended that pipework is constructed minimising horizontal flanged sections and with sufficient slope in order to facilitate self-drainage in the event of shut-down or maintenance – recommended minimum pipework slope 1 in 100.

1.2.2.4 All pipeworks to be designed in accordance with ASME B31.3. The design pressure should be in accordance with design codes and corresponding to a design temperature which takes account of maximum operating temperature and pressure. Pipework should also be adequately strong and robust for all foreseeable conditions of work. Allowance must also be made for the hydraulic expansion of liquid caused by high ambient temperature.

1.2.2.5 Materials of Construction should normally be seamless carbon steel. Elbows, tees and reducing pieces should be forged or hot formed without reduction in wall thickness

1.2.2.6 The minimum corrosion allowance should be 2 mm. Pipework should be suitably protected to prevent external corrosion.

1.2.2.7 Radius of curvature of any pulled bends should be a minimum of 5 times the pipe nominal diameters. Bending procedures and tolerances should conform to ASME B31.3 Section 332 “Bending and Forming”.

1.2.2.8 Bolting should be to BS 4882 - Specification for bolting for flanges and pressure containing purposes. ASTM A193 B7 Bolts and ASTM A194 2H Nuts or equivalent standard.

1.2.2.9 The number of flanges should be limited as far as possible and those should be to the requirements of a recognised design code. It is however advisable to locate some flanged joints strategically (recommended at 6m intervals and at bends) to facilitate de-choking in the event of pipeline blockages. Also, creation of “dead ends” should be avoided, as this could subsequently lead to pipeline blockages.

1.2.2.10 Steel used for fabrication of flanges or welded connections to the pipe must be compatible with that of the pipe itself.

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1.2.2.11 Gaskets should be as described in paragraph 1.2.1.10.

1.2.2.12 Where flexible hoses are to be used, for example in some off-loading applications, they should be of the armoured type and manufactured from materials compatible with TiCl_4 . If PTFE Stainless Steel Braided hoses are to be used, these should be antistatic type to prevent breakdown of the PTFE liner due to static discharges. Choice of flexible hoses and a scheduled inspection programme should be agreed with the supplier and in accordance with the local regulations about the use of flexible hoses.

1.2.2.13 The following controls should be applied during construction. It is recommended that at least 100% of all butt welds should be radiographed examined. All pipework should be pressure tested in accordance with the design code, followed by a leak test with dry air before introduction of the product. Where hydrostatic tests are made it is essential that the complete piping system be dried before re-jointing, then purged with dry air or nitrogen to at least dewpoint of -40°C (at atmospheric pressure) prior to the introduction of TiCl_4 .

1.2.2.14 Any extension, modification or repairs should be carried out to a standard at least equivalent to the original design and construction code and must be fully documented.

1.2.3 Valves

1.2.3.1 The valves used in installations handling TiCl_4 may come into contact with the liquid or with a gas phase containing TiCl_4 vapour. Care is therefore essential in the choice of valves to meet the required duty.

1.2.3.2 The valve bodies should preferably be manufactured of carbon steel. For ball valves and plug valves, stainless steel should be used for balls and stems; PTFE should be used for seats and seals.

1.2.3.3 In circumstances where the TiCl_4 is being supplied by a manufacturer to a user, the user is advised to seek advice from the manufacturer regarding the selection of the appropriate type of valves. Valves of the following types have been used successfully for handling TiCl_4 liquid and vapour.

- a) Ball valves
- b) Plug valves
- c) Butterfly valves

Note: that ball valves and plug valves will contain liquid TiCl_4 unless they were opened during decontamination. Precautions are essential if an assembly is to be dismantled for repair or maintenance and a valve has been presented to the workshop in the closed position.

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Ball valves and plug valves are normally used for isolation purposes. Butterfly valves are not suitable for isolation but may be used for control purposes.

1.2.3.4 In all cases it is emphasised that valves must be completely dry before installation.

1.2.3.5 When undertaking maintenance activities on liquid TiCl_4 plant, reliance should not be placed on individual valves of whatever type for isolation. Suitable methods for achieving isolation include two valves in series with the ability to drain the space between them (double block and bleed) or the insertion of a suitable slip-plate on the downstream side of a valve.

1.2.4 Instruments

Control instrumentation on storage tanks and elsewhere in the installation should, wherever possible, be designed to fail-safe. Electrical and electronic equipment, unless specifically protected against corrosion, should not be placed in areas where it could be affected by TiCl_4 leaks or by the gas resulting from the hydrolysis of TiCl_4 .

As a minimum all the information from the instrumentation equipment should be grouped and indicated locally in a well-defined place. Consideration should also be given to displaying essential information in the control room in those installations where one is provided.

For safe operation of the plant and especially to prevent overfilling, the amount of TiCl_4 in each storage tank must be continuously measured and displayed.

Measuring devices commonly used are weighing devices, level measurements with use of contact level sensors or non-contact level sensors (like a gamma ray beam for example).

The instruments should be capable of providing high and low level alarms, according to the plant operating requirements.

An extra-high level alarm is recommended for safety reasons. This should be provided by an instrument separate from the one that initiates the high alarm. Where appropriate the extra high alarm should provide automatic pump trip.

Regular testing and efficient maintenance is essential to keep instrumentation in effective operation.

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1.2.5 Pumps and Pumping Systems

1.2.5.1 This section considers pumps and pumping systems associated with transferring TiCl_4 between a storage facility and a processing operation.

The selection of the appropriate type of pump should be reviewed with the supplier of TiCl_4 who will be able to suggest manufacturers whose equipment has given satisfactory service.

This will reduce the risk of installation of pumps that have a potential safety or reliability problem.

1.2.5.2 Various types of pumps have been developed for use with liquid TiCl_4 . Two commonly used types are

- Submersible pumps
- Externally Mounted Centrifugal pumps

1.2.5.3 Submersible Pumps

These pumps are of a vertical cantilever shaft constructions having no bearings within the pumped liquid and they are mounted within the storage vessel. They are usually fitted with a packed gland having a nitrogen purge to the lantern ring. A further nitrogen supply is installed below the gland area within the stuffing box for emergency purposes. The gland is designed to contain gaseous TiCl_4 and an internal spillback system is incorporated to avoid liquid TiCl_4 reaching the gland area. Control of vessel inventory is also recommended to avoid liquid reaching the gland area.

This type of pump may be operated dry for limited periods.

1.2.5.4 Externally Mounted Centrifugal Pumps

Externally mounted centrifugal pumps can be used for pumping TiCl_4 particularly if high pressures are involved and complete emptying of the vessel is necessary.

These pumps are usually supplied via a bottom off-take connected to the storage vessel.

The selection of the shaft seal is very important for this type of pump and should be made in conjunction with the supplier. Note: seal-less / magnetic drive pumps are the preferred option.

This type of pumping system should include remotely operated suction and delivery valves, in addition to manual isolation valves, to enable shut down of the system in emergencies.

It should be noted that certain types of centrifugal pumps must not be run dry.

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1.2.5.5 Pumps must be completely dry before use and should be stored under dry conditions. It is recommended that all openings should be sealed to avoid ingress of moisture prior to installation.

1.2.5.6 Care in preparation for pump changes is essential to avoid liquid TiCl_4 being retained in the pump and pipework systems. Maintenance preparation procedures should ensure the pump and pipework are completely drained. Where appropriate a vent system to a scrubbing unit should be provided to avoid release of gaseous titanium tetrachloride to atmosphere. All personnel should be protected from exposure to gaseous TiCl_4 by the use of appropriate respiratory protective equipment (R.P.E.).

1.2.6 Safety/Security Equipment

1.2.6.1 Systems capable of being operated from safe locations accessible under all conditions should be provided to stop transfer of TiCl_4 in an emergency. These will include facilities for stopping pumps and operating remote actuated valves as referred to in paragraph 1.2.5.4.

1.2.6.2 Facilities should be readily available for the application of vapour suppressing substances to spillages of TiCl_4 . Substances which can be used include foam and paraffin oil. Further information can be obtained from TiCl_4 manufacturers.

1.2.6.3 Water supplies, capable of providing sufficient volume and pressure of water to enable the emergency services to set up water curtains, which will help to minimise the downwind concentration of HCl, could be located around the storage facility. Training in the use of such equipment is vital, and this aspect of emergency procedures should be discussed in advance with the emergency services.

Note: Directing the water curtain onto a pool of TiCl_4 will increase the generation of fume. Therefore it is very important that the position of any water spray system is carefully considered.

1.2.6.4 In cases where the storage area is not subject to regular visits by operating personnel warning of TiCl_4 emissions may be given by the installation of HCl detection/alarm systems placed around the storage area and/or CCTV.

1.2.7 Vent Disposal Systems

1.2.7.1 Installations handling TiCl_4 should include suitable equipment for handling and disposal of fugitive emissions of TiCl_4 vapour. This equipment can also be used for the disposal of vapour containing TiCl_4 which is displaced from vessels or transport containers when they are being filled or which arises from the use of purges on instruments etc.

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1.2.7.2 Suitable methods of disposing of TiCl_4 vapour include scrubbing systems with recirculating HCl followed by scrubbing with a caustic solution to prevent HCl emission to the atmosphere. Further advice is available from TiCl_4 manufacturers.

Note: Pipework design should prevent reverse flow of scrubbing liquid to the tank.

1.2.7.3 Arrangements must also be made for ensuring that when liquid is removed from a vessel or storage container the gas replacing it is completely dry. This may be achieved by the use of dry inert gas such as nitrogen or atmospheric air, which has been dried to a dew point of below -40°C (at atmospheric pressure).

1.2.7.4 A dedicated fixed network of gas suction pipe to an adequate vapour disposal system, provided with hosed couplings facilities at regular/adequate intervals, may also help to facilitate local intervention (i.e. for maintenance) by allowing immediate trapping of the fumes, which may be generated during the intervention, by positioning the gas suction hoses ("snake") inlet at their point of emission.

1.3 Operation

Selection and training of operators is extremely important for efficient and safe operation.

Detailed operating instructions are recommended for all process work and procedures involved in the loading and unloading of TiCl_4 tankers, operation of the storage installation and utilisation of the TiCl_4 .

Procedures need to be defined in detail for plant commissioning and shutdown, for periodic plant testing and inspections, and for emergency action to deal with TiCl_4 spillages. (See sections 4.1 and 4.2).

It is recommended that operating procedures are reviewed and/or audited regularly to ensure that they remain effective.

1.3.1 Operator Selection

Careful selection of operators for bulk TiCl_4 handling installations is necessary. It is essential that the personnel selected are of adequate physical fitness and they should pass a medical examination before engagement. Operators need to be capable of effective communication and be reliable under stressful conditions. Previous experience in the chemical or similar industry is very desirable.

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1.3.2 Operator Training

Operator training should comprise both off-the-job and on-the-job training. Off-the-job training should include basic information on the physical and chemical properties of TiCl_4 , including its safe handling and use as well as detailed descriptions of the process operations required of the operators. Operators should be provided with personal protection, clothing, eye protection etc., as appropriate, and be trained in its use. On-the-job training should be carried out under the guidance of an experienced operator who is familiar with the process; management and supervisory staff should also be involved in operator training.

Emphasis must be given to safety precautions and methods of dealing with emergencies. Training and practice with breathing apparatus should also be carried out.

Refresher training should be carried out to maintain operator competence.

1.3.3 Operating Instructions

Written operating instructions are required for all foreseeable routine and emergency operations, ranging from guide cards for simple operations to complete manuals.

The operating instructions should cover each process operation in detail and should be formally issued by the manager responsible for the operation of the plant section concerned.

Copies of the instructions, which should include a flowsheet and indicate valves to be closed in emergency, should be available in the working area for operators and in the control centre for supervisors.

Supervisors should check regularly that operations are carried out according to the instructions and/or standard site practices.

1.3.4 Loading Operations

The operation of filling any containers with TiCl_4 is a potential hazard. It is therefore important that loading facilities and transport equipment are correctly designed, constructed, properly used and maintained.

The design and construction of transport equipment is described in Section 3 of these Guidelines.

Written operating instructions should be available at all filling points covering the loading of TiCl_4 into tank containers and rail tank wagons. Personnel involved should be fully trained in their implementation. The instructions should recognise the specific hazards of TiCl_4 and ensure the correct operation of filling equipment in both normal and emergency situations.

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All necessary personal protective equipment should be available for loading operations, and operators should be trained in the correct use of this equipment.

It is not the intention in this section of the guidelines to attempt to set detailed operating instructions for filling TiCl_4 containers, since these of necessity will depend upon local operating conditions. However, as part of the operating instructions, an inspection of the transport equipment should be carried out by the loading terminal staff before, during and after loading.

This inspection does not replace or diminish the responsibility of the owner of the tank container or rail tank wagon to ensure that the equipment is properly tested, maintained and fit for purpose. It is meant to ensure that the transport of TiCl_4 is conducted as safely as possible.

1.3.5 Unloading Operations

The operation of unloading any tank container or rail wagon of TiCl_4 is a potential hazard. It is therefore important that unloading facilities are correctly designed, constructed, properly used and maintained.

Unloading facilities should be designed and located having due regard to the potential hazards with TiCl_4 . The equipment should be subject to regular checks to ensure maintenance of the standards set.

Written operating instructions should be available for unloading TiCl_4 from tank containers and rail tank wagons. Personnel involved should be fully trained in their implementation. The instructions should recognise the specific hazards of TiCl_4 and ensure the correct operation of unloading equipment in both normal and emergency situations.

All necessary personnel protective equipment should be available for unloading operations and operators should be trained in the correct use of this clothing and equipment.

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1.4 Maintenance

A high standard of maintenance of all plant, equipment and instrumentation associated with TiCl_4 storage and transfer systems is an essential part of safe operation of the user's facility.

Maintenance systems and procedures should be prepared to cover:

- Scheduled maintenance procedures
- Inspection procedures
- Maintenance preparation procedures
- Post maintenance procedures
- Maintenance procedures
- Permit to work system
- Training
- Selection
- Control of modifications and changes
- Protective devices

1.4.1 Scheduled Maintenance

A scheduled maintenance programme should define the frequency for inspection, testing and servicing of all plant and equipment.

1.4.2 Inspection Procedures

A written scheme of work should be specified for the inspection of all vessels and pipework systems taking into account any statutory or local authority requirements.

It is recommended that a visual external inspection is carried out at least annually supported by non-destructive testing if deterioration is observed e.g. breakdown of protective coating or surface corrosion.

For vessels, an internal inspection is recommended at intervals to be determined by the user based upon operating experience. Where operating experience is not available new users are advised to consult their suppliers.

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1.4.3 Maintenance Preparation Procedures

The importance of pre-planning maintenance activities cannot be over-emphasised. An appropriate safe system of work should be adopted, which identifies:

- equipment to be worked on
- isolations to be made
- precautions to be taken during the work
- protective equipment to be worn
- any special equipment to be used
- any residual risks remaining
- numbers of people necessary for work
- necessary tools, material and replacement parts for performing the job.

1.4.4 Post Maintenance Procedures

Before re-commissioning plant after maintenance work, procedures should be determined in advance to ensure that the plant is completely dry and in a satisfactory condition to accept TiCl_4 e.g. pressure testing and instrument loop checks.

1.4.5 Maintenance Procedures

Procedures covering maintenance operations should be determined in advance and communicated to the maintenance personnel.

1.4.6 Permit to Work System

A Permit to Work system should be established to cover all maintenance work associated with TiCl_4 storage and handling.

The permit to work is a signed statement from production personnel confirming that the plant has been suitably prepared. Both maintenance and production personnel must satisfy themselves that the permit has been completed correctly and should subsequently check for compliance with the stated precautions.

On completion of the maintenance work the permit must be signed off by the designated maintenance and process personnel before the plant or equipment can be returned to service.

Only personnel trained in the permit to work system should be allowed to issue/accept permits.

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1.4.7 Training

All maintenance personnel should be trained in the safe handling of TiCl_4 including:

- Physical, chemical and toxicological properties of TiCl_4
- Permit to work procedures
- Personal protective equipment
- Respiratory protective equipment
- Emergency procedures

1.4.8 Selection of Maintenance Personnel

Maintenance personnel should be physically fit and should pass a medical examination before engagement. Previous experience in the chemical industry is desirable.

1.4.9 Control of Modifications and Changes

Modifications/changes should not be carried out without specific authorisation. A formal written procedure should be in place to ensure approval is obtained from designated personnel. Such a procedure is generally called "Management Of Change" (or MOC) procedure.

1.4.10 Protective Devices

A checking/testing schedule should be in place to ensure all protective devices are in good working order; this schedule should be strictly adhered to.

A protective device includes any protective control or monitoring equipment considered essential to prevent a dangerous situation arising, i.e. trips alarms and pressure relief systems.

SECTION 2 - LOADING AND UNLOADING OF TRANSPORT CONTAINERS

Information on the design of transport containers is provided in Section 3.

A typical installation for loading liquid TiCl_4 into transport containers via "padding" is shown in Fig. 1.

In addition to the general principles for TiCl_4 storage set out in Section 1, the following points should be considered.

Each filling line should preferably be equipped with an on-line counting device allowing pre-selection of the quantity of TiCl_4 to be transferred. When the pre-selected amount of TiCl_4 is reached, the device should automatically stop the transfer. This may be backed up by a high-level trip device.

Adequate measures should be taken to prevent movement of the container during the loading (or unloading) process. Examples include physical barriers, electrical or mechanical interlocks and proximity switches.

It is recommended that an operator be present at the loading station during loading (or unloading). In addition HCl detectors and/or TV monitors displaying in an appropriate location could be considered.

See also Section 1.2.6 regarding safety/security equipment.

The installation of TiCl_4 pipework should allow self-draining of the liquid when the transfer process is stopped.

2.1 Equipment - An example is given in Fig. 1

2.1.1 The filling tank

- The weight detector (WQX) displays permanently the weight of TiCl_4 contained in the tank.
- The low-level detector (WSL) alerts the operator and stops the loading process when the tank is empty.
- The high level detector (WSH) alerts the operator and stops the filling of the tank.
- An extra high level switch (LSH) provides a back-up to the high level switch and also automatically stops transfer of TiCl_4 into the tank to prevent over-filling.
- The filling tank should be maintained at the required pressure by a regulated nitrogen (or dry air) supply and a regulated vent to the gas treatment plant. Protection against under or overpressure should be provided by an appropriately rated relief system that vents to the gas treatment plant or other safe location.

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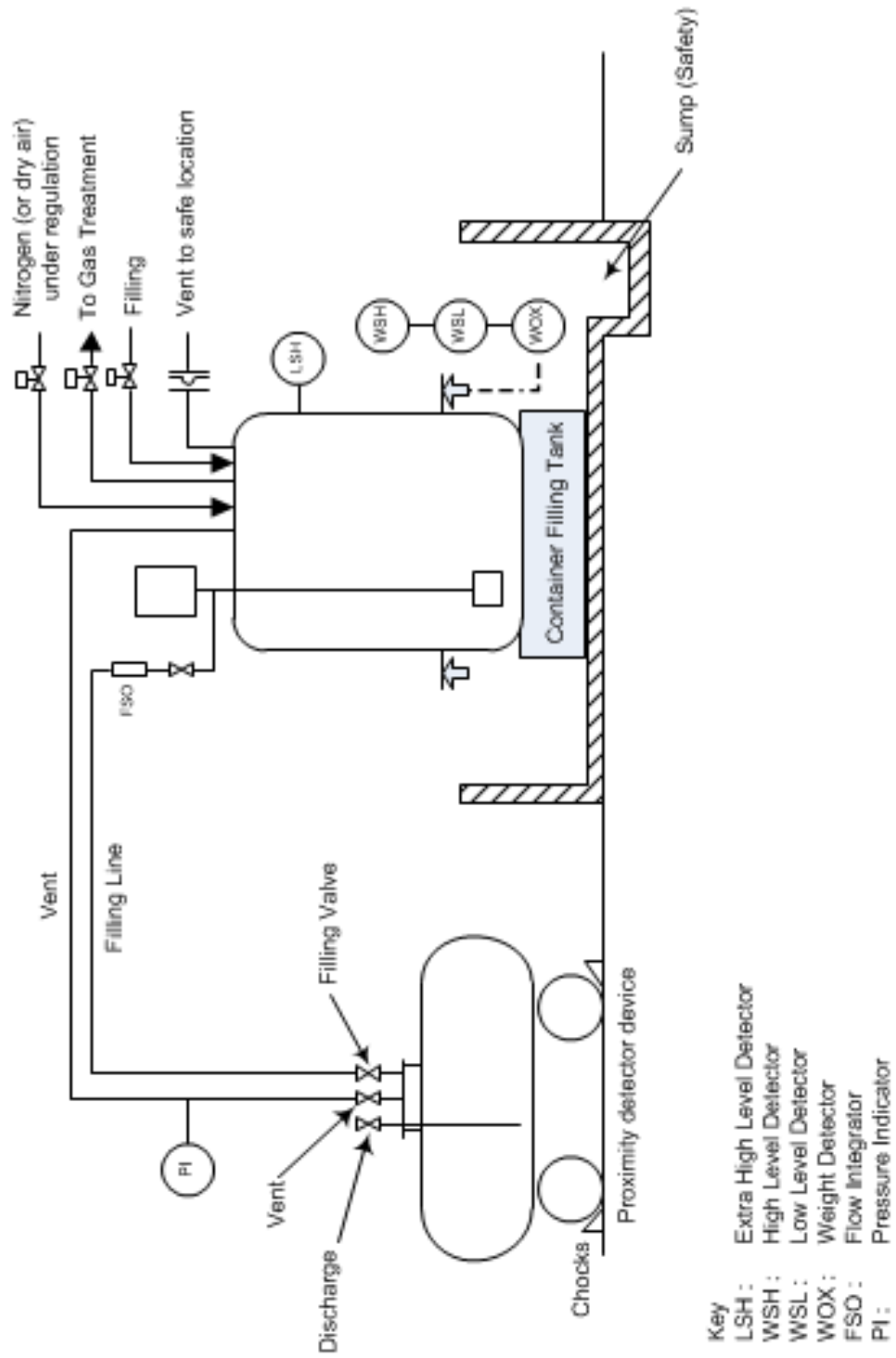


Fig 1 - LOADING A TICl₄ TRANSPORT CONTAINER

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2.1.2 The transport container

- The connections for venting, filling and emptying should be correctly identified before connections are made. The use of a colour code or other valve identification system may be helpful (see Section 3). Specially designed fittings may also be considered.
- In figure 1 a vent line connects the top of the transport container to the top of the filling tank through a hand valve and flexible hose and thus to the gas treatment plant.
- The filling line connects the transfer pump to the transport container through valves and a flexible hose.

2.2 Loading of Transport Containers

The procedure for loading TiCl_4 into transport containers is as follows (referring to Fig. 1)

- Put the transport container in position, locate wheel chocks correctly and set the proximity detector device.
- Identify correctly the valves for venting, filling and emptying the container.
- Carefully remove the blank flange from the vent valve.
- Connect the vent hose to the top of the container's vent valve.
- Open the vent valve slowly to vent the transport container to the filling tank.
- During the venting process, check that the valve operates correctly and is gas tight.
- Remove the blank flange from the filling valve and dip through the valve to confirm that the container is empty.
- Determine the quantity to be loaded into the container.
- Connect the filling hose to the filling valve using a new gasket.
- Set the flow integrator (FSQ) to the required quantity of TiCl_4 to be transferred.
- Start the filling process.
- When the required quantity of TiCl_4 has been transferred, the pump should stop automatically.
- Shut the container's filling valve after allowing the line to drain, carefully disconnect the filling hose and fit the blank flange to the filling valve using a new gasket.
- Shut the vent valve, carefully disconnect the vent hose, and fit the blank flange to the vent valve using a new gasket.
- Remove the proximity detector device and wheel chocks.

2.3 Unloading from Transport Containers to Storage Installations

Fig. 2 shows a typical installation for unloading of liquid TiCl_4 from transport containers into a fixed storage facility. This figure also gives an example of a TiCl_4 storage installation.

In addition to the principles set out in Section 1 and 2, the following points should be considered.

2.3.1 General Layout and Siting

The transfer from transport containers to the storage installation is affected by the application of dry nitrogen gas (or dry air) under pressure. (Padding)

The nitrogen supply is regulated and equipped with a relief system to prevent over-pressurisation of the transport container.

- Adequate measures should be taken to prevent movement of the container during the unloading process. Examples include physical barriers, electrical or mechanical interlocks and proximity switches.
- It is recommended that an operator be present at the loading station during unloading. In addition HCl detectors and/or TV monitors displaying in an appropriate location could be considered.
- The installation of TiCl_4 pipework should allow self-draining of the liquids when the unloading process is stopped.

2.3.2 Equipment

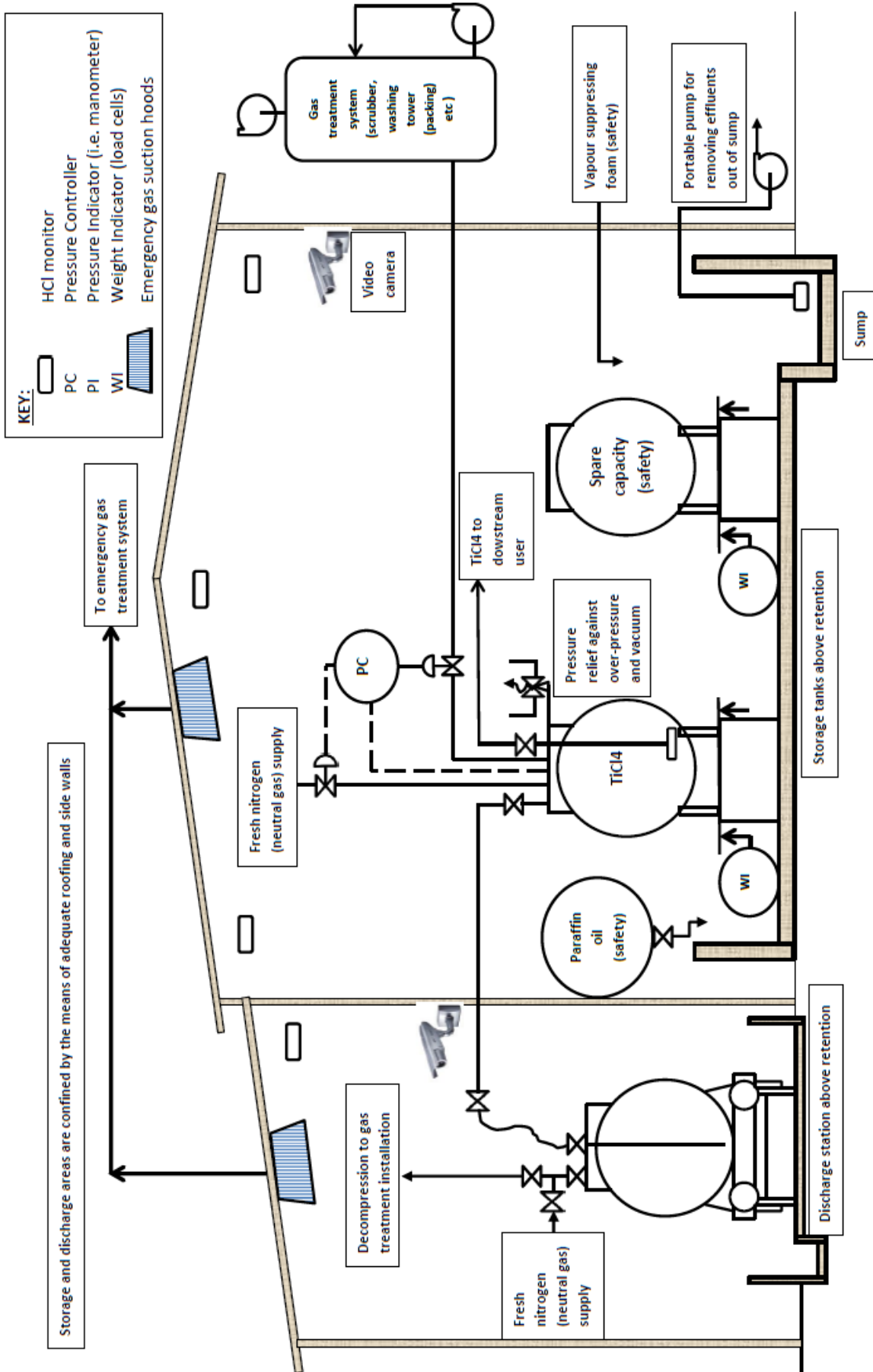
An example is given in Fig. 2.

2.3.2.1 The transport container:

- The connection for venting, emptying and filling should be correctly identified before connections are made. The use of a colour code or other valve identification system may be helpful.
- Either the vent valve or the filling valve used in the loading process will now be connected to a regulated nitrogen, argon or dry air supply. The transfer is achieved by the application of minimum padding pressure, sufficient to overcome the differential pressure between the transport container and storage tank.

An alternative system, using a suitable pump, may also be adopted. The advantage of using a Pumped (rather than Padding) offloading system is that in the event of an Emergency, the TiCl_4 transfer can be stopped either locally or remotely by stopping the offloading pump. With a Padding offloading installation, after isolating the offloading valve and the motive force, (nitrogen, argon or dry air) you must then safely depressurise the transport container by venting via a fume scrubber facility.

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2.3.2.2 Storage Tank:

- The free capacity must be significantly greater than the full capacity of the transport container.
- The storage filling line is connected to the transport container's emptying valve through a flexible hose and valves.
- The storage tank should be fitted with a vent to a gas scrubbing system to prevent overpressure and release of $TiCl_4$ fumes to atmosphere, during the offloading operation.
- The vent should be designed to prevent moist air, or liquor from the gas scrubber entering the storage tank after filling, by use of a suitable non-return device and application of a minimum positive pressure to the tank (taking into account the pressure rating of the tank).
- If an aqueous media is used in the gas scrubbing system, there is the potential for hydrochloric acid to form in the vent line. The specification of the vent line should therefore take this into account.

2.3.3 Operation

The principle for transfer from transport containers to storage installation by Padding is as follows (referring to Fig. 2):

- put the transport container in position, locate wheel chocks correctly and set the proximity detector device.
- ensure that the free capacity of the storage tank is greater than the full capacity of the transport container.
- identify correctly the valves for venting, filling and emptying the container.
- carefully remove the blank flange on the transport container's vent/padding valve and connect it to the decompression line to gas treatment installation.
- decompress slowly the container to the gas treatment installation.
- once decompression is complete, carefully remove the blank flange on the transport container's liquid outlet (emptying) valve.
- connect the emptying hose to the transport container's liquid outlet (emptying) valve using a new gasket.
- carefully remove the blank flange on the transport container padding valve and connect the nitrogen (or dry air) to the pressurising line.
- open all the valves on the emptying line.
- start the transfer process by opening the nitrogen (or dry air) inlet valve.
- when all $TiCl_4$ has been transferred from the transport container to the storage tank, shut the nitrogen inlet valve and allow the transport container to vent down and decompress to gas treatment installation. Carefully disconnect the nitrogen (or dry air) delivery line and vent line.
- Fit the blank flange on the vent/padding valve using a new gasket.
- shut the valves on the emptying line after allowing sufficient time for natural drainage.
- carefully disconnect the emptying flexible hose (beware of $TiCl_4$ dripping) and fit the blank flange using a new gasket.

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- remove the proximity detector device and the wheel chocks.

See Section 2.3.2.1 regarding Pumped offloading.

SECTION 3 - TRANSPORT CONTAINERS

3.1 Engineering Procedure

3.1.1 Scope

This document states the necessary requirements relating to the design, registration construction, maintenance, periodic examination, repair or modification of all transport containers used for the distribution of TiCl₄.

3.1.2 Definitions

3.1.2.1 General

The job titles identified and defined in this document may vary in different companies and locations worldwide. It is intended that the responsibilities, detailed below, be allocated to appropriate individuals, regardless of their specific title. Where necessary, the appropriate individual may be a contracted person.

3.1.2.2 Transport Containers

Transport Containers include rail and portable tanks – see Appendix 1 and 3

3.1.2.3 Returnable Containers

Returnable Containers are those transport containers that are designed to be used more than once without reconditioning or refurbishment, i.e. road tank, rail tank and multi-modal portable tanks.

3.1.2.4 Product Description for Transportation Documents

UN 1838 Titanium Tetrachloride, 6.1 (8), PG I, (C/D) according ADR/RID regulation

3.1.2.5 Operated

The word "Operated" refers to the "operator" of the transportation container. Tank container/portable tank operator means any enterprise in whose name the tank container/portable tank is registered.

The "operator" is responsible for the provision, operation, maintenance and registration of equipment used for distribution.

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3.1.2.6 Periodic Examination

Periodic Examination is the process of internal and/or external examination, inspection and/or testing carried out at defined intervals.

3.1.2.7 Responsible Executive

The Responsible Executive is the person or persons identified by the TiCl₄ manufacturer to carry out the responsibilities in 3.1.4.1.

3.1.2.8 Responsible Engineer

The Responsible Engineer shall have understanding, practical knowledge and experience of relevant transport engineering, and shall be appointed by the Responsible Executive to carry out the responsibilities in 3.1.4.2.

3.1.2.9 Operating Manager

The Operating Manager is the manager of a production unit/facility on the TiCl₄ manufacturer's site/location or the manager of a distribution function, appointed to carry out the responsibilities in 3.1.4.3.

3.1.3 Principles

3.1.3.1 General

Statutory requirements shall be complied with; however, where the requirements of this document exceed statutory requirements then this document shall also apply.

3.1.3.2 Design and Construction

Transport containers used for the distribution of TiCl₄ shall wherever possible comply with an appropriate national or international standard.

Inspection during manufacture, repair or modification shall be by the relevant Responsible Engineer or by an inspection service approved by the Responsible Executive.

All containers used for the distribution of TiCl₄ and all other operated returnable containers, shall have their design and construction (including repairs, modifications and selection of appropriate materials of construction) approved by the Responsible Engineer.

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3.1.3.3 Registration

All returnable containers and their pressure relief devices shall be registered.

Registration requires that:

- a) each container is allocated and marked with a unique number;
- b) there is a notification system which prevents the use of containers whose due date for periodic examination has passed or will be passed before it is returned to the TiCl_4 manufacturer;
- c) a file is created and maintained containing documentation relating to design, manufacture, initial inspection, periodic examination, maintenance, repair and modification.

3.1.3.4 Maintenance

Transport containers shall be maintained in such a manner as to avoid danger and shall be periodically examined at intervals specified in legislation, or otherwise appropriate to the duty.

3.1.3.5 Auditing

The maintenance and registration schemes of transport containers used for the distribution of TiCl_4 should be subjected to an engineering audit at appropriate intervals by the Responsible Engineer.

3.1.4 Responsibilities

3.1.4.1 Responsible Executive

The Responsible Executive (or Executives) is the person (or persons) identified by the TiCl_4 manufacturer as having the following responsibilities:

- a) ensuring that engineering procedures are provided in accordance with this document and that they are implemented;
- b) approval, in consultation if appropriate, of the appointment of the Responsible Engineer(s) and other key individuals required by this Procedure.
- c) ensuring that staff with the required competence are appointed in writing.

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3.1.4.2 Responsible Engineer

The Responsible Engineer shall approve the design of transport containers as specified in 3.1.3.2, using an external design/inspection authority where required by the relevant national or local authority, and shall carry out the audits as specified in 3.1.3.5.

3.1.4.3 Operating Manager

The Operating Manager is responsible for ensuring that transport containers and storage tanks used for the distribution of $TiCl_4$ are:

- a) designed and constructed in accordance with 3.1.3.2;
- b) subject to registration as detailed in 3.1.3.3;
- c) maintained in accordance with 3.1.3.4.

Remark: the naming of these responsibility holders may differ between companies.

3.2 Engineering Guide

INTRODUCTION

Engineering Guides explain how the Engineering Procedures should be implemented. The Procedure states the necessary engineering requirements related to safety, health and environmental matters.

The principles given in the Procedure are intended to ensure that transport containers are correctly designed and manufactured and that they are managed effectively with respect to periodic examination, modification and repair once they have entered service.

3.2.1 Scope

This Guide covers the implementation of the Engineering Procedure for transport containers used for the distribution of $TiCl_4$. Within the general framework provided by the Procedure, this Guide sub-divides transport containers into tankers (rail and portable) and packages.

3.2.2 Definitions Additional to those in the Procedure

3.2.2.1 Rail Tank

A rail tank is a tank permanently mounted on a chassis for the conveyance of products by rail.

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3.2.2.2 Portable Tank

A Portable Tank is a "multi-modal tank with a capacity of more than 450 litres in accordance with the definition in Chapter 6.7 (of ADR/RID regulation) or the IMDG Code and indicated by a portable tank instruction (T-code) in column (10) of Table A of chapter 3.2 of the Dangerous Goods Transportation Regulation."

"A tank container means an article of transport equipment meeting the definition of a container, and comprising a shell and items of equipment, including the equipment to facilitate movement of the tank-container without significant change of attitude, used for the carriage of gases, liquid, powdery or granular substances, and when used for the carriage of gases as defined in 2.2.2.1.1 (of ADR), having a capacity of more than 0.45 m³ (450 litres)."

3.2.3. Application of Principles

3.2.3.1 General

The operation of transport containers often crosses the areas of responsibility of several departments. It is important to ensure that the responsibilities detailed in the Procedure are clearly defined without introducing unnecessary constraints.

3.2.3.1.1 Registration

A registration system is required which ensures that each returnable container is adequately identified and the product, payload and restrictions on use are defined and that it is subjected to periodic examination at the required intervals. The registration system is required to cover all containers presented for filling, e.g., customers own containers.

3.2.3.1.2 Lapsed Containers

The requirements for the periodic examination of a transport container whose due date for periodic examination has passed will be deemed to be satisfied if it is examined before its next filling operation. Filling a transport container whose due date for periodic examination has passed is strictly prohibited.

3.2.3.1.3 Margin on Intervals for Periodic Examination

If there is likely to be a delay between the filling and despatch of a transport container, then this is required to be allowed for in selection of containers for filling: it is not allowable for containers to leave the Works, or be in transit to their final destination, after the due date for periodic examination has passed.

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3.2.3.1.4 Maintenance

In addition to the formal periodic examinations carried out at the prescribed intervals, transport containers are required to undergo visual external inspection before each filling so as to ensure that they are suitable for continued use.

3.2.3.2 Tankers

References to tankers include those rail or portable tankers that operate solely within the confines of a site.

3.2.3.2.1 Design and Construction

Tankers are required, wherever possible, to comply with the requirements of an appropriate national or international standard. Many regulations (particularly the international ones such as IMDG, ADR, RID CFR 49 or US DoT) have prescribed forms for design approval. Fittings and pressure relief valves are required to be included in the approval system.

Portable tankers are required to comply with the requirements of the International Convention for Safe Containers (CSC) (implementation is by national legislation; in the UK for example, The Freight Containers (Safety Convention) Regulations 1984). In France for example, Ministry of Development Durable, Division 431-1 and its Annexes regarding Maritime Transportation of Dangerous Goods.

See Appendix 1 for an example of a typical specification.

3.2.3.2.2 Periodic Examination and Maintenance

There should be a formal written scheme for the procedures to be adopted for the periodic examination and maintenance of $TiCl_4$ tankers. It is required by the Transportation Regulations and CSC (Container Safety Convention) that portable tanks/tank containers must be subject to an internal examination every 2.5 years, and in addition a hydraulic test is performed every 5 years.

Regarding the rail tankers, this time frame is 4 and 8 years respectively.

One example of an inspection procedure is given in Appendix 2 for further guidance.

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3.2.3.3 Packages

3.2.3.3.1 Design and Construction

The designs of packages are defined in performance specifications in the United Nations Recommendations on the Transport of Dangerous Goods. Packages conforming with the UN requirements are embossed or marked at manufacture with a United Nations approval number allocated by a testing station authorised by the competent authority of the country concerned.

Packages used for TiCl_4 should comply with the United Nations requirements. There should be a specification relating to design, prepared by a designated person (e.g., a package advisor) and in compliance with the packaging instruction specified in the current ADR regulation.

See Appendix 3 for a typical specification.

Packages should be identifiable against a batch or manufacturing number. Re-conditioned packages should not be used for TiCl_4 .

The returnable pressure cylinders complying with Packing Instruction P602 are specially designed to allow the shuttle transportation of TiCl_4 between supplier and customer.

Each pressure cylinder complying with Packing Instruction P602 is identified by its owner's name engraved on the top of the cylinder, plus the cylinder ID and additional labels carrying all the regulatory information. These cylinders are transported fixed on a specially designed metal pallet, which allows the transport of 2, 4 or 6 cylinders on each pallet. The cylinders are immobilised on the pallet during the transport with a special clamping device.

3.2.3.3.2 Periodic examination and maintenance

The returnable pressure cylinders complying with Packing Instruction P602, are required to be periodically examined and maintained in the same manner as tanks, but with a different schedule. (intermediate visual inspection every 20 shuttle deliveries or at least every 5 years, visual inspection associated with hydraulic test every 10 years).

3.2.4 Auditing

3.2.4.1 General

An independent auditor or audit team should periodically audit the implementation of and compliance with the principles of the Procedure. A more detailed engineering audit is required to be carried out on the maintenance and registration schemes for transport containers used for the distribution of TiCl_4 .

SECTION 4 - BASIC HEALTH HAZARDS AND SAFETY MEASURES

4.1 Exposure of TiCl₄ Fume

Inhalation of TiCl₄ should be avoided and appropriate respiratory equipment should be worn.

TiCl₄ fume consists of hydrochloric acid mist, together with solid particles of hydrolysed titanium compounds. The fume is irritating to the eyes and to the respiratory system and will cause thermal as well as chemical burns. As the particulate content can be within the respirable size range, the particulates may be carried into the lungs.

The fume has a sharp, irritant odour and an acid taste, its irritant nature making continued work in dangerous concentrations intolerable. Indeed, the fume is sufficiently irritating at relatively low concentrations to encourage withdrawal from the contaminated atmosphere. A further safety feature is that the fume is clearly visible even at the lowest concentrations.

Exposure to low concentrations may result in a sore throat, perhaps with coughing and a tightness of the chest. A period of rest in fresh air is often sufficient to quickly clear these effects.

More severe exposure may lead to a choking sensation and difficulty in breathing. In such cases artificial respiration or oxygen should be administered immediately by trained personnel. Such cases could show signs of pulmonary oedema and shock. First Aiders should transfer serious cases to a hospital without delay. Exposure to high concentrations can be fatal.

There should be no chronic ill effects if the respiratory system is protected at all times by the wearing of a mask whenever fume is present or is expected.

Exposure to small amounts of fume can aggravate a condition in persons with a history of respiratory problems.

Circumstances in which severe exposure might occur would include a person drenched with liquid TiCl₄ or someone trapped in a high concentration of fume without a suitable gas mask.

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4.2. Contact with Liquid TiCl₄

4.2.1 Skin Contact

If TiCl₄ is allowed to remain in contact with the skin, it will react with moisture present to produce hot hydrochloric acid causing both thermal and acid burns.

Skin contaminated with TiCl₄ should be wiped with a dry cloth before being washed clear in order to limit the burning effect when water is applied, unless this causes exposure to be unduly prolonged.

Saturated clothing, including rubber gloves and boots, must be removed and excess liquid wiped off the skin before water is applied, otherwise serious scalding would occur.

The skin should then be drenched with large volumes of water and washing should continue for 20 minutes.

The effect can range from blistering to destruction of tissue. Skin burns should receive immediate attention.

TiCl₄ fume will also cause skin irritation, particularly when associated with perspiration.

4.2.2 Eyes

If liquid TiCl₄ enters the eye it will cause irritation immediately it comes into contact with the moisture present, forming titanium oxychloride solids and hydrochloric acid, as well as generating heat. Emergency action must be swift. Providing there is absolutely no delay, the eyelids should first be wiped with a dry and clean cloth to remove excess liquid. The eye should then be washed with large quantities of water, ensuring that irrigation is complete by holding the eyelids open. Washing should continue until professional assistance is provided.

If emergency action is not carried out swiftly and correctly damage could result in impairment of vision or even total loss of sight.

4.2.3 Ingestion

If liquid TiCl₄ is swallowed it will cause severe burns to the mouth, oesophagus and stomach.

If conscious, the patient should be made to swallow copious amounts of water. Sodium bicarbonate should not be used and vomiting should not be induced.

Prompt medical attention is vital.

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4.3. Personal Protective Equipment

4.3.1 Respiratory Equipment

TiCl₄ fume contains hydrochloric acid (initially anhydrous) and very fine particles of oxychlorides that are drawn deeply into the lungs on inhalation.

Cartridges for air-purifying respirators must remove HCl and at least 99.97 percent of particulates > 0.3 microns. If cartridge respirators are used, the cartridges must have an end-of-service-life indicator (ESLI), a system that warns the user of the approaching end of adequate respiratory protection.

If the cartridges do not have an ESLI the user must have a process to ensure that the cartridges are changed after a defined period of exposure to TiCl₄ fumes.

The ori-nasal mask is preferred as a general escape mask. It is recommended that escape masks should be carried by all personnel, entering a TiCl₄ area, but they are not recommended for use as working masks because they do not protect the eyes against TiCl₄ fume. They will afford protection up to 50 ppm HCl in the atmosphere.

Never re-use an escape mask without renewing filter cartridges and cleaning the mask to remove residues.

The general working mask for TiCl₄ fume protection is the full face canister respirator. This mask protects the eyes and will give respiratory protection up to 2000 ppm HCl. At this relatively high concentration the canister would last for two and a half hours at an average working breathing rate. In practice, canister respirators should not be chosen if the expected TiCl₄ fume concentration is likely to approach this limit. Compressed air breathing apparatus should be used in such cases.

Neither cartridge or canister respirators must be used in confined spaces or in an atmosphere deficient in oxygen. Again, breathing apparatus would be necessary.

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A number of positive pressure breathing apparatus are available for protection against any concentration of TiCl_4 fume. For example:

- ONE HOUR air line sets (trolley sets). They are generally preferred for maintenance jobs of extended duration or for work in a confined space.
- HALF HOUR self-contained breathing apparatus for both general and emergency use.
- TEN MINUTE escape sets for special circumstances where concentrations of TiCl_4 fume could be high. They must not be used as working masks.

There must be effective procedures for the selection, issue, inspection and maintenance of all respiratory protective equipment.

4.3.2 Protective Clothing

General Protection

TiCl_4 is a corrosive liquid that must be prevented from coming into contact with the skin.

If there is any possibility of contact, suitable protective equipment must be worn. As an absolute minimum this would include chemical goggles and PVC or rubber gloves with a suitable respirator readily at hand.

The level of protection should then reflect the level of risk, being prepared for the unexpected and erring on the side of safety.

For example, where fastenings are provided (e.g. boots, overalls) they should be of a quick release type.

When the risk is high a one piece PVC suit, complete with hood (green acid suit), should be worn with Wellington boots inside the trousers and PVC gloves inside the sleeves, sealing the wrists with elasticated armlets. Complete coverage of head and face with a gas tight seal can be achieved between a full face mask or breathing apparatus set and the hood. A bump cap is recommended with this arrangement as it fits better than the normal helmet.

Acid resistant PVC clothing provides complete protection against TiCl_4 splash up to temperatures approaching boiling point.

Other types of protective material, e.g., 'Corroguard', a lightweight polyethylene - material, is suitable for TiCl_4 temperatures up to 80°C and can be used in the form of a coverall, neck cape, sleeves, jacket, trousers etc.

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If a person wearing such impermeable equipment becomes contaminated, all traces of $TiCl_4$ must be washed off his protective clothing before it is removed.

Any pockets of liquid should be cleared before water is applied. Anyone giving assistance must be suitably protected. The water should be applied in large quantities under an emergency shower with additional water from Hosepipe.

If only partial protection was worn, the equipment, along with any contaminated clothing, should be carefully removed before water is applied.

SECTION 5 - EMERGENCY PROCEDURES

Introduction

All installations that use $TiCl_4$ should have a written Site Emergency Plan which should be formed in conjunction with the Emergency Services.

5.1 General points when Handling Spillages within a Factory

5.1.1 Environmental Effects

The safety of personnel, both workers and the general public, is of paramount importance when dealing with spillages, and some estimation of the degree of risk which people are exposed to should be made when evaluating the best means to tackle the spillage.

5.1.2 Informing Neighbours

It is important to inform people close to the scene of a spillage about such incidents, before they become affected by the fume so that they can adopt sensible measures from the onset.

Take particular care before using water to wash away spillage because large volumes of fume will be generated immediately which could exacerbate the incident.

5.1.3 Upwind Approach

Approach spillages from upwind. This will provide a better view of leakage in general and will also reduce exposure time and gas mask exhaustion.

Check the site wind sock to confirm air flow direction when available. Take care that the wind direction displayed by a wind sock located on the top of tall buildings may not be representative of the wind direction at ground level, due to the impact of the local buildings lay-out.

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5.1.4 Isolate Source of Leak

Identify the source of spillage and isolate immediately if this is feasible. If the source cannot be identified, shut off all flows and transfers within or into the affected area. Check instruments for evidence leading to identification of the source.

5.1.5 Minor Spillages

In some instances minor spillages of TiCl_4 can be dealt with quickly and effectively without raising a major alarm. However, every situation must be judged individually and incidents involving personal injury or where environmental effects could be severe (e.g., TiCl_4 falling from the top of a structure creating extraordinary amounts of fume) will require the operation of an emergency plan which may involve external emergency services.

All spillages need to be given the same degree of urgency and planning irrespective of size. Water curtains should be erected downwind for maximum knock down of fume and the boundaries of the immediate area should be monitored continuously. Any escalation of fume which carries to an adjacent area will require communication with any neighbours in the direct path of the fume.

5.1.6 Containment

If the spill is confined, consider transferring it to acid resistant drums using a pump. Chalk can be spread around the edges to prevent spreading. Depending on the climatic conditions, location etc., it might be possible to delay such transfer to a quieter period when there are few people in the vicinity, leaving the spillage barriered off but permanently manned to ensure no interference, and covered with a suitable foam agent or polythene sheets with hygiene hoses attached to lead away any fume.

Take great care in order to avoid any inlet of the spilled product into drains. Such inlet may create a rapid hydrolysis of the product in a location having not enough room to accommodate the volume of fumes. This may lead to a "pressurized" like fume volume expansion with violent gas /liquid projections out of the drain.

A number of foam systems are commercially available for containment of TiCl_4 (mainly hydrochloric acid) fumes. Consult supplier for details. It is important that foam systems are applied correctly to gain maximum effect and training by the supplier is essential.

Systems for the application of paraffin oil to contained spillages may also be used.

Safety Advice for Storage and Handling of Anhydrous Titanium Tetrachloride

5.1.7 Quenching Using Fire Hoses

For spillages which are thinly dispersed the only course of action will be to flush away with large quantities of water. Water sprays set up downwind must be turned on before any flushing is started and full protective clothing should be worn. Fire hoses are usually required to ensure a deluge of water.

The use of water-curtains may also help to absorb and block some hydrogen chloride contained in drifting fumes generated by a TiCl_4 spillage and therefore, contribute to protect downwind buildings.

- Note:
- a. Water getting inside a ruptured or leaking container may cause an explosion.
 - b. Water may be effective in mitigating an incident involving a water reactive material, only if it can be applied at sufficient flooding rate for an extended period. Be aware that the products from the reaction with water are both toxic and corrosive.
 - c. The environmental fate of contaminated firewater entering drainage systems must be considered.

5.1.8 Use of Solid Alkali Compounds

After flushing thoroughly spread solid alkali compounds for example chalk over the affected area, unless it is acid tiled, in order to neutralise any remaining liquor, and to prevent damage to steelwork, foundations, concrete surfaces etc.

5.1.9 Drains and Gulley's

TiCl_4 which has entered closed drains or gulley's can be the cause of "explosion" when water is poured into them. Ultimately such drains must be cleared out, but this must be done with the full knowledge that manholes can be thrown into the air when water is directed down the TiCl_4 filled drain and also corrosive substances can be ejected violently from drain openings, due to the water reaction.

5.2 Major Incidents

5.2.1 Major Spillage

Bring the spillage under control as quickly as possible and estimate where the spillage will spread to. Prevent the spread by laying a barrier of chalk, lime or dolomite etc. Fumes from the surface of the spillage (puddle) may be suppressed using foam or by spreading chalk over the surface, if safe to do so. For spillages in bunds paraffin oil may be used to suppress fumes, then access to bund is possible to enable the re-pumping of the spilled product into secured certified containers.

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5.2.2 Spillage Transfer

If the spillage can be limited by transferring $TiCl_4$ from the leaking section to other tanks, do so. Sufficient empty tank capacity must be maintained in groups of interconnected tanks to enable any one tank to be emptied into the others in an emergency. Ensure that the leaking section is vented when pumping to another tank. This is to avoid vacuum collapse if large volume are transferred from a vessel with a choked vent.

5.2.3 Emergency Service

Major spillages will require involvement of the appropriate emergency services (e.g., Police, Fire Brigade) and activation of the Site Emergency Plan.

No decision should be taken to direct water hoses onto the spillage until the full implications of the effect of a large increase in fume density has been considered. Temporary evacuation of buildings inside the factory may be necessary.

5.2.4 Fire Brigade

The services of the Fire Brigade shall be used to supplement the numbers of water sprays downwind of the spillage. Containment of the $TiCl_4$ pool should be a first priority using chalk to prevent ingress into drains etc. If an approach can be safely made upwind of the fume, chalk should be spread evenly over the surface of the pool using a mechanical shovel. All necessary precautions need to be taken at this stage, however guard against change of wind direction resulting in personnel being caught in dense pockets of fume.

5.2.5 $TiCl_4$ 'Pools'

Consideration should then be given to find means of pumping the contained $TiCl_4$ pool back into acid resistant vessels or drums, wearing full protective clothing and breathing apparatus.

Remark: $TiCl_4$ itself is not compatible with High Density Polyethylene (HDPE) and High Density Polypropylene (HDPP) receptacles.

These materials become fragile and brittle if in contact with liquid $TiCl_4$.

5.2.6 Effects on Visibility

Following a major spillage, exposed areas would fill with dense white, choking fumes, making the task of searching for missing persons almost impossible until the fume began to clear, even though breathing apparatus would be used. High concentrations of $TiCl_4$ fume not only reduces visibility almost to zero, but also deadens sound to an alarming degree.

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The open design of a plant has both advantages and disadvantages in this respect. Fume will spread quickly up through the building, but this same natural ventilation will prevent prolonged internal fume accumulation.

5.2.7 Escalation of an Incident

If TiCl_4 fume is in danger of affecting adjacent areas, then a decision must be taken on potential evacuation of such areas. Wind direction and weather conditions influence these decisions. The worst conditions for dispersion would be on a still, damp day when there is a temperature inversion.

5.2.8 Evacuation

A large, uncontrolled spillage of TiCl_4 may require total site evacuation if the safety of persons remote from the incident cannot be ensured by selective evacuation. This should entail total shutdown and evacuation of the site, followed by roll call and may involve additional emergency measures by the local authorities.

Alternatively, for on-site personnel, suitably designed toxic refuges may be provided.

Note also, depending on location, there may be significant off-site impact due to a visible cloud / fog resulting from a spillage of TiCl_4 .

5.3 Transport Emergencies

5.3.1 General Points

The general points outlined in Section 4 also apply for emergencies during transport. However, for an incident during transport the risks may be greater because: -

- a) The general public may be at risk.
- b) The spillage may be less controllable than at a factory site.
- c) The dense white fumes from a TiCl_4 leak may impair visibility and lead to secondary road traffic accidents (e.g., on a busy motorway).
- d) Emergency equipment available immediately at the scene is likely to be limited to that carried by the driver of the vehicle.
- e) The driver of the vehicle may be familiar with the product carried but is unlikely to have experience of dealing with an accident. At maximum, the driver will comply with the content of the document entitled "Instructions in writing" that he received from the haulier company. (refer § 5.4.3 of the ADR regulation).

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5.3.2 Instructions in Writing - Hazardous Chemical Information

Transport Emergency Cards (Tremcards) as carried under ADR regulations for all hazardous substances were replaced with "Instructions in Writing" in the 2009 edition of the ADR regulations - See ADR Regs Section 5.4.3 for more information.

"Instructions in Writing" as defined in ADR Regulations, contains basic information regarding a range of hazardous chemicals, this information can be used as an aid during an accident emergency situation.

Before the start of each road journey, the members of the vehicle crew shall inform themselves of the dangerous goods loaded, and consult the "Instructions in Writing" for details on actions to be taken in the event of an accident or emergency.

5.3.3 Control at the Scene of an Incident

The majority of countries have specific schemes involving the management of chemical transport incidents and this is controlled by the emergency services. The Emergency Services may call upon assistance from the chemical industry in the form of agreed schemes such as TUIS (Germany), CHEMSAFE (UK), TRANSAID (France) and DUCHEM Help (EMEA). The CEFIC TiCl₄ supply companies are members of such schemes.

Under the remit of the CEFIC I.C.E. initiative, the systems for emergency response (for all chemicals) are being upgraded and integrated across Europe and this will operate in parallel to any product specific agreements on providing assistance for TiCl₄.

CEFIC ICE website --> <http://www.cefic.org/Industry-support/Transport--logistics/Transport-Emergency-Scheme-/Transport-Emergency-Scheme/>

CEFIC has also developed emergency instructions providing guidance on the initial actions to be taken by fire brigades in case of chemical transport accidents. These instructions are called **Emergency Response Intervention Cards** (ERICards).

ERICards are currently available in 19 languages directly on corresponding website --> <http://www.ericards.net/>

The advice in the US 2012 Emergency Response Guidebook (published by the US Department of Transport) indicates that: -

For small spill (defined as < 200 litres), an initial isolation zone of 30m radius, and a protection zone of 0.1km (day) or 0.2km (night) downwind are to be established.

For large spills (defined as > 200 litres), the equivalent distances are an initial isolation zone of 30m radius, and a protection zone of 0.4km (day) or 0.7km (night).

SECTION 6 - CHEMICAL AND PHYSICAL PROPERTIES OF TiCl₄

6.1 General Information

CAS-No: 7550-45-0
EINECS-No: 231-441-9
IUPAC-Name: Titanium Tetrachloride

General Substance Information:

Molecular Formula: Ti Cl₄
Molecular Weight: 189.73
Substance Type: Inorganic
Physical Status: liquid
Typical Purity: >= 99% w/w

6.2 Typical Impurities

CAS-No.	EINECS-No.	IUPAC-Name	Value
13780-39-7	237-430-5	TiOCl ₂	<0.15% w/w
7646-78-8	231-588-9	SnCl ₄	<0.1% w/w
7647-01-0	231-595-7	HCl	<0.05% w/w
10026-04-7	233-054-0	SiCl ₄	<0.025% w/w
7446-70-0	231-208-1	AlCl ₃	<0.025% w/w
7784-34-1	232-059-5	AsCl ₃	<0.001% w/w
7705-08-0	231-729-4	FeCl ₃	<0.003% w/w
10213-09-9	233-517-7	VOCl ₂	<0.003% w/w
7758-89-6	231-842-9	CuCl ₂	<0.002% w/w
7773-01-5	231-869-6	MnCl ₂	<0.002% w/w
7719-12-2	231-749-3	PCl ₃	<0.001% w/w

6.3 Labelling and Classification - Labelling as in Directive 67/548/EEC is no longer in effect and has been replaced by Section 6.4

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6.4 Labelling as in regulation EC n° 1272/2008 Annex VI :

Symbols : toxic , corrosive, toxic by inhalation (GHS 06, 05 and 08)

Signal word = Danger

Hazard statements:

H330: Fatal if inhaled.

H314: Causes severe skin burns and eyes damages.

H370: Causes damage to lung following inhalation.

H372: Causes damage to lungs through prolonged or repeated exposure by inhalation.

EUH014: Reacts violently with water.

EUH071: Corrosive to the respiratory tract.

Precautionary Statements:

P260: Do not breathe dust/fume/gas/mist/vapours/spray.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P284: Wear respiratory protection.

P303+P361+P353 : If on skin (or hair): Remove/take-off immediately all contaminated clothing. Specific treatment: BEFORE rinsing with water, carefully wipe away with dry cloth until product is fully removed from skin. Rinse skin with water/shower.

P304 +P340: IF INHALED : Remove to fresh air and keep at rest in a position comfortable for breathing.

P402 + P404 :Store in dry place. Store in closed container.

P403: Store in a well-ventilated place.

6.5 Occupational Exposure Limit Values

Type of Limit MAK (D) (maximum work-place concentration (Germany))

Value 9.1 mg/m³

Short Term Exposure Limit Value

Value 18.2 mg/m³

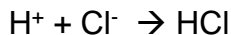
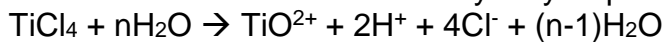
Time Schedule 5 min

Frequency 8 h.

Country: Germany

Remark:

MAK-value results from HCl as hydrolysis product:



7 mg HCl/m³ corresponds to 9.1 mg/m³ TiCl₄.

18.2 mg TiCl₄/m³ depending on the degree of hydrolysis.

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Type of Limit: Industrial Standard UK
Value: 0.5 mg/m³
Country: United Kingdom
Remark: Voluntary
Type of Limit Other: ERPG-1
(Emergency Response Planning Guideline)
Short Term Exposure Limit Value
Value: 5 mg/m³
Time Schedule: 1 h

Remark:
The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour.

Type of Limit Other: ERPG-2
Short Term Exposure Limit Value
Value: 20 mg/m³
Time Schedule: 1 h

Remark:
The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

Type of Limit other: ERPG-3
Short Term Exposure Limit Value
Value: 100 mg/m³
Time Schedule: 1 h

Remark:
The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

Type of Limit: EU OEL for HCL
Short Term Exposure Limit
Value: 15 mg/m³
Time Schedule: 15 minutes

Time Weighted Average
Value: 8 mg/m³
Time Schedule: 8 hours

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6.6 Source of Exposure

Under normal conditions no exposure as TiCl_4 is produced in a closed system. Each leakage results in a visible cloud containing HCl and TiOCl_2 .

6.7 Physico-Chemical Data

6.7.1 Melting Point

Value: -24.3 °C

6.7.2 Boiling Point

Value: 136.5 °C
Pressure: 1013 hPa

6.7.3 Density

Value: 1.71 - 1.73 g/cm³
Temperature: 20 °C

6.7.4 Vapour Pressure

Value: 12 hPa
Temperature: 20 °C

Remark:

Vapour pressure "p" [Torr] can be calculated by following equation:

$$\log p = -1764.65/T + 1.75 \log T - 0.000665T + 2.90055$$

range: 20 °C < temperature < 135 °C

6.8 Water Solubility

Decomposes in water with formation of clouds containing HCl and TiOCl_2 .

6.9 Environmental Fate and Pathways

6.9.1 Stability in Water

Degradation pH: 1 at 4°C: 100% after 0.1 minute

Reaction time depends on $\text{H}_2\text{O}/\text{TiCl}_4$ ratio as well as mixing intensity.

Result: Degradation products:

HCl (Solution) 7647-01-0

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6.10 Toxicity

6.10.1 Acute Oral Toxicity

Type: LD₁₀₀
Species: Rat
Value: 464mg/kg

6.10.2 Acute Inhalation Toxicity

Type: LC₅₀
Species: Rat

Exposure Time:	LC ₅₀		
	(1)	(2)	
4 h	0.46		mg/l
2 h	1.1	0.1	mg/l
1 h	1.3		mg/l
30 min	3.0		mg/l
15 min	5.5		mg/l
5 min	36.0		mg/l
2 min	108.0		mg/l

6.10.3 Acute Dermal Toxicity

Type: LD₅₀
Species: Rabbit
Value: 3610 mg/kg
Type: LD₀
Species: Rabbit
Value: 1000 mg/kg,

6.10.4 Reference

(6.10.1) Material Safety Data Sheet
TIT.514.S.Pittsburgh, Pa.: Stauffer Chemical Co. 1986

(6.10.2) (1) "Acute Inhalation Studies with Titanium Tetrachloride"
Haskell Laboratory Report No. 658-80, Date issued Oct. 31, 1980.

(6.10.2) (2) Izmerov, N.F., et al.: "Toxicometric Parameters of
Industrial Toxic Chemicals Under Single Exposure", Moscow, Center of
International Projects GKMT, 1982 -, 111,82

(6.10.3) Material Safety Data Sheet
TIT.514.S.Pittsburgh, Pa.: Stauffer Chemical Co. 1986

APPENDIX 1 - TYPICAL TRANSPORTABLE TANK SPECIFICATIONS

(Reference to proprietary equipment is **for example only and equivalent alternative equipment may be used**)

SPECIFICATION:

14,000 – 14,500 litres total capacity, maritime tank container IMO Type 1 or UN multi-modal portable tank T20 (or higher in accordance with requirements of Transportation Regulation for Dangerous Goods), with 6.67 bar (or higher) Maximum Allowable Working Pressure, 20' x 8' x 8' 6" Isotank frame, single compartment (with possibility of baffles), carbon steel or stainless steel tank for Titanium Tetrachloride ADR/RID/IMO UN 1838 6.1 (8) Packing Group I .

Capacity

Typically, 14,000 -14,500 litres nominal (or as required).

Material

Vessel: Carbon steel to BS1501-224-490A/B 10 mm thick barrel and heads (including 2 mm corrosion allowance)
Stainless Steel also possible (Please consult your TiCl₄ Supplier for Advice) SANS 50028-7 1.4402/ASME SA-240 316/316L, max carbon content 0.03%

Tubes: Carbon steel to API 5L

Flanges: Carbon steel to SA350 LF2.

Corrosion Allowance

2.0 mm on barrel, heads and other pressure bearing parts.

Tank Size

1,880 mm id x 4,500 mm barrel x 5,600mm over heads (to suit capacity).

Manhole

508mm diameter (20 inch) flat bolted ASA 150lb flanged manhole located at top longitudinal centre of tank or at the rear. Two lifting handles provided on blank flange.

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Fill/Empty

Top rear of tank fitted within a 3" NB x Sch 80 carbon steel tube and a carbon steel 3" ASA 150lb slip-on flange. A removable 2" NB x Sch 40 double flanged stackpipe in carbon steel extends to bottom sump. In series with stackpipe is a carbon steel 2" NB Ball or Plug valve terminating with a 2" ASA 150lb carbon steel blank flange. Connection will be fitted with a stainless steel label 'Fill/Empty' in 25mm high engraved letters filled black. Bottom stackpipe support bracket supplied. (Flange drillings will be off centres).

Remark: some Isotanks may have a dedicated filling port and a dedicated liquid outlet port, while others may have a unique port (with stackpipe used for both filling and discharging).

Vent

Forward of Fill/Empty is fitted 3" NB x Sch 80 carbon steel tube and a carbon steel 3" ASA 150lb slip-on flange. A 3" NB Ball or Plug valve with suitable joints fitted to flange. Termination is a 3" ASA 150lb carbon steel blank flange. Connection will be fitted with a stainless steel label 'Vent' in 25mm high engraved letters filled black. (Flange drillings will be off centres).

Nitrogen Pad

Forward of vent connection is fitted a 2" NB x Sch 80 carbon steel tube and a carbon steel 2" ASA 150lb slip-on flange. A 2" NB Ball or Plug valve. Termination is a 2" ASA 150lb carbon steel blank flange. Connection will be fitted with a stainless steel label 'Pad' in 25mm high engraved letters filled black. (Flange drillings will be off centres).

Remark: vent and nitrogen (dry air) pad may be the same port. In such case, a T shaped piece equipped with valves and fixed above the port will allow to separate both circuits. (nitrogen (dry air) inlet and vent outlet)

Pressure Relief

Manhole blank flange fitted with a 3" NB x Sch 80 tube and a 3" ASA 150lb flanged connection to receive a 2.5" Fort Vale stainless steel maxi-highflow pressure relief valve preceded by an 80mm composite inconel or Teflon lined rupture disc with stainless steel vacuum support.

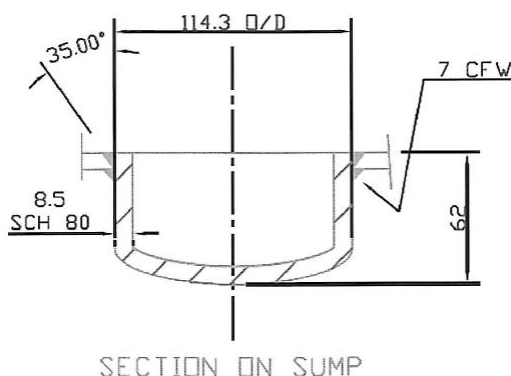
Rupture Disc set at 8.1 bar at 20°C and Relief Valve set at 7.3 bar for an Isotank having a Maximum Allowable Working Pressure (M.A.W.P) equal to 6.67 bar.

The Rupture Disc pressure always being set higher than your Relief Valve, so offering the Relief Valve protection until a fault (over pressure) condition is reached. Such setting is required by Regulations for Transportation of Dangerous Goods.

Sump

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4" NB x Sch 80 butt weld end cap forms sump beneath top Fill/Empty facility.



Walkway

Safe access to the container's top for filling and/or discharging process has to be in place. Consideration to be given to fall protection devices for Personnel who may require access to top of Isotank.

Iso Frame & Mounting

20' x 8' x 8'6" Series One ISO 1496/3 frame constructed from structural hollow steel EN 10219 S355 J2H. Rear end frame fitted with special label plate.

Ladder

Incorporated in nearside frame. Two grab handles provided adjacent to ladder.

Tank Finish

All seams butt welded and ground to even bead internally and left as welded externally with spatter removed. Bottom 400 mm of circumferential seams dressed flush with parent metal for tank drainage.

HAZCHEM Holder/Warning Label

Front, rear and each side of tank fitted with a 3 mm thick stainless steel HAZCHEM holder with plate for warning label. (All labels supplied and fixed by client). HAZCHEM plate to be supplied un-drilled.

Typical size of the Hazchem plate = 1125 mm (horizontal) x 560 mm (vertical)

Design Pressure

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Higher or at least equal to 6.67 bar internal.

Calculation Pressure

10 bar for ADR to comply with T20 Tank Specification
Minimum thickness weld joint factor 1.0 for heads and 1.0 for barrel.

Test Pressure: (example of a T20 tank)

Tank tested to: 10 bar hydraulic.

Max. Working Pressure: 6.67 bar

Design Temperature: - 40 to 130 °C

Radiography

All welded seams subjected to 100 % x-ray

Design Code: ASME Section VIII Division 1.

Painting

Tank and frame shot blasted to SA 2 ½ then painted with a suitable external corrosion protection system to suit the tanks working environment.

Frame Testing

Each end frame will be subjected to a stretch test in accordance with International Convention for Safe Containers (ICSC) requirements.

Bolting

All bolting will be carbon steel to BS EN 20898-1 Grade 8.8.

Document Holder

3" diameter x 12" long polypropylene document holder fitted behind nameplate bracket.

Earthing Pin

Lower nearside of frame fitted with a brass earthing pin.

Gaskets: See 1.2.1.10

Insurance Inspection: 3rd Party Authorised Inspection Agency.

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Code Requirements

ISO, ADR/RID/IMDG, UIC, CSC

Tare: 5,840 kgs approximately.

MGW: 30,480 kgs.

APPENDIX 2 - INSPECTION GUIDELINES

INTRODUCTION

These guidelines are intended to supplement the International Maritime Dangerous Goods (IMDG) Code and the European Agreement on the Carriage of Dangerous Goods by Road/Rail (ADR/RID). Should these guidelines conflict with the requirements of either of these Codes, then the Code will take precedence.

In countries where there are government requirements for safety at work (such as those of the UK's Health and Safety Executive), these requirements must be adhered to in all cases. In particular, there may be special precautions to be taken in carrying out air leak tests.

2.5 YEAR INSPECTION

Tank Shell

The tank should be visually inspected internally to check for signs of contact damage, cracking, indentation, pitting or other corrosion or any other signs of weakness. Before entering the tank, the surveyor should satisfy himself that the tank is clean and free from odour. The surveyor should insist on a valid gas-free and cleanliness certificate before entering. Local regulations should be complied with regarding "Confined Space Entry"

Particular attention should be paid to the following areas:

- Any indentations on shell or frame.
- Welds, for porosity, cracks, etc.
- Inside the tank at the points/areas where the frame is anchored to the shell, for distortion and possible cracking.
- The ullage level opening, for corrosion.
- Welding where internal baffles meet the shell for cracking.
- Throughout, for deep scratches or surface imperfections due to abrasion.
- Throughout, for pitting, chemical attack, breakdown of surface finish.

If the surveyor is in any doubt, non-destructive testing such as dye penetrant inspection should be carried out.

The Tanks exterior should be examined in the same manner.

Safety Advice for Storage and Handling of Anhydrous Titanium Tetrachloride

Any product found inside or adhering to the exterior of the tank should be reported on an attachment sheet, "Tank requires cleaning internally (externally)".

Having passed internal and external visual inspection, the tank should be subjected to a hydraulic leakage test.

5 YEAR INSPECTION

In addition to the inspection program performed during the 2.5 years inspection, an hydraulic test must be performed every 5 years.

Hydraulic Test

A hydraulic test should be conducted to the full test pressure of the tank. The water should not be too cold as water starts to expand as the temperature falls below 4 °C.

The pressure should be maintained for a minimum of 30 minutes without loss. Check for leakage around the tank. It should be noted that where rain water has been trapped inside the tank cladding it can drip out over a period of time. Consequently, the hydraulic test should, if possible, be performed on the tank after it has been under shelter.

When the tank has been emptied, the remainder of the inspection can be carried out. This should include a low pressure (1 bar) pneumatic leakage test as specified, in addition to the hydraulic test.

Ultrasonic thickness measurements may be conducted at the surveyor's discretion should he deem it necessary. Random thickness measurements are recommended on all tanks aged more than ten years where pitting and scoring is observed.

Equipment

All discharge filling valves should be stripped, cleaned, overhauled, refitted and checked for correct type and operation.

Joint surfaces on all openings should be visually checked and new gaskets installed.

Frangible (bursting) discs should be replaced with discs of the same design and pressure rating.

Relief Valves

Pressure Relief valves should be tested on a separate test rig, having a current calibration certificate. The pressure should be increased gradually and the "start-to-discharge" pressure noted.

This should be within +/- 10% of Set Pressure.

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Remark: for $TiCl_4$ there are normally no vacuum relief valves on Isotanks.

After the relief valve has opened, the air supply should be closed, and the pressure at which the relief valve closes again should be noted. This pressure should be not less than 90% of the "start-to-discharge" pressure. The integrity of the closed relief valve should be tested with a soap solution.

Pressure relief valves should be adjusted so that they are fully open, i.e., discharging at their maximum capacity, at 10 % above the maximum working pressure of the tank.

Frame

The frame should be checked for indentation or deformation. Any cracks, splits, punctures or excessive corrosion damage should be repaired. (See "Repairs" section below). Sharp indentations or dents deeper than 19mm (0.75") must be repaired. Deformed corner posts should be replaced. Deformed top or bottom beams, rails or struts must be repaired at the surveyor's discretion. Any frame damage resulting in deformation of the tank shell must be repaired.

Where a repair to a frame has been made without consultation in advance with the surveyor, or when un-documented repairs are observed, a note must be made on an attachment sheet to the inspection certificate in the form: "Frame found repaired" giving a brief description of the repair. Corrective action to maintain the integrity of the frame may be ordered by the surveyor at his discretion.

Box section end frame supports should be hammer checked for integrity, some types have no internal drainage or extra corrosion protection and internal corrosion can occur. Where repair is necessary, the entire box section should be replaced.

For skirt-mounted tanks, any deformation of the skirt necessitates replacement of the complete segment of the skirt to the existing welded butt joints. Small inserts are not acceptable.

RELIEF VALVE FLOW CAPACITIES

The total flow capacity required is specified in the IMDG Code Section 13.1.13.3. This table lists flow rates for un-insulated tanks according to the surface area of the tank.

TANK MARKINGS (Decals)

These should be legible and complete. Damaged or missing decals should be replaced in accordance with the owner's/operator's requirements.

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STAMPING THE DATA PLATES

Data plates are positioned in a variety of places depending on the model of tank. Any plates found to be missing must be replaced.

The marking on the plate should identify the month and year of the regulatory inspection in accordance with the policy on periodicity of inspections. For TiCl₄ the next inspection will be a 2.5 year, the date marked on the CSC (Container Safety Convention) plate should be exactly 2.5 years after the previous inspection, the date marked should be 2.5 years after the present date.

In addition, the tank manufacturer's plate should be marked with the date of the inspection.

The date of the next inspection should be marked in the form of three letters denoting the month (in English or French, as both are similar), followed by two numbers denoting the year. This should be followed by an A or H to denote whether the present inspection included Air or Hydraulic testing, and the stamp of the Inspection Body.

If the inspection was carried out following repair work on the tank shell, then this should be denoted by marking with the word "REPAIR". In this case the cycle of 2.5 year inspections should be re-started.

Example: DEC 92 H

REPAIRS

Tank Shell

Repairs should be carried out in accordance with the design code to which the tank was built. Where there is any doubt, repairs will be carried out according to the ASME VIII Code for pressure vessels.

Repairs

Surveyors should ensure that depots intending to repair Tank Containers have documented weld procedures and that welder qualification certificates are available.

Frame

All welding on frames must be carried out to British Standard 4870 (for carbon steel) by welders certified to BS4871, or equivalent.

Dents in frames greater than 19 mm (0.75") deep must be repaired.
All repairs must be checked by an appropriate NDT method.

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Corner Posts

Inserts in corner posts are only permitted to cover up to 25 % of the cross-section of the post. Both ends of any insert should be scarfed. The end of any insert should be more than 300 mm (12") from a corner casting. No more than two inserts are permitted in any corner post. Patches or doubler plates are not permitted.

If any repair exceeding these limits is required, then the entire corner post, including its top and bottom corner castings, must be replaced. In this case batch material and test certificates for the corner post used must be checked.

When major repairs are carried out to a number of corner posts it is recommended that at least one post be subjected to a tensile test of $0.5 \times R$.
 R = twice the maximum load (including the tare weight of the container).

Top Rails, Bottom Rails, Transverse Beams, etc.

Inserts or replaced beam sections should be scarfed wherever possible. Patches or doubler plates are not permitted except on the top near the corner castings (provided the puncture is evident) to repair and protect against pounding damage. Any sharp indentations or punctures must be repaired by replacing sections of the beam.

No more than two butt welds are permissible on one transverse top rail. No butt weld should be less than 300 mm (12") from any other weld.

Tank Mountings

Heating and fairing are only permitted on tank mountings where the deformation is less than 19mm (0.75"), otherwise the mounting must be replaced. Welding to the tank shell must be carried out according to the ASME VIII Code.

Frame Damage:	Maximum Tolerances Allowed
Corner posts:	19 mm on flat areas 19 mm on formed radii 6 mm on flat area or formed radii if within 300 mm of a corner casting. 19 mm bowed full length
Top rails (side):	19 mm bowed full length
Top beams (front and rear):	19 mm bowed full length
Bottom side rails:	19 mm on flat area or web 19 mm bowed full length

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Front bottom beam:	19 mm bowed full length 19 mm on flange surrounds
Rear bottom beam:	19 mm bowed full length
Bottom members:	19 mm bowed full length
Bolted	40 mm bowed full length or when against cladding and/or valves. 25 mm on brackets.
Side members:	19 mm bowed full length or when against cladding.
Top members:	19 mm bowed full length or when against cladding.
Ladder:	19 mm bowed full length
Walkways:	To be secure at all times.

QUALITY AT INSPECTION

Surveyors have a responsibility to advise on correct working practices on tank containers. Each Repairer should have a sign-off sheet for each tank. Surveyors cannot release a tank on their own authority. The tank should be released by the Repairer only when it has been signed off by the Insuring Company and by the Tank Cleanliness contractor.

IMPORTANT

Surveyors should always double-check the correct stamping of the tank plates. If there is a separate CSC (Container Safety Convention) plate it should always be stamped in addition to the manufacturer's data plate with the date when next inspection is due. The CSC plate is not stamped with the Insurers stamp.

In recent years regulatory authorities have placed increasing importance on the marking of the plates, and many tanks are detained in transit as a result of incorrect marking.

REMARK

Further information to establish a basic minimum tank condition throughout the industry, and to assist in maintaining the excellent safety record of the tank containers worldwide.

See International Tank Container Organisation's web site <http://www.international-tank-container.org/>

for latest publication of "Acceptable Container Condition" (ACC)

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APPENDIX 3 - PACKAGING PURCHASING SPECIFICATION

Packaging for Titanium tetrachloride must comply at minimum with the packing instruction

- P602 (ADR/RID 2015 issue) or
- § 173.227 for non-bulk packaging (US DoT CFR 49)

Drums complying with ADR/RID (2015 issue) Packing Instruction P602 sub-chapter 3 can still be used for transporting Titanium Tetrachloride. However, TDMA does not recommend this option.

Contact your product supplier for further information and details.

APPENDIX 4 - CLEANING PROCEDURES

We strongly recommend that a risk assessment and written method statement is available for all cleaning work of equipment that comes into contact with TiCl_4 . Further specific advice may be obtained from the TiCl_4 suppliers.

These procedures should cover the following aspects: -

- Personal protective equipment:
Type of gloves, eye and body protection, respiratory protective equipment
- Environmental protection
Use of vent system, water curtain, effluent collecting and cleaning
- Prerequisite for cleaning
Draining of equipment, disconnection of equipment from the plant, dismantling, connection to vent system, complying with written method statement
- Cleaning
In compliance with the written method statement one should consider the possibility of residual TiCl_4 being present

Typical Tank Cleaning Procedure:

1. Empty the tank as completely as possible and ensure it is at atmospheric pressure.
2. Gauge the remaining amount in the tank with a rigid metallic dip rod. The height of the wetted part can be translated into a corresponding volume of TiCl_4 , taking into account the dimensional characteristics of the tank.
3. If the wetted height is above 20 - 25mm, complete the emptying of the tank.
4. The estimated volume of the remaining amount of TiCl_4 can then be translated into an equivalent HCl amount.
5. Prepare (in composite IBC or other tank) an amount of caustic soda (NaOH typically 23%) sufficient to neutralise the equivalent HCl amount, in order to have a targeted pH after neutralisation of around 8 - 9. (This avoiding acidic corrosion of the tank internals during cleaning)

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6. Open manhole located on the top of the tank and install a hygiene suction hose routed to a suitable scrubber unit. (Specifically designed for TiCl_4 maintenance work and emergencies)
7. Start scrubber and check the gas suction flow, if suction sufficient proceed further.
8. Put in place the NaOH inlet hose/pipe and the water inlet hose.
9. Introduce rapidly the prepared amount of caustic and then the water.
10. Stop the water addition when the tank is 90% full.
11. Check the pH, add more caustic if acidic until pH is around 8 - 9.
12. Empty completely the tank contents to the waste liquid effluent drain.
13. Refill the tank with water (rinsing) to 95% and re-check pH.
14. If needed, repeat the cycle of emptying/rinsing until neutral pH is reached.
15. When the pH is neutral, empty the tank completely as possible.
16. Complete entering-permit procedure including atmosphere control.
17. One operator (with adequate PPE and safety harness) enters the tank to finish the cleaning and emptying, while a second person remains outside the tank to watch over him.

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APPENDIX 5 - DESIGN SPECIFICATIONS PORTABLE TANKERS

International Maritime Dangerous Goods (IMDG)
European agreement on the transportation dangerous goods by road (ADR)

Summary of T Codes				
Portable Tank Instructions				
T1 - T22				T1 - T22
These portable tank instructions apply to liquid and solid substances of classes 3 to 9. The general provisions of IMDG Sections 4.2.1 and the requirements of Section 6.7.2 shall be met.				
Portable tank instruction	Minimum test pressure (bar)	Minimum shell thickness (in mm-reference steel) (see IMDG 6.7.2.4)	Pressure-relief requirements (see IMDG 6.7.2.8)	Bottom opening requirements (see IMDG 6.7.2.6)
T1	1.5	>or = 6mm	normal	int + ext
T2	1.5	>or = 6mm	normal	int+ext+cap/blank
T3	2.65	>or = 6mm	normal	int + ext
T4	2.65	>or = 6mm	normal	int+ext+cap/blank
T5	2.65	>or = 6mm	normal + rupture disc	not allowed
T6	4	>or = 6mm	normal	int + ext
T7	4	>or = 6mm	normal	int+ext+cap/blank
T8	4	>or = 6mm	normal + rupture disc	not allowed
T9	4	6mm	normal	not allowed
T10	4	6mm	normal + rupture disc	not allowed
T11	6	>or = 6mm	normal	int+ext+cap/blank
T12	6	>or = 6mm	normal + rupture disc	int+ext+cap/blank
T13	6	6mm	normal	not allowed
T14	6	6mm	normal + rupture disc	not allowed
T15	10	>or = 6mm	normal	int+ext+cap/blank
T16	10	>or = 6mm	normal + rupture disc	int+ext+cap/blank
T17	10	6mm	normal	int+ext+cap/blank
T18	10	6mm	normal + rupture disc	int+ext+cap/blank
T19	10	6mm	normal + rupture disc	not allowed
T20	10	8mm	normal + rupture disc	not allowed
T21	10	10mm	normal	not allowed
T22	10	10mm	normal + rupture disc	not allowed



Table 1

The portable tank instructions as per Table 1 specify the requirements applicable to a UN portable tank when used for the transportation of a specific hazardous material. The T Code- portable tank instruction - specifies the applicable minimum test pressure, the minimum shell thickness (in reference steel – see IMDG Section 6.7.2.4), bottom opening requirements and pressure relief equipment's.

Since January 1. 2011, the EU Classification of Titanium Tetrachloride has been amended from Hazard Classification 8 (Corrosive) Packing Group II, to Hazard Classification 6.1 (Toxic) Subgroup 8 (Corrosive) Packing Group I (refer Issue 2011 of ADR and RID Regulations). This re-classification was entered in the January 1. 2012 version of the IMDG. To comply with these new Classification amendments, the new portable tank instruction for Titanium Tetrachloride has become T 20 as a minimum requirement.

The 2011, 2013 and 2015 versions of ADR, RID and IMDG also specify, in the special provision TP37, that :

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[TP37 Portable tank instruction T14 may continue to be applied until 31 December 2016 except that until that date:

- (a) For UN Nos. 1810, 2474 and 2668, T7 may be applied;
- (b) For UN No. 2486, T8 may be applied; and
- (c) For UN No. 1838, T10 may be applied.

Knowing that ADR/RID and IMDG regulations are subject to revision on a two years' basis, the reader is strongly advised to refer to the latest version of these regulations.

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APPENDIX 6 - DESIGN CODE REQUIREMENTS TO ADR (2015 issue)

UN No.	Name and description	Class	Classification code	Packing group	Labels	Special provisions	Limited and excepted quantities		Packaging			Portable tanks and bulk containers	
							3.4.6	3.5.1.2	Packing instructions 4.1.4	Special packing provisions 4.1.4	Mixed packing provisions 4.1.10	Instructions 4.2.5.2 7.3.2	Special provisions 4.2.5.3
(1)	(2)	(3a)	(3b)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9a)	(9b)	(10)	(11)
1838	TITANIUM TETRACHLORIDE	6.1	TC3	I	6.1 +8	354	0	E0	P602		MP8 MP17	T20	TP2 TP37

ADR tank		Vehicle for tank carriage	Transport category (Tunnel restriction code)	Special provisions for carriage				Hazard identification No.	UN No.	Name and description
Tank code	Special provisions			Packages	Bulk	Loading, unloading and handling	Operation			
(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(1)	(2)
4.3	4.3.5, 6.8.4	9.1.1.2	1.1.3.6 (8.6)	7.2.4	7.3.3	7.5.11	8.5	5.3.2.3		3.1.2
L10CH	TU14 TU15 TE19 TE21	AT	1 (CD)			CV1 CV13 CV28	S9 S14	X668	1838	TITANIUM TETRACHLORIDE

Table 2

Whereas the meaning of the columns are as follows:

- (1) UN Number: 1838
- (2) Name of Substance: Titanium Tetrachloride
- (3a) Hazard Class: 6.1 (Toxic)
- (3b) Classification Code T : toxic, C3: Acid Substances (C1-C4), Inorganic Liquid
- (4) Packing Group: I, Substances Presenting High Danger
- (5) Labels: 6.1 + 8
- (6) Special Provision 354 means: "This substance is toxic by inhalation".
- (7a): Specifies maximum amount which can be transported under "Limited quantities" conditions . For UN 1838 it is zero.
- (7b): Specifies maximum amount which can be transported under "Excepted quantities" conditions . For UN 1838 it is zero.
- (8): Packing instruction = P602. specifies requirements for the packaging.
- (9): The absence of IBC xx instruction means that IBC even made of steel, are not authorized for transporting this substance.
- (10) Portable Tank Instructions: T 20 – see table 1
- (11) Special provisions: TP 2 – specifies “Degree of Filling”
TP37 means " previous instruction T10 may continue to be applied until 31 December 2016 for the portable tanks in use before 1 January 2011.
- (12) Tank Code L10CH
Type of Tank L=tank for substances in the liquid stage
Calc pressure 10=minimum calculation pressure in bar
Openings C=tank with top-filling and discharge openings with only cleaning openings below the surface of the liquid.

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Safety Devices H=hermetically closed tank (see ADR §1.2.1).

Remark 1 : the here above tank code and portable tank instruction are the required minima. Any higher level material according table 1 for portable tank code or according the rationalized approach specified in ADR for ADR tanks, may be used.

Remark 2: The tank code displayed in column 12 is L10CH.
However, TDMA recommends to use tank code L10DH for UN 1838, where D means "tank with top-filling and discharge openings with no openings below the surface of the liquid." (cf. ADR § 4.3.4.1.1.)