

Fourth Edition
May 2011

Guidance on Storage and Handling of Chlorinated Solvents

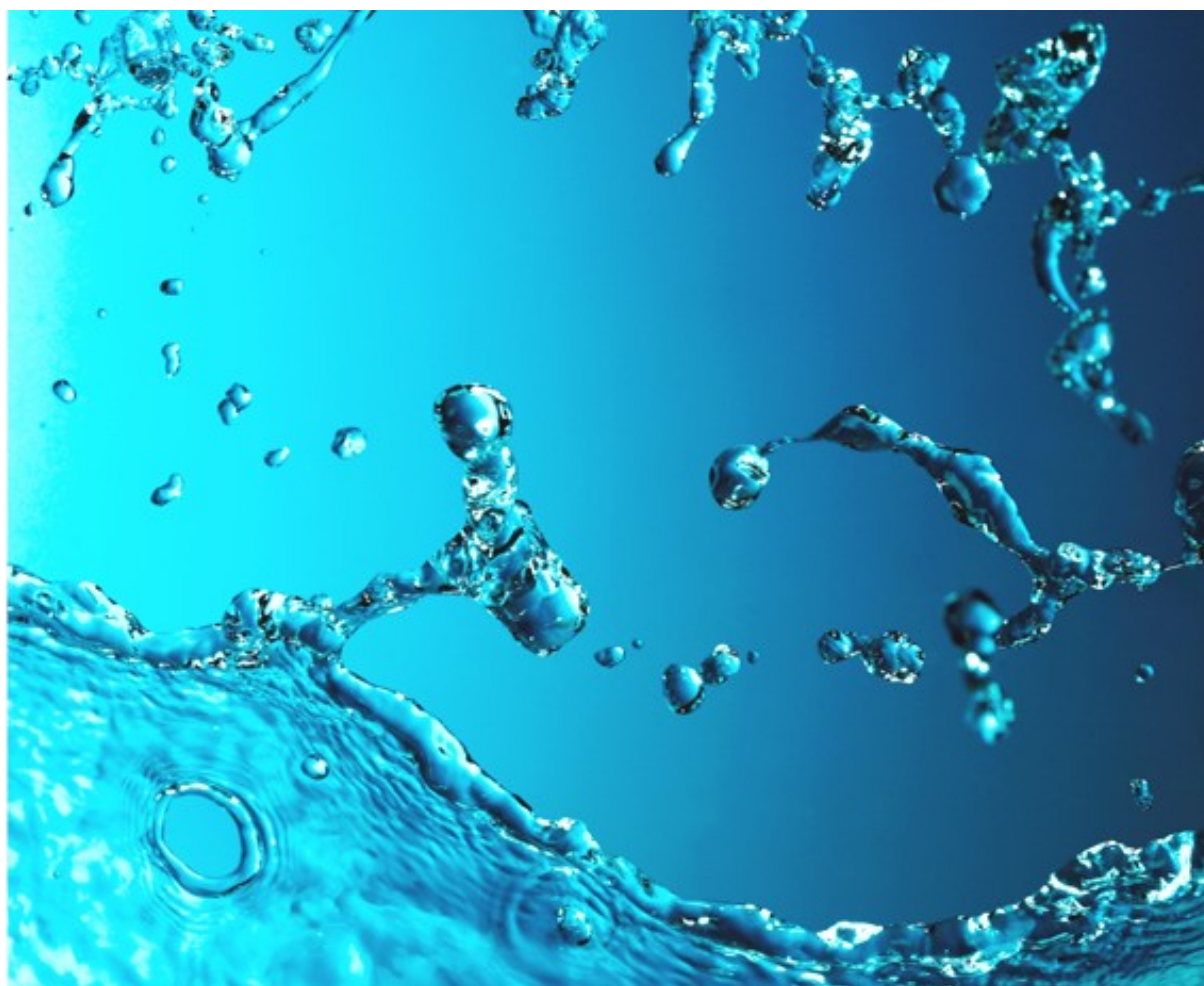


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INTRODUCTION TO THE 4th EDITION

The chlorinated solvents **Methylene Chloride (Dichloromethane, DCM)**, **Perchloroethylene (PER)** and **Trichloroethylene (TRI)**, can, if not handled and used in the proper way, pose certain risks to human health and the environment.

This guidance, produced by ECSA is intended to help distributors and users of chlorinated solvents to handle those products safely and with care, thus protecting man and nature against possible negative impact.

As the main issues, this guidance deals with:

- Construction and operation of bulk storage facilities and the handling of drums.
- Precautions to be taken.
- Relevant European regulations, impacting the use of chlorinated solvents.

Since the issue of the 2nd edition of this guidance, in 1988, significant changes have taken place regarding regulations on the use of chlorinated solvents in Europe. Since the issue of the 3rd edition of this guidance, in 2000, additional care has been taken to illustrate modern equipment in surface and dry cleaning for a safe & sustainable use of chlorinated solvents. In this 4th edition the storage part of this guidance has been adapted with recommendations to the use of state-of-the-art equipment.

The recommendations provided in this guidance are based on the understanding and experience of the chlorinated solvents producers in their respective countries and the European Union at the date of issue of this document. In some locations more stringent measures may be necessary and these recommendations are in no way intended as a substitute for the relevant national or international regulations which should be consulted and respected. This document is established in good faith and should be used as a guide to be consulted and which may be modified in the future to take technical progress into account.

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Important Note:

ECSA is not in the resource position to regularly follow the evolution of all the national regulations and standards listed below and to update the listing accordingly.

It is also important to note that a regulation with respect to the handling and use of solvent is different from country to country and sometimes even from region to region within countries. In addition, regulations are often not specific to Chlorinated Solvents but apply for solvents in general.

Therefore, it is strongly recommended to contact the authorities before building any installation for, or starting any operation with, Chlorinated Solvents.

ABBREVIATIONS

BS	British Standard
CHC	Chlorinated hydrocarbon solvent (often used instead of chlorinated solvent)
CS	Chlorinated solvent (often used instead of CHC)
DIN	Deutsche Industrie Norm (German Standard)
EN	European Standard
ECSA	European Chlorinated Solvent Association
PTFE	Polytetrafluoroethylene

1. STORAGE

Chlorinated solvents need special attention to avoid ground contamination and structural damage because of their high specific gravity and low surface tension (see A.1.). Tanks shall be of suitable design and material, visibly in good condition and well maintained. They shall have a double wall or be erected in a chlorinated solvent tight basin of adequate design, material and retention capacity. Wall thickness measurements shall be done on a regular base. For double wall tanks it is recommended to monitor wall space for leakage detection.

Packed material (in drums, small containers) shall only be stored in areas where contamination of the ground is protected, unless special safety packaging (e.g. double walled safety containers) is used.

1.1. RECOMMENDED MATERIALS FOR THE CONSTRUCTION OF STORAGE VESSELS

1.1.1. Bulk tanks and small containers

Carbon steel of welded construction is the usual material for storage and handling of chlorinated solvents in bulk tanks. If rust contamination can not be tolerated, an appropriate grade of stainless steel may be preferred; hot-dip galvanised steel (though not steel galvanised by electroplating or spraying) should be suitable, or a coating may be applied to the steel.

Section 1.2.2.1. should be consulted for details.

1.1.2. Drums

Carbon steel is generally suited for drums.

Product contamination can be controlled by using a special solvent-resistant coating, but a loss of integrity of the coating by mechanical deformation of drums may give problems in view of quality requirements. Galvanised steel, in particular steel galvanised by electroplating or spraying is not recommended.

Aluminium, magnesium and their alloys should not be used in chlorinated solvents service. Plastics are not generally suitable for bulk chlorinated solvents service, but may be acceptable for very small one-way containers as long as their suitability has been specially proven (most of today's generally used plastic containers are regarded as not suitable).

Reconditioned metal drums are not recommended for use with chlorinated solvents, as undiscovered material defects could increase the risk for spills.

1.2. BULK STORAGE OF CHLORINATED SOLVENTS

1.2.1. General Requirements

The individual product quality of the chlorinated solvents (CHCs) will determine the materials of construction to be used. Freshly produced, stabilized, and dry CHCs are not corrosive and require less material investments than contaminated CHCs. In case of regenerated substances, the quality of the product will determine the materials of construction to be used.

All parts of plants and protective installations have to be able to endure the projected mechanical, thermal and chemical stresses. They have to meet the following basic standards:

- Containers and pipelines must be designed to endure the static fluid pressures as well as over- and under pressures encountered during operations. They have to be resistant to external mechanical stresses. Adequate structural design and resistance qualifications are required.

- The materials must be impervious against and resistant to the liquid chlorinated hydrocarbons and their vapours.

In contact with water some CHCs tend to hydrolyse slowly, causing formation of acid (HCl) and thus corrosion of metals. Most CHCs are stabilised against acid formation by the manufacturers. However, depending on the use, regular analytical control may be recommended.

For the bulk storage of CHCs ECSA strongly recommends to respect the following conditions:

- The substance is free of water and acid (HCl); see the delivery specification of the manufacturer.
- Transport & (un)loading should be done under nitrogen blanket to exclude moisture. If moisture could enter into the tank via seals or valves, it should be blanketed by slight overpressure of nitrogen.
- The temperature of the bulk liquid during transport and storage should not exceed 30 °C.

1.2.2. Storage Tanks

This chapter lists European (and where available also national) standards. The national standards given are considered examples only. It is recommended by ECSA that further national standards and practices are investigated and consulted by users of chlorinated solvents on a needs basis.

1.2.2.1. Tanks for Storage Above Ground

For design, fabrication, testing and service of tanks including accessories the requirements of legal regulations for flammable liquids and legal regulations for water contaminating media have to be considered.

1.2.2.1.1. Without Containment

Double-walled storage tanks with leakage indicator:

- EN 12285-2 Workshop fabricated steel tanks. Horizontal cylindrical single skin and double skin tanks for the aboveground storage of flammable and non-flammable water polluting liquids
- DIN 66232 Vertical double-wall steel tanks with less than 1000 litre capacity, for the above ground storage of flammable and non-flammable water polluting liquids
- DIN 6624-2 Horizontal double-wall steel tanks with capacities between 1000 and 5000 litres, for the above ground storage of flammable and non-flammable water polluting liquids

1.2.2.1.2. With Containment

Single-walled tanks:

- EN 12285-2 Workshop fabricated steel tanks. Horizontal cylindrical single skin and double skin tanks for the aboveground storage of flammable and non-flammable water polluting liquids
- DIN 6618 - 1 Vertical single-wall steel tanks for the above ground storage of flammable and non-flammable water polluting liquids - DIN 6623 - 1 Vertical single-wall steel tanks with less than 1000 litre capacity, for the above ground storage of flammable and non-flammable water polluting liquids

- DIN 6624 - 1 Horizontal single-wall steel tanks with capacities between 1000 and 5000 litres, for the above ground storage of flammable and non-flammable water polluting liquids
- DIN 4119-1 Above-ground Cylindrical Flat-bottomed Tank Installations of Metallic Materials; Fundamentals, Design, Tests

Note:

Flat-bottom tanks according to DIN 4119 should have a double bottom together with a leak detector. Flat bottom tanks without double bottoms should be erected in a way (e.g. lifting on steel members) that leaks at the bottom may be detected by a visual inspection. (Remark: this note depends on requirements of different local country codes).

- BS 5500 Specification for unfired fusion welded pressure vessels (applies to pressure vessels and
- BS 2594 Specification for carbon steel welded horizontal cylindrical storage tanks (applies to low pressure tanks).
- BS 2654 would be used for large capacity storage tanks and requires full support of flat-bottomed tanks which precludes inspection underneath (cf. DIN 4119-1 above)

1.2.2.1.3. Containment materials

Metals suitable for construction of containment in chlorinated solvents service are steel, according to EN 10025 respectively EN 10028-2 and stainless steel, according to EN 10088-3.

For containment of concrete construction, a concrete of minimum BII quality according to EN 1992 and local codes is needed. Local regulations and requirements will govern the choice of surface protection for the concrete.

1.2.2.1. Suitable Materials of Construction

1.2.2.1.1. Metals

The following table contains recommendations as developed by the German Chemical Industry Association (VCI) together with the German Chemical Distributor Association (VCH) for their common guidance on handling of chlorinated solvents¹. The table has been re-edited by ECSA to reflect the replacement of DIN standards by EN Standards and the changes in material designations in accordance with EU standards.

¹ Verband der Chemischen Industrie, Verband Chemiehandel, *Innerbetrieblicher Umgang mit leichtflüchtigen chlorierten Kohlenwasserstoffen, Boden- und Umweltschutz*, 2nd edition, 1990

Materials		
Material Type (referenced EN standard)	Material No. (EN10027-2 ¹⁾)	Designation (EN10027-1 ²⁾)
General purpose construction steels (EN 10025-1 ³⁾)	1.0036 1.0038 1.0038/ 1.0116 1.0553/ 1.0570	S235JRG1 S235JRG2 S235JRG2/G3 S355JO/J2G3
Weather-resistant construction steels (EN 10025-5 ³⁾) (#) these materials have been part of the original standard SEW 087 but have not been taken over into the replacing EN standard	1.8960(#) 1.8961 1.8963	S235JRW (#) S235J2W S355J2G1W
Boiler steel sheets (EN 10028-2 ⁵⁾)	1.0345 1.0425 1.0481	P235GH P265GH P295GH
Weldable fine grain steels (EN 10028-3 ⁶⁾) (*) these materials have been part of the original standard DIN 17102 but have not been taken over into the replacing EN standard	1.0461, 1.0486	S255N (*) P275N
	1.0505 1.0562	P315N (*) P355N
Corrosion resisting steels (EN 10088-3 ⁷⁾)	1.4541 1.4571	X6CrNiTi18-10 X6CrNiMoTi17-12-2
	1.4306 1.4404	X2CrNi19-11 X2CrNiMo17-12-2

¹ EN 10027-2: Designation systems for steel - Part 2: Numerical system

² EN 10027-1: Designation systems for steels - Part 1: Steel names

³ EN 10025-1: Hot rolled products of structural steels - Part 1: General technical delivery conditions

⁴ EN 10025-5: Hot rolled products of structural steels - Part 5: Technical delivery conditions for structural steels with improved atmospheric corrosion resistance (former EN 10155, former SEW087)

⁵ EN 10028-2: Flat products made of steels for pressure purposes - Part 2: Non-alloy and alloy steels with specified elevated temperature properties.

⁶ EN 10028-3: Flat products made of steels for pressure purposes - Part 3: Weldable fine grain steels, normalized (former DIN 17102).

⁷ EN 10088-3: Stainless steels - Part 3: Technical delivery conditions for semi-finished products, bars, rods, wire, sections and bright products of corrosion resisting steels for general purposes (former DIN 17440).

In addition to the recommendations in the table above, there might be national recommendations / guidances. ECSA recommends that you check for national recommendations / guidances or rules in order to ensure you stay in full legal compliance.

Examples for such additional national recommendation are e.g. the

- DIN 6601² - listing suitable materials for the construction of CHC storage tanks.
- BAM List³ - a list established and published by the German Federal Institute for Materials Research and Testing, BAM.

1.2.2.1.2. Plastics

Plastics as materials for tanks are generally not suitable because they do not meet certain basic requirements, such as vapour tightness (permeability) and resistance to chemicals, under continuous exposure to CHCs.

If, in special cases, plastics are proposed for installation in new constructions, the suitability has to be proved by the supplier of the material or an expert, and a qualification approval has to be obtained from the authorities.

1.2.2.2. Construction of Storage Tanks

The design calculation should be based on the specific gravity of the material to be stored.

Carbon steel is generally satisfactory but stainless steel can be used in special cases where high quality and purity of the product is demanded (for tank materials see 1.2.2.1., for coating of the tank see 1.2.2.2.1.).

Steel sheets are to be butt-welded, i.e. without overlapping.

If the tank is to be lined inside, welding should ground smooth in order to have a regular surface. 10% X-ray control of the welding [plus 100 % dye penetration test, if required] is recommended, otherwise according to design specifications.

Tanks must be hydraulically tested in accordance with the terms laid down in the design specification.

Heat absorption and resulting vapour losses can be minimised by using light reflecting paint on the outside of the tank.

Tanks must be clean, dry, and free from grease and carefully checked before being put into service.

1.2.2.2.1. Coating of the Tank

Rust contamination of the solvent can be avoided by using a solvent-resistant inner coating. Special coatings such as high baked phenolics give good results as do zinc silicate coatings. Ease of repair should be considered when selecting the type of coating. Smaller tanks or containers can be made of hot dip-galvanised steel (steel galvanised by spraying or electro-plating is not recommended). In any case a certificate of the suitability of the coating should be obtained from the supplier/manufacturer.

1.2.2.2.2. Standardized Storage Tanks

Steel tanks are often available in standard designs for the storage of flammable liquids, however their individual suitability would need to be proved if they are to be used in chlorinated solvents service. It is

² DIN 6601- *Beständigkeit der Werkstoffe von Behältern (Tanks) aus Stahl gegenüber Flüssigkeiten (Positiv-Flüssigkeitsliste)* [Resistance of materials of steel tanks against liquids (positiv-list of liquids)], (currently revision of April 2007, only available in German), DIN Deutsches Institut für Normung e.V. Berlin, Germany (<http://www.din.de>). All standards of DIN are published exclusively by the Beuth Verlag GmbH, Berlin, Germany (<http://www.beuth.de>)

³ BAM List - *Requirements for tanks for the carriage of dangerous goods*, BAM - Bundesanstalt für Materialforschung und -prüfung [German Federal Institute for Materials Research and Testing]; (<http://www.bam.de>)

especially important to take into account the large density difference between chlorinated solvents and other common solvents like hydrocarbons, alcohols or esters.

These storage tanks are not made to any definite design specification and are usually of very low pressure design. Since they do not provide design specifications and drawings, these types of tanks are not normally recommended for chlorinated solvents.

1.2.2.3. Location of Storage Tanks

In order to minimise the risk of unnoticed leakage, storage tanks should be sited above ground and as close as is reasonably possible to the vehicle delivery point, providing easy access for the delivery vehicle.

Tanks and vehicle delivery area must be sited on containment to avoid escape of any spill or leakage to the environment (see 1.2.3.1.).

Tanks should be located away from traffic and from any source of heat or flames or from flammable materials, and secured against impact of moving vehicles (road tankers, fork-lifts, etc.).

Where space permits, tanks should be located so that an incident on one tank does not affect adjacent tanks (domino affect). This is particularly the case for other flammable chemicals.

Plant permits and specific national or local regulations on fire security, water and ground protection should be carefully checked.

Provisions must be made to keep unauthorized people out of the storage area.

1.2.2.3.1. *Pressure rating of tanks*

Transfer of chlorinated solvents by air pressure requires that both receiving and delivery tanks are suitably pressure rated. As a pressure surge at the end of unloading by air pressure can cause problems of over-pressurisation and often leads to excessive atmospheric losses, discharge should preferably be completed by means of a pump.

1.2.2.3.2. *Second-hand tanks*

Before a second-hand tank is purchased and put in operation, detailed drawings and technical data are needed to check its suitability for the intended chlorinated solvents service. The tank should also be designed and constructed to withstand any sub-atmospheric pressures when removing liquid from the tank (pressure during emptying depends on vent size, etc).

1.2.3. Safety devices

A number of important safety devices are incorporated to warn of failures and to avoid damages. Their purpose is especially to prevent leakage of CHCs and they include: containment to collect drips and leaks, leakage indicators, laminations, external sealings, liquid level indicators, exhaust installations, high level trip and high and low level alarms.

1.2.3.1. Containment

1.2.3.1.1. *General*

In case of failure or spillage, chlorinated solvents must not be allowed to contaminate the ground or any local water course.

A bund or catchment area, capable of holding the total volume of the largest tank involved, would provide appropriate protection for the environment. For installations which can hold only minor quantities, such as drum storage and containers, drip pans should be used to contain drips or spillages. Drip pans should be tight, sufficiently resistant, and water- and CHC-proof.

Containment installations must not have floor gullies or other openings discharging directly into the environment. They have to be equipped with devices for the removal of liquids. After correct identification these liquids may be removed by a pump. Design of the sump should be such as to allow safe removal and treatment of rain water whilst retaining the higher density solvent for subsequent handling.

Where regular (minor) spills are difficult to avoid, e.g. at loading / unloading facilities, drumming / de-drumming stations, a full enclosure is needed to ensure that spills can be collected separately and that they will not enter the surface water drainage system.

Concepts of containment and materials of construction for containments are often described in national storage and handling regulations for CHCs.

1.2.3.1.2. *Containment made of metal*

Steel and stainless steel of types suitable for chlorinated solvents service, may be used (see table in 1.2.2.1).

The following precautions against corrosion should be considered:

- Protection from water and other liquids
- Leakage detection and control
- Suitable laminates.

CHC-resistant materials which have proved to be suitable are available for laminates (see 1.2.3.1.3). An official certificate of the suitability of any metal coating should be requested from the supplier/manufacturer.

1.2.3.1.3. *Containment made of concrete*

Unprotected concrete surfaces, including waterproof concrete, are not impervious to CHCs, therefore concrete requires, when necessary, the application of a surface protection, allowing the covering of capillary cracks, to render it impervious to CHCs.

Expansion- and differential settlement-joints constitute special weak points and should be avoided as far as possible. Where they are mandatory for technical reasons, they should be constructed in such a way that deformation of joint strips and the sealing material will not impair the tightness of installation. Joints should be inspected regularly and deficiencies repaired immediately.

Suitable surface protections for concrete include:

- linings of sheet metals (see 1.2.3.1.2) or plastic sheeting
- laminates (see below).

1.2.3.1.3.1. Laminates on concrete

For CHC-proof laminates a suitable quality of concrete is required, for example A.1.2.1.3).

CHC-proof laminates are based on:

- phenolic resins or;
- furan resins.

In addition, one form of epoxy resin has passed the rigorous tests for CHC-proof laminate.

Other substances are either considered not sufficiently impervious to CHCs or are suited for certain CHCs only.

Furan resin laminates may contain chemical modifiers to overcome cracking by improving their plasticity. However modifiers reduce chemical durability; this is of special importance with Methylene Chloride.

Furan resins cannot be used as sealing materials in joints due to their limited plasticity.

To obtain sufficient durability, phenolic or furan resins have to be combined with glass fiber mats. Elastic intermediate layers are required to cover and fill cracks in the concrete, e.g.

- layers of elastomers (e.g. polyisobutylene, several rubber products);
- layers on a bituminous basis;
- so-called liquid foils, which are poured on the concrete and when hardened will form an elastic layer (e.g. polyurethane)

The CHC-impervious laminate is then applied on the top of the elastic intermediate layer.

If resistance to considerable mechanical wear is required of this laminate, then a cover must be applied, e.g. of tiles in a mortar bed.

Duroplastics should be processed in coordination with the manufacturer and installed only by expert and sufficiently experienced companies.

1.2.3.1.3.2. Sub-surface protection of concrete

Concrete construction may require an additional protection from below against moisture and aggressive subsoils. This protection prevents vapours from creeping behind the laminate and detaching it from the concrete.

In cases of non-cohesive soils and low groundwater-level, a capillary moisture stop of coarse gravel will be sufficient as a base for the concrete.

The following multi-layer construction will provide improved protection: An approximately 5-10 cm thick concrete layer is placed on the soil and covered with a barrier of elastomeric layers (e.g. polyisobutylene, various derivatives of rubber) or with bitumen. Then the actual concrete construction is built on these layers.

1.2.3.1.4. Containment made of Plastics

In general, ECSA does not recommend the use of plastic containment for Chlorinated Solvents.

Plastics considered to be suitable for chlorinated solvents should have an official approval certificate.

1.2.3.2. Leakage Control Equipment for double-walled Tanks

The following systems are state of the art for chlorinated solvents stored in double-walled tanks:

- Liquid level indicator systems:

A leak in the wall of the tank is indicated by lowering of the level in the leakage indicator liquid container.

- Overpressure systems:

A leak in the tank wall is indicated by a pressure increase in the control space.

Any suitable leakage indicator may be used. Leakage control equipment requires regular checks of correct functioning. The instructions of the manufacturer for installation, adjustment and maintenance have to be followed.

1.2.3.3. Leakage Sensors for Bunds

Leakage sensors may be used for bunds.

1.2.3.4. High and Low Level Alarm/Trip for Tanks

A high level alarm linked to a “shut-off valve” is recommended to discontinue the filling process of a tank before the maximum permissible filling level is exceeded. If a pump is used to fill the tank then the high level alarm could also be set to trip the pump.

If a pump is used for the removal of solvents from a stock tank then a low flow trip could stop the pump; if an alarm is incorporated then there will be advance notice that the tank is nearly empty. These devices would prevent damage to the pump arising from dry running.

1.2.3.5. Liquid Level Indicator

Liquid level indicators are necessary for the storage tanks for CHCs.

When combined with an optic or acoustic alarm, the liquid level indicator may serve as a fill control against overfilling. The liquid level indicator should preferably not be a sight glass because of the risk of accidental breakage. In case a sight glass is in place, it has to be of a caged and impact resistant type.

1.2.3.6. Sealing Material

Table 1 presents a survey on the CHC-resistance of plastics for laminates and sealings.

Note:

This compilation is given as orientation for basic selection and based on general experience. However, it is recommended to obtain approval from the manufacturer of the material for the suitability of an individual material in contact with a specific Chlorinated Solvent.

Table 1: Resistance of plastic laminates and sealings to chlorinated solvents *

Duroplastics		Thermoplastics		Natural and synthetic elastomers	
Resistant ¹⁾	Non-resistant ²⁾	Resistant ¹⁾	Non-resistant ²⁾	Resistant ¹⁾	Non-resistant ²⁾
Furan resins phenol-cresol resins	Most EP-resins (epoxy resins) cold/hot hardened	PTFE (poly-tetrafluoroethylene)	PIB (polyisobutylene)	FCM (fluoro-rubber)	NR (polyisoprene)
phenol resins cresol resins					
		PFEP (poly-fluoroethylene propylene)	PVC (poly-vinylchloride)		SBR (styrene butadiene copolymer)
	PUR resins (polyurethane resins)	PVDF (poly- vinylidene fluoride)	HDPE / LDPE (high + low density polyethylene)		NBR (acrylonitrile-butadiene-copolymer)
	UP resins (unsaturated polyester resins)	Other fluoro- synthetics (copolymers)	PP (polypropylene)		CR (poly-chlorobutadiene)
			PC (polycarbonate)		IIR (isobutylene-isoprene copolymer)
Exception					
vinyl-ester resins ³⁾ towards PER	vinylester-resins ³⁾ towards DCM			thiokol (polysulphide rubber) towards PER	Rubber
TRI					CSM (chloro-sulfonated polyethylene)
Range of application					
concrete laminates		metal laminates (containers, pumps, fittings, pipelines)		Sealings (containers, pumps, fittings, pipelines)	
sealing of clay-concrete pipes		sealings, linings			
joint sealings				joint sealings	

Notes:

^{1), 2)} Chemical resistance/ impermeability: Information is based on tests with pure solvents.

Other results in the resistance of plastics may be observed if mixtures of solvents are stored or transported.

In these cases specific user-oriented tests should be made.

³⁾ The varying data for trichloroethylene were furnished by different manufacturers of vinyl ester resins.

ECSA recommends to check particular national guidances or rules in order to ensure you are in full legal compliance e.g. the BAM List⁴ on approved materials for tank containers and portable tanks designed for the carriage of dangerous goods.

⁴ *BAM List - Requirements for tanks for the carriage of dangerous goods*, BAM [Federal Institute for Materials Research and Testing], Berlin, Germany.

1.2.3.7. Other Tank Accessories

1.2.3.7.1 *Manholes*

Manholes should be fitted to larger tanks in order to facilitate inspection and cleaning; manholes should be sized for the entry of a man equipped with self-contained breathing apparatus, and should be sited in the vapour space of the tank. (See also Chapter 6).

1.2.3.7.2 *Atmospheric Vent Dryer*

The atmospheric vent of the tank should be fitted with an air dryer in order to prevent moisture from entering the storage tank and to minimise corrosion of exposed internal metal surfaces. An air dryer may use as a drying agent the anhydrous forms, e.g. silica gel (re-usable), calcium sulphate or calcium chloride; caustic soda flakes (sodium hydroxide) are incompatible as they decompose chlorinated solvents. A non-return valve in the dryer line may be helpful to prevent the dryer from becoming saturated with solvent fumes when filling the tank.

1.2.3.7.3 *Pressure-Vacuum Relief Valve*

A pressure-vacuum relief valve should be fitted and should be of stainless steel, cast iron or brass to avoid oxidation. It prevents damage to the tank, should the vent become blocked. Tank design and the pressure/vacuum setting of the valve should be compatible. Consideration should be given to the provision of an emergency relief vent.

Maintenance of a dry nitrogen blanket over chlorinated hydrocarbons in the tank may be helpful to maintain product quality.

1.2.3.8. Vent Gas Treatment

When unloading by gravity or pumping, chlorinated solvent vapours should be kept inside the system by connecting the vapour-phase of the tank to be filled to the vapour phase of the tank or vehicle to be emptied, i.e. a closed system operation.

If vent gases containing chlorinated solvents cannot be kept inside the system, they may be treated by:

- adsorption, e.g. on activated carbon or on resins; for big gas streams, an absorber that can be regenerated is recommended; the adsorbed chlorinated solvents would then be recovered and the adsorbent would be reactivated for re-use. A one-way cartridge can be used to treat the breathing of the tanks;
- incineration with adequate flue gas treatment;
- vent scrubber (if traces of aqueous hydrochloric acid need to be removed).

1.2.3.9. Related Equipment

1.2.3.9.1. *Filters*

A filter, e.g. cartridge or basket type, made of materials compatible with chlorinated solvents will be helpful in maintaining product quality by catching particles (abrasion, rust). The mesh size needs to be adapted to the desired retention requirements, taking into account the flow rate of the liquid and the pressure requirements. Filters should be equipped with pressure indicators at in the in- and outlet to notice unacceptable pressure drop by blocking of the filter.

1.2.3.9.2. *Pumps*

Centrifugal pumps of cast iron or steel construction are recommended, as are canned (hermetic) type pumps or pumps having mechanical seals (solvent resistant).

Pumps have to be placed inside a CHC-resistant containment (see 1.2.3.1.).

(<http://www.bam.de>)

1.2.3.9.3. Gaskets

Gaskets must be solvent resistant. Suitable materials include fluoro rubbers, PTFE or carbon fibre. Specialised gasket suppliers will be able to recommend the right product for each solvent and application.

1.2.3.9.4. Valves

Valves can be of stainless steel, cast steel or brass. Ball valves should have a PTFE seat. Where throttling is necessary, globe valves may be used; globe valves should have a metal seat. PTFE diaphragm valves are also acceptable but not for stock tank isolation.

1.2.3.9.5. Meters

Meters should not have any aluminium, magnesium or zinc component, nor any alloys of these metals. Brass is acceptable.

1.2.4. Pipelines

Pipelines are rigid or flexible lines including elbows and fittings. Underground pipelines should be the exception and they require special precautions; they must be constructed as a jacketed pipe system with leakage alarm system for the outer space. Pipelines should be installed with a slight fall to ensure drainage. Relief valves should be considered to prevent damage due to thermal expansion where the pipe run is long and could become full of liquid.

1.2.4.1. Steel Pipelines

Piping may be of carbon steel or stainless steel

1.2.4.1.1. Steel types suitable for pipelines are:

EN Standards		Steel types	
		Material # EN10027-2	Designation EN10027-1
Seamless pipes	EN10216 ¹⁾	1.0254; 1.0421	P235TR1 P355T1
	EN 10088-3 ²⁾	1.0405 1.0305(#) 1.4541 1.4571	P255 G1 TH P235 G1 TH(#) X6CrNiTi18-10 X6CrNiMoTi17-12-2
Welded pipes	EN 10217 ³⁾	1.0254; 1.0256; 1.0421 1.0315 (*); 1.0498	P235TR1 P275T1 P355T1 P235G2TH (*) P255G2TH
	ISO 1127	1.4541 1.4571	X6CrNiTi18-10 X6CrNiMoTi17-12-2

#) was referenced in withdrawn DIN 17175, not further referenced in EN 10216-2 replacing DIN 17175

*) was referenced in withdrawn DIN 17177, not further referenced in EN 10217-2 replacing DIN 17177

- 1) EN 10216 part 1 to 5: Seamless steel tubes for pressure purposes - Technical delivery conditions
- 2) EN 10088-3: Stainless steels - Part 3: Technical delivery conditions for semi-finished products, bars, rods, wire, sections and bright products of corrosion resisting steels for general purposes
- 3) EN 10217 part 1 to 7: Welded steel tubes for pressure purposes - Technical delivery conditions
- 4) EN ISO 1127: Stainless steel tubes - Dimensions, tolerances and conventional masses per unit length (takes over DIN 2463-1)

The following types of steel may be used for adaptors and prefabricated parts:

- same as in Table above
- made of sheet steel

e.g. material P255GH, EN 10028-2 with inspection certificate 3.1 B, EN 10204

- cast steel

e.g. material GS-C 25 (material-#: 1.0619), **EN 10213-2**
with inspection certificate 3.1 after EN 10204

Pipe connections

Since pipe connections are one of the weak points of pipelines, they should be reduced to a minimum, although this should not unnecessarily obstruct maintenance.. Connections between pipe sections are usually either welded or flanged. Slip-on socket and soldered connections are not acceptable for service with CHCs. Sealing materials for flanged connections are given in Table 1, Section 1.2.3.6. Only bolts with quality certificates and appropriate test marks are acceptable. Suitable chemical-resistant gasketing materials shall be used (see 1.2.3.9.3).

All welding is to be carried out only by qualified welders.

All shut-off devices in these pipelines should be easily accessible and functioning; they should be supported if they would cause overloading of the pipe.

Fabrication and erection

Fabrication and erection of pipelines should be in compliance with local regulations.

The external walls of the pipeline and supports shall be protected against corrosion by a priming coat followed by a coat of paint or by a suitable jacket (e.g. plastic).

If pipelines are underground they have to be double-walled. Special devices (over- or underpressure, control of inner space between pipe and jacket) are used to detect leakage.

1.2.4.2. Pipelines made of Plastics

Pipelines for CHCs made of plastics are only suitable for above-ground installation and in any case have limited durability. They should be designed for total drainage and due note should be taken of their susceptibility to mechanical damage.

Chemically resistant against CHCs and to be used under certain conditions are:

- PTFE (polytetrafluoroethylene)
- PFEP (polyfluoroethylenepropylene)
- PCTFE (polychlorotrifluoroethylene) and ECTFE (ethylene-chlorotrifluoroethylene-fluorocopolymer)

- PVDF (polyvinylidene fluoride)

As plastic materials tend to lose mechanical properties at elevated temperatures, it is generally not recommended to use any sort of plastic piping for Chlorinated Solvents above ambient temperature.

Local regulations should be followed for the design and construction of fibre-reinforced plastic (FRP) pipelines. In general, such pipelines are not recommended for chlorinated solvents.

2. UNLOADING OF BULK SOLVENT

Note: Operators involved in the unloading of Chlorinated Solvents should be trained and in the possession of written guidances and procedures.

Chlorinated solvents are transported in bulk in rail and road tankers and in ISO containers of various volumes.

There are three methods of unloading from these bulk transport containers:

- Gravity

Gravity flow is used to unload into a customer's pump or to a storage tank at a lower level. Gravity unloading is uncommon today since most storage facilities are nowadays located above ground.

- Pumping

Pumping discharge includes the situation where the pump is part of the road tanker, as well as with a pump at the receiver's site. For safety reasons, the use of positive displacement pumps is not recommended for discharging chlorinated solvents. Centrifugal pumps are recommended, in particular those with magnetic transmission.

- Air pressure

For safety and environmental reasons (no vapour return possible) discharging by air pressure is not recommended.

2.1. SOLVENT SAMPLING

Because ionic materials, moisture and other contaminants usually cannot be detected by visual inspection, the chlorinated solvents should be carefully sampled according to recommended procedures to avoid any further contamination of the sample.

The detailed analytical procedures for these solvents are available from the producers on request.

General guidances:

- Sealed sampling containers should be made of brown glass with metal lined or plastic screw caps compatible with the chlorinated solvents. If clear glass bottles are used, storage should be in the dark. Aluminium in any form should not be used for storing retained sample or for the screw cap.
- Glass thief tubes or siphons are preferred as sampling devices. Those made of metals (stainless steel or other metals except light metals and their alloys) may be used but are less satisfactory. Plastic is not recommended and rubber equipment must not be used.
- All sampling material must be clean (free from rust and grease) and dry.
- Underfill the container to allow for thermal expansion of the sample.
- Label the sample container properly.
- Store samples in tightly sealed containers in a cool place and away from direct sunlight.
- Sampling from tank or tank cars.

The analysis should be done before unloading. Any pressure in the vessel should be relieved prior to opening the manhole cover. Open the dome cover cautiously and avoid breathing vapours.

Obtain a sample by means of a lecture bottle under vacuum that sucks up the liquid via the gas phase opening or by immersing a clean glass container that has been securely wired to a stiff metal rod. Close the cover immediately. Samples may be also taken from a sampling point in the unloading line or pump.

- Sampling from storage tanks.

If sampling takes place after unloading, material should be withdrawn from the centre of the storage tank. Metal sample lines preferably of stainless steel may be used. Valves should have polytetrafluoroethylene packing to avoid contamination of the solvent.

Any sampling from a tanker or tank wagon should not expose the person to falls from height, therefore top sampling should only be carried out from fixed gantry or other safe means of access.

2.2. PREPARATION FOR UNLOADING

2.2.1. The unloading operations should be carried out only by properly trained employees under adequate supervision. The appropriate personal safety equipment, such as gloves and eye protection, must be worn.

2.2.2. The unloading point should be correctly labelled with:

- a) Type of solvent
- b) Method of unloading

Also labelling the discharge point with the UN number on an orange plate (to mimic that on the tanker) is recommended

2.2.3. The stock tank should also be labelled with the type of solvent stored. (Results of laboratory control should be available before unloading into storage tank in case supply contract does require analysis upon delivery).

2.2.4. Check that there is sufficient capacity in the stock tank to receive the full delivery.

2.2.5. Inspect the safety vent system on the storage tank to ensure that it will work properly and that it is not frozen or obstructed. To avoid vapour emissions to the atmosphere, a vapour return line should be installed between storage tank and tanker, through which the displaced air and vapour out of the storage tank is fed back into the tanker.

2.2.6. Rail and road tankers should be in a position where connections can be made quickly and easily, preferably on level ground. Precautions should be taken to ensure that any spillage or leakage is contained and that there is no contamination of drains, etc. Absorption of contained spills and leakages will keep evaporation to air at a minimum.

2.2.7. Emergency showers and eyewash fountains should be located in the unloading area in case of accidental skin or eye contact.

2.2.8. Unloading should preferably take place during daylight hours. When it is necessary to unload in the dark, adequate lighting should be provided.

2.3. UNLOADING HOSE

The requirements for flexible hoses are the same as for rigid pipelines, i.e. temperature and pressure ratings, as well as being chemically resistant.

Couplings and connections are weak points of flexible hoses as well as hose pipes and require a constant control.

Permanent, rigid pipelines are preferred to flexible hose because of the more secure connections. Interlocked, spiral-type hose should not be used since there will be solvent leakage through the packing. Hoses should be reinforced by steel spirals or meshed steel.

The following pipe materials are acceptable for chlorinated solvents:

- Seamless, flexible metal hose made of stainless steel (in which case it is important that moisture be excluded).
- PTFE-lined composite hose with internal and external wire reinforcement of Monel (or of stainless steel of appropriate grade), braided with PET polyester film laminate, and with chloroprene cotton fabric with nylon chloroprene outer cover.

Other types of linings that can be used are:

- vinyl hexafluoropropylene;
- tetrafluorethylene - fluoromethylene - vinylether;
- fluoro-rubber.

Hose should be ordered in the required lengths with fittings already installed by the manufacturers.

Manufacturers' advice on chemicals resistance should be followed.

All unloading hoses should be subjected to regular inspection and testing, and when not in use should be blanked to prevent ingress of dirt and moisture.

2.4. UNLOADING FROM RAIL TANKERS

The paperwork has to be checked before unloading to confirm that the correct chemical will be discharged into the correct tank.

2.4.1. Suitable stops should be placed on the rail to avoid collision between the rail wagon and other wagons which may be shunted on the discharging line. WARNING flags should be placed at appropriate points. A safety system may be installed, where possible, that closes the unloading valve in case of displacement of the rail tanker.

2.4.2. Set hand brake and block wheels with a brake shoe. However the brakes must be released before unloading commences or damage to the brake mechanism could occur due to the tanker rising during unloading.

2.4.3. If the discharge is to be made with compressed air then it is essential that a high pressure limit (often 1.3 bar (20 psig) but dependent on site conditions) is not exceeded. This can be accomplished by installing a pressure reducing valve and relief valve in the customer's air supply pipework.

2.4.4. Ensure that the internal plug valve is closed.

2.4.5. Connect the vapour return line to the vent valve. Open slowly the vent valve on top of the rail tanker to release any pressure or vacuum. Make sure that this valve remains open during the entire unloading period of delivery by gravity or by pumping.

2.4.6. Check that all liquid outlet valves are closed (ie the internal and the external one) and remove the blanking cap.

2.4.7. Connect the flexible hose to the tanker and to either the customer's pump or intake pipework.

2.4.8. Check the entire system for proper valve arrangement.

2.4.9. Open the external outlet valve on the tanker.

2.4.10. Open the internal outlet valve on the tanker.

2.4.11. Open the customer's intake valve and feed to the stock tank. If the delivery is pumped, start the pump.

2.4.12. Periodically check for leaks in pipes, hoses and connections during delivery. Collect any drips in metal cans.

The paperwork has to be completed.

2.5. UNLOADING FROM ROAD TANKERS

The paperwork has to be checked before unloading to confirm that the correct chemical will be discharged into the correct tank.

2.5.1. Barriers and flags should be positioned to warn personnel of the unloading. Brakes should be set and the wheels chocked. The truck should be earthed.

2.5.2. Carry out instructions as 2.4.4. to 2.4.10.

2.5.3. Open the customer's intake valve and feed to the stock tank.

If a pumped delivery is involved, start the pump.

2.5.4. Periodically check for leaks in pipes, hoses and connections during the delivery.

The paperwork has to be completed.

2.6. PROCEDURE AFTER UNLOADING

- Close the outlet valve.
- Disconnect and drain the delivery hose to a drum or other container to avoid any spillage. An unloading arm (rigid pipeline) can be left filled with solvent provided that it is properly valved and that suitable hydraulic protection is ensured. Disconnect the vapour return line.
- Close and secure the top valves and dome.
- Replace blanking caps to tanker and delivery pipework.
- Any spillage should be absorbed and disposed of properly in accordance with local regulations, to avoid contamination of water, air and ground.

3. TRANSFER FROM STORAGE TANK INTO SMALL TRANSPORT CONTAINERS

Transfer of chlorinated solvents from the storage tank to the point of use can be made in several ways depending on the transfer distance and the number of enduse points.

- Gravity
- Pumping
- Transport containers (which need to be closed during transport).

Each unloading pipe should be labelled with the name of the product.

3.1. MATERIALS FOR SMALL TRANSPORT CONTAINERS

Containers used for transport should be made of steel (cf. 1.2.2.1.) and should be kept tightly closed during transport.

Reconditioned metal drums are not recommended for use with chlorinated solvents since undiscovered material defects could increase the risk for spills. The containers should be inspected for cleanliness before use. Bungs and plugs should be fitted with gaskets chemically resistant to the solvent.

Use of special containers respectively drum storage areas are strongly recommended by ECSA for storage, transport and handling of chlorinated solvents and are obligatory in certain countries.

3.2. LEGAL REQUIREMENTS FOR SMALL TRANSPORT CONTAINERS

Any packaging (drums, IBCs, small containers up to 3 tonnes) used for transportation by road, rail, air and sea (ADR/RID/IATA/IMDG) shall have an appropriate UN packaging code suitable to the relevant solvent (e.g. UN 1A1/X1.2/250/...).

For non-returnable steel drums with non removable head (usually ca. 200 L volume) the general X type drum (UN 1A1/X1.2/250/...) is suited for liquids of packaging group III with a density of max 2.7 kg/l and vapour pressure of max. 250 kPa (= 2.5 bars) at 55 °C. The wall thickness (top, bottom, side walls) of the drums is recommended to be minimum 1.0 mm, preferably 1.2 mm. For hot climate zones drums with higher wall thickness might be required. Bulging of drums (even with higher wall thickness) has been observed in some cases (particularly bulging of top and bottom) if drums have been stored at significantly higher temperatures due to increasing vapour pressure and expanding liquid. This physical phenomenon usually does not affect the chemical quality of the solvents as long as the shelf-life is not exceeded.

The maximum volumetric filling grades of small transport containers (90 % for DCM, 92 % for TRI, and 94 % for PER) need to be observed, as well as other relevant provisions of the ADR, Annex A, Chapter 4.

Containers used for transport by road, rail, air and sea must bear the appropriate transport and chemicals labels according to international, European and national regulations (in particular after ADR/RID/IATA/IMDG and the CLP regulation⁵); if only used on site, the chemicals label is sufficient.

3.3. REPACKAGING

Drums and other transport containers are filled by

- volumetric measurement using a meter or dip stick, or by

⁵ REGULATION (EC) No 1272/2008 of 16 December 2008 on classification, labelling and packaging of substances and mixtures, and its amendments for the purposes of its adaptation to technical and scientific progress.

- weighing.

Filling pipe must be self-draining or have provision for draining.

Transfer of solvent from rail tanker, road tanker or tank installed above ground into small tanks/containers or drums should be done with appropriate ventilation. A closed filling system (emission free filling line with vapour return line) is preferred in order to prevent emissions and to protect workers.

Where drums/containers are sited and filled indoors openly (through the bung hole), the storage room should be well ventilated to prevent accumulation of solvent vapour displaced from the drum during filling or adequate point vapour extraction should be used; however, a closed filling system (emission free filling line with vapour return line) is preferred in order to prevent emissions and to protect workers best.

In addition adequate precautions should be taken during these operations to prevent soil and ground-water pollution. A steel retainer basin is the best way to achieve this and in some countries this is required.

Controls and switches for the pump, drum filler, etc. should be located with the convenience and safety of the operator in mind. An emergency stop of the total operation is recommended.

4. RECOMMENDATIONS FOR HANDLING DRUMS AND SMALL CONTAINERS

For handling storage and transport of chlorinated solvents, ECSA strongly encourage to use and promote special containers which as such assure in all cases safe handling, transport and storage of the chlorinated solvents by end-users (safety containers or equivalent closed loop systems). This is of special importance if storage and handling premises and equipment at the customer site are not specifically designed for safe handling and storage of chlorinated solvents (e.g. lack of ground protection measures, lack of substance specific training, lack of equipment to prevent air emissions).

4.1. STORAGE OF DRUMS

Drum storage facilities for chlorinated solvents should be segregated from other types of products, e.g. flammable solvents.

Drums should be stored in cool ventilated areas and be tightly closed when not in use. Storage facilities for filled drums (also for empty drums unless new or thoroughly cleaned) need to be protected against rain and other ingress of water to prevent contamination of the surface water drainage system.

Storage for sealed drums should be out of direct sunlight and remote from sources of heat to avoid generation of pressure. Drums should be stored at ground level and measures taken to prevent corrosion of the drum base. A retention basin of adequate design (made of chlorinated solvent tight material and with sufficient retention capacity) shall be in place.

If stacked one upon the other, drums should not be stacked more than two high unless they are empty. Storage outside the workroom is desirable although limited storage of a working supply in the workroom should be allowed.

Adequate ventilation must be available to ensure that in case of incidental release of solvent (vapour) the vapour concentration is as low as possible, and in any event within the regulatory requirements.

In certain countries there are requirements for a drip or leak retainer basin constructed of a solvent-impervious material such as steel.

Provision must be made to keep unauthorised persons out of the storage area.

4.2. DISPLACEMENT

Full drums should be handled with care and should not be moved without mechanical assistance. Rolling of 200-litre drums by hand with all the weight on the bottom rim is not recommended and should be avoided.

A portable tank on wheels or a skid is sometimes used to dispense solvent and this can be constructed of either stainless steel or mild steel, with a suitable lining if corrosion control is required. The unit should have its own permanently mounted pump, used exclusively for solvent transfers, and an adequate pressure relief valve. Any tank opening should have an attached cover to prevent accidental contamination of the unit. A drip retainer basin is recommended and may be required.

4.3. UNLOADING

Small containers (to about 25 kg) are readily emptied by hand. Removing the contents of 200-liter drums should be done by using a pump. Gravity unloading is possible but not recommended. Under no circumstances should a drum be emptied by using air pressure as the drum may burst.

To avoid soil contamination the drum to be emptied should be put on a metal grating over a metal drip pan or a collector pan of prefabricated polymer concrete. A retention basin of adequate design (made of chlorinated solvent tight material and with sufficient retention capacity) shall be in place.

4.3.1. Gravity unloading

Gravity unloading of drums is not recommended, because of a higher risk for spills and exposure. Pump unloading using secured dry connections and vapour return lines is preferred. Should notwithstanding gravity unloading be selected, the drum has to be fitted with a valve or draw-off faucet to facilitate unloading.

Protective clothing including goggles must be worn. Cautiously loosen the 1.8 cm bung just enough to allow drum to breathe, then carefully remove the bung and replace it by a suitable valve. The drum should be placed in a horizontal position and rotated until the 5 cm plug is aligned directly above the draw-off valve. While emptying the contents, the 5 cm plug should be slightly loosened to relieve the internal vacuum. It is also recommended to use a point vapour extraction to minimize exposure.

4.3.2. Pump unloading

Pump unloading is the preferred unloading method for drums. It is also suitable where the point of use is higher than the drum or portable container. The same precautions as in 4.3.1. apply to the opening of bungs when a drum is emptied by pumping.

Self-priming portable centrifugal pumps of adequate power (for instance having a ¼ to 1/3 h.p motor, being capable of delivering 40-120 liters per minute of 1.6 specific gravity liquid against a head of 6 m), are satisfactory. They can be placed directly on the bung head of the drum.

Either rigid piping or flexible solvent-resistant hose may be used. It is recommended to use fixed dry connections where ever possible to eliminate/minimize the risk of spills / exposure.

The use of special containers for solvent delivery instead of drums brings the advantage that the containers are already equipped with a permanently mounted pump, used exclusively for solvent transfers, an adequate pressure relief valve as well as dry connections and a drip container. In addition special containers are equipped with a skid for easy displacement. All this ensures a safe solvent transfer with lowest possible risks for spills and exposure. For the use of the special containers guidance issued by the supplier should be followed.

4.4. HANDLING OF EMPTY CONTAINERS

Before being returned, drums should be thoroughly drained, if possible also freed from vapours and then sealed with their original plugs.

Drums with remnant solvent can be disposed as hazardous waste according to waste regulations, but preferably should be returned to the supplier for re-use. Labelling must not be removed in this case.

Fully cleaned drums without remnant solvent or solvent vapour can be disposed off as simple waste according to the waste regulations, but preferably should be returned to the supplier for re-use.

TORCH CUTTING of drums that have been filled with halogenated solvents is hazardous (see A.2) and must not be permitted.

4.5. STORAGE OF DRUMS WITH SOLVENT WASTE

When storing waste solvents in drums/containers, it is advisable to ensure that they should not be tightly closed to avoid pressure build-up in case of uncontrolled reaction between waste products. An automatic fire extinguishing system should be installed in the waste storage area as uncontrolled reactions could cause a fire.

The same caution to avoid ground contamination as for the storage of fresh solvent should be applied. - Storage of drums with chlorinated solvent waste should be done in areas with impermeable floors and leakage containments, depending on local regulations this might be mandatory.

5. MAINTENANCE

General maintenance recommendations for all storage, handling and use installations / equipment

- 5.1. All equipment should be maintained and serviced according to the manufacturer's recommendations.
- 5.2. The entire storage system requires careful and regular visual inspection to detect any leakage as quickly as possible.
- 5.3. A small leak under pressure can result in solvent losses without any warning pool of liquid. A simple halide leak detector, such as is employed by refrigeration maintenance workers, can be used to check connections, valves, pump packing, and any other easily accessible parts of the system. **WARNING:** The halide detector employs a small propane gas flame or electric element, which may make it unsuitable for use in areas containing combustibles.
- 5.4. Be sure that all connections are painted with a material that will not be affected by the solvent. Several commonly used plant maintenance paints fall into this category.
- 5.5. As appropriate, a maintenance program should be put in place.

6. SAFETY PRECAUTIONS FOR TANK CLEANING AND REPAIRS

Tank cleaning and repairs should be performed by thoroughly trained/qualified personnel who are completely familiar with the hazards, safety precautions and equipment, and with the rescue and first aid procedures appropriate to chlorinated solvents.

Depending upon the state of contamination and/or need for repair in practice, cleaning/repair is carried out either by own qualified personnel or with the assistance of specialized cleaning/repair companies.

In addition to observing any relevant local regulations, the following precautions must be taken.

- 6.1.** Entry into tanks and working in them requires a work permit, to be signed by the supervisor.
- 6.2.** Isolate the tank from the circuit and prepare it for the cleaning/repair operation by locking-out power feeds, etc.
- 6.3.** Disconnect all in- and outgoing pipes of the tank after emptying and after closing the valves in question. Cover the ends of the pipes with a cap or a blind flange to protect against “human errors” or unsuspected leaks.
- 6.4.** Empty, dry and purge the tank of all solvent vapours. Warm air purging (1 to 2 days, observing local emission regulations) is suggested until tests with a solvent detector (e.g. Dräger tube or similar) indicate that it is safe.
Cleaning of the tank is carried out (after purging) by filling with water and draining.
Dirt is sprayed away from the walls by means of high-pressure water.
Rinsing water containing chlorinated solvents should be disposed of according to local regulations.
- 6.5.** Ventilate the tank during the entire cleaning or repairing operation, with proper attention to observing local air quality standards. In practice this is done by opening the inlet at the bottom of the tank and placing the ventilator on top of the manhole above the tank; in this way air is circulated through the tank. Do not use air from compressed air systems for this purpose.
- 6.6.** In case operators have to enter the tank during this cleaning, a qualified person has to determine that there is no oxygen deficiency. In principle, entering the tank should wait until the chlorinated solvent concentration has decreased below the national Occupational Exposure Level (OEL) value. If in exceptional situations the chlorinated solvent vapour concentration is higher than the Occupational Exposure Level value, fresh air masks or self-contained breathing equipment (air respirator) should be used.
- 6.7.** The people in the tank should be equipped with a rescue harness and lifeline. There must always be a qualified man outside at the manhole, who will keep the people in the tank under constant observation, and to get assistance in case of unforeseen emergency situations.
- 6.8.** An air respirator or self-contained breathing apparatus of which proper operation has been checked, together with a rescue harness and air-line should always be nearby, regardless of the type of respiration equipment or air supply inside the tank.
- 6.9.** Anyone entering the tank for rescue purposes should be equipped with an externally supplied air respiration.
- 6.10.** More specific local regulations and laws may be applicable.

7. Recommendations for Cleaning Machines for the use of Chlorinated Solvents in dry cleaning and surface cleaning

Recommendations for Cleaning Machines for the use of Chlorinated Solvents in Dry Cleaning and Surface Cleaning

The benefit to use modern closed cleaning machines

Chlorinated solvents (Perchloroethylene (PER), Trichloroethylene (TRI) and Dichloromethane (DCM)) are used since many decades as cleaning solvents in metal or more generally speaking surface cleaning. Perchloroethylene specifically, is also used since many decades as the major cleaning solvent in dry cleaning of textiles.

Over the last decades, since the mid 1980ies, cleaning machines have undergone a huge evolution from simple very basic equipment with high emissions to highly sophisticated, closed or sealed equipment as commercialized today. Modern machines are incorporating many innovations like

- equipment internal closed loop air flows with solvent abatement and regeneration
- continuous solvent recycling
- the use of vacuum technology in surface cleaning.

The use of modern cleaning machines has lead to a very strong decrease of emissions from over 150g of Perchloroethylene per kg of garments to less than 10g/kg in dry cleaning and from over 10kg/h to less than 20g/h in surface cleaning.

ECSA and its member companies are heavily supporting the development and market introduction of modern cleaning machines and have developed adequate solvent formulations and stabilisation packages to fit the requirements of modern machines. This allows to fully use the advantages of such equipment leading to a strongly extended life time of the solvent in the equipment. E.g. in surface cleaning, the life time of a machine filling with solvent could be extended from less than a month in simple equipment to up to 2 years of solvent performance and up to even more in modern equipment. This means that the cleaning efficiency of a solvent molecule could be increased by a factor of 20 and more. The cleaning efficiency of chlorinated solvents used in modern equipment is currently unmatched because of the unique recycling properties of chlorinated solvents. This heavily increases the eco-efficiency of the chlorinated solvents.

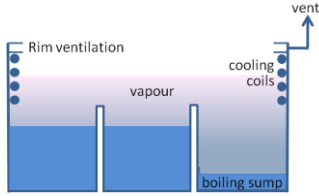
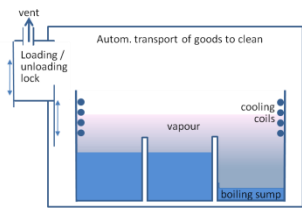
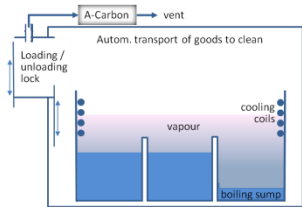
ECSCA strongly recommends the use of modern closed equipment of Best Available Technology (BAT). It is recommended to use at least 4th -Generation or higher for dry cleaning equipment. And it is recommended to use machines of at least type III or higher for surface cleaning⁶. These modern machines are designed to fulfil the emission requirements of the European VOC directive. Higher machine generations (dry cleaning) or machine types (surface cleaning) will not only contribute to reach legal compliance but also ensure the sustainable use of solvents in surface or textile cleaning by minimizing emissions and ensuring the safe handling, transfer and take-back of the solvent. The machines can easily be equipped for an emission free solvent transfer in combination with emission free delivery and take-back containers (closed loop safety containers). Modern BAT cleaning machines are available from all leading manufacturer of machines for surface or dry cleaning.

Review and description of the different cleaning machine generations and types

The development of the machines used in surface cleaning and dry cleaning is summarized in the following tables 1 and 2. The tables describe the different machine types / generations. The nomenclature follows for surface cleaning the nomenclature adopted by ECSCA in 2001 and for dry cleaning the nomenclature adopted by the Leonardo da Vinci E-DryClean training program (www.cinet-online.net/edryclean/), which has been prepared in partnership with ECSCA. Both tables give cross-references / equivalences to different nomenclature used in other documents.

⁶ For the use of Trichloroethylene (TRI) in surface cleaning confirmation of use in machines of type III or higher is a pre-condition for delivery. This voluntary commitment is fixed in the **ECSCA TRI Charter for the safe use of Trichloroethylene** (<http://www.eurochlor.org/index.asp?page=813>) which has been signed by producers and importer of TRI.

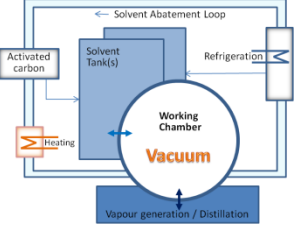
Table 1: Types / Generations of Surface Cleaning Machines

Current ECSA Nomenclature ¹⁾	Schematic Drawing	Key characteristic (Key improvement in red)	Legal compliance	Nomenclature Reference /equivalence in European Standard EN 12921-4 ³⁾	Nomenclature Reference /equivalence in J.von Grote, ETH Diss. #15067 of 2003 ⁴⁾
Type I Open Top		<ul style="list-style-type: none"> • Open Top • Rim ventilation • Cooling with water or Refrigerated cooling (2°C). • Typical air emission: between 1-16 kg/h, average 4.7 kg/h 		As “ Open top tank ” in Figure A.4 of Appendix A.	Water cooling: As Type I “open top water cooled”
					Refrigerated cooling: As Type II “open top electro- cooled”
Type IIa enclosed (vented directly to atmosphere)		<ul style="list-style-type: none"> • Encased (all side closed) • Vented Air lock for loading / unloading of goods • Refrigerated cooling • Automatic transport of goods • Typical air emission: 2.0 kg/h 		As “ Type II – enclosed open cleaning machine ” in Figure A.3 of appendix A.	As Type III “ encased machines”
Type IIb Enclosed & abatement (vented through external A-Carbon filter)		<ul style="list-style-type: none"> • As type IIa but with additional external A-carbon filter for solvent abatement from exhaust air. • Typical air emission: 1.0 kg/h 	<ul style="list-style-type: none"> • May fulfil German Emiss. Directive “2.BImSchV” in old Version of 1986 • May enable the fulfilment of limits set by EU-SED²⁾ directive 		

Type III Closed with internal air cleaning prior to opening		<ul style="list-style-type: none"> • Closed single chamber or use of a collection chamber (air-lock to seal against solvent bathe(s)) • Solvent abatement loop with refrigeration (<-20°C) to clean air prior to opening (<2g/m²) • Typical air emission: 155g/h 	<ul style="list-style-type: none"> • Generally fulfils requirements of German Emiss. Directive "2.BImSchV" . • Designed to comply with SED limits. 	Type I – sealed cleaning machines differentiated by Type Ia – Collection chamber systems Fig. A.1 of Appendix A. and Type Ib – Single chamber cleaning machine Fig. A.2 of Appendix A.	As Type IV "one chamber" machines
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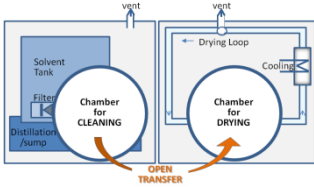
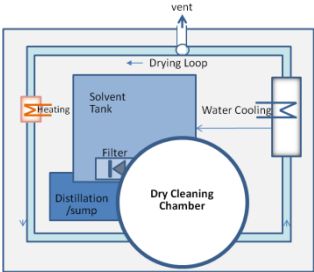
Table 1 (cont.): Types / Generations of Surface Cleaning Machines

Current ECSA Nomenclature ¹⁾	Schematic Drawing	Key characteristic (Key improvement in red)	Legal compliance	Nomenclature Reference /equivalence in European Standard EN 12921-4 ³⁾	Nomenclature Reference /equivalence in J. von Grote ⁴⁾
Type IV Closed with closed loop air drying without vent		<ul style="list-style-type: none"> • No exhaust air (Fully closed air loops) • Equipm. Internal A- carbon in addition to refrigeration. • Better drying also of goods with difficult shapes. • Typical air emission: 1-100 g/h, average about 38 g/h 	<ul style="list-style-type: none"> • Generally fulfils requirements of German Emiss. Directive "2.BImSchV" . • Designed to comply with SED limits. 	Not yet known to EN 12921-4	As Type V "closed loop drying one chamber" machines
Type V Closed without vent		<ul style="list-style-type: none"> • As type IV but with • Vacuum technology, keeping the working chamber and distillation 	<ul style="list-style-type: none"> • Generally fulfils requirements of German Emiss. Directive 	Not yet known to EN 12921-4	Was not yet known to the thesis

and operation under vacuum		under reduced pressure during operation <ul style="list-style-type: none"> • Improved drying • Reduced emissions • Reduced waste • Increased solvent life time (because of lower temperature) 	“2.BImSchV” . <ul style="list-style-type: none"> • Designed to comply with SED limits. 		
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- 1) first time used in ECSA publication: “Annex to Perchloroethylene Risk Assessment Report, ECSA Response to UK Environment Agency regarding Perchloroethylene Emission Reduction from the Solvent Emissions Directive (1999/13/EC), 30 April 2001”
- 2) EU Solvent Emission Directive (COUNCIL DIRECTIVE 1999/13/EC) also referenced sometimes as EU VOC Directive
- 3) EN 12921-4 “Machines for surface cleaning and pre-treatment of industrial items using liquids or vapours - Part 4: Safety of machines using halogenated solvents”
- 4) 4J. von Grote, Occupational Exposure Assessment in Metal Degreasing and Dry Cleaning – Influences of Technology Innovation and Legislation, Dissertation (no 15067), ETH Swiss Federal Institute of Technology Zurich, Zurich, Switzerland, 2003

Table 2: Types / Generations of Dry Cleaning Machines

Current ECSA Nomenclature	Schematic Drawing	Key characteristic (Key improvement in red)	Legal compliance	Nomenclature Leonardo da Vinci E-DryClean Training program ³⁾	Nomenclature Reference /equivalence in in ETH Dissertation of Julia van Grote ⁴⁾
1st Gen. Transfer Machines		<ul style="list-style-type: none"> • Separate equipment for cleaning and drying. • Open transfer of wet garments • Typical total PER consumption: ab. 300 to 500 g / kg textiles ³⁾ 		Same as current ECSA Nomenclature: 1st Generation machines	Same as current ECSA Nomenclature: 1st Generation machines
2nd Gen. dry-to-dry vented machines with water cooling		<ul style="list-style-type: none"> • Single equipment machines combining cleaning and drying in one equipment • Water cooling (15°C) in drying loop • Vented to atmosphere • Typical total Per consumption: ab. 100 to 150 g / kg textiles ³⁾ • Introduced in the late 1950s ³⁾ 		Same as current ECSA Nomenclature: 2nd Generation machines	Same as current ECSA Nomenclature: 2nd Generation machines
3rd Gen. Dry-to-dry vented machines		<ul style="list-style-type: none"> • As Generation II, but with • external activated carbon filter for post cleaning of 		Same as current ECSA Nomenclature:	Same as current ECSA

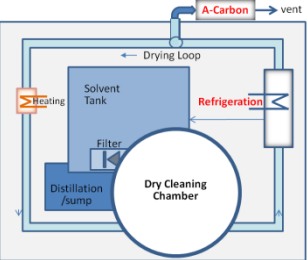
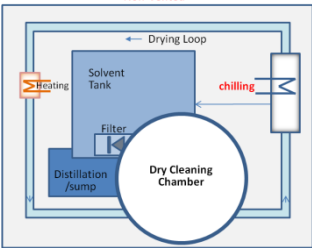
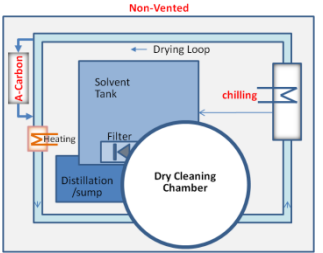
with refrigerated cooling and external activated carbon filter		<ul style="list-style-type: none"> vented air Water and later refrigerated cooling (ca.-15°C) in the Drying loop and Typical total Per consumption: ab. 40 to 80 g / kg textiles ³⁾ Introduced in the late 1960s, ³⁾ 		3rd Generation machines	Nomenclature: 3rd Generation machines
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Table 2 (cont.): Generations of Dry Cleaning Machines

Current ECSA Nomenclature	Schematic Drawing	Key characteristic (Key improvement in red)	Legal compliance	Nomenclature Leonardo da Vinci E-DryClean Training program ³⁾	Nomenclature Reference /equivalence in in ETH Dissertation of Julia van Grote ⁴⁾
4th Gen. Single equip., not vented, closed loop drying machines with chilling system for cooling		<ul style="list-style-type: none"> Single equipment Closed loop drying loop No vent Chilled cooling (-20°C) in drying loop Typical total Per consumption: 20 to 40 g / kg textiles ³⁾ Introduced in the early 1980s ³⁾ 	Designed to enable user to achieve emission limits set by the EU-SED ¹⁾	Same as current ECSA Nomenclature: 4th Generation machines	Same as current ECSA Nomenclature: 4th Generation machines
5th Gen. single equip., un- vented,		<ul style="list-style-type: none"> As Generation IV with in addition 	Designed to comply with the 2 nd		

<p>closed loop drying machines with chilling system + integrated A-carbon.</p>		<ul style="list-style-type: none"> • Activated carbon integrated in drying loop (to efficiently achieve residual concentration of 2g/m^3 after drying required by 2.BlmSchV of 1990) • Typical total Per consumption: $< 10\text{ g / kg textiles}$ ³⁾ • Developed in the late 1980s and introduced in the early 1990s ³⁾ 	<p>BlmSchV (German Emission Directive) of 1990 ²⁾</p> <p>Designed to enable user to achieve emission limits set by the EU-SED ¹⁾</p>	<p>Same as current ECSA Nomenclature: 5th Generation machines</p>	<p>Same as current ECSA Nomenclature: 5th Generation machines</p>
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- 1) EU Solvent Emission Directive (COUNCIL DIRECTIVE 1999/13/EC) also referenced sometimes as EU VOC Directive
- 2) German 2nd Federal Immission Protection Directive (2.BlmSchV, Zweite Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes, Verordnung zur Emissionsbegrenzung von leichtflüchtigen Halogenkohlenwasserstoffen) of 10.Dezember 1990.
- 3) Module 5 of "E-DryClean, Sustainable dry cleaning processing", a training program in six modules having as objective to improve and adapt the educational level of entrepreneurs and employees working in dry cleaning sectors across the European Union, CINET (Comité International de L'Entretien du Textile)
- 4) J. von Grote, Occupational Exposure Assessment in Metal Degreasing and Dry Cleaning – Influences of Technology Innovation and Legislation, Dissertation (no 15067), ETH Swiss Federal Institute of Technology Zurich, Zurich, Switzerland, 2003

APPENDICES

A.1. FLAMMABILITY AND DECOMPOSITION OF CHLORINATED SOLVENTS

Experience shows that there is usually no danger of fire or explosion when the chlorinated solvents are used under appropriate conditions.

The chlorinated solvents discussed here exhibit neither flash point nor fire point by standard methods, though with stabilized solvents under certain conditions and test procedures a flash point can be demonstrated (consult manufacturers for details). These solvents, except for perchloroethylene, do however have flammable limits in air (FLA), so that at certain concentrations of vapours of chlorinated solvents in air, these vapours might burn in contact with a source of high energy such as electric arc or oxyacetylene welding flame or a cutting torch. For this reason electrical equipment approved for use in hazardous locations is recommended for work in closed tanks, in accident situations or in locations where high concentrations of solvent vapour may accumulate. In addition: all tanks should be grounded (earthed).

The flammable limits in air (FLA), ignition energies and self ignition temperatures at atmospheric pressure are:

	Unit	Methylene Chloride	Trichloroethylene	Perchloroethylene
Lower flammability limit	% (v/v)	13	8	none (non-flammable)
Upper flammability limit	% (v/v)	22	45	none (non-flammable)
Minimum ignition energy	mJ	9100	510	n.a.
Self ignition temperature at a steel surface	°C	605	410	none

Note: the flammable limits in air will be different under pressure or in atmospheres with higher or lower oxygen fraction.

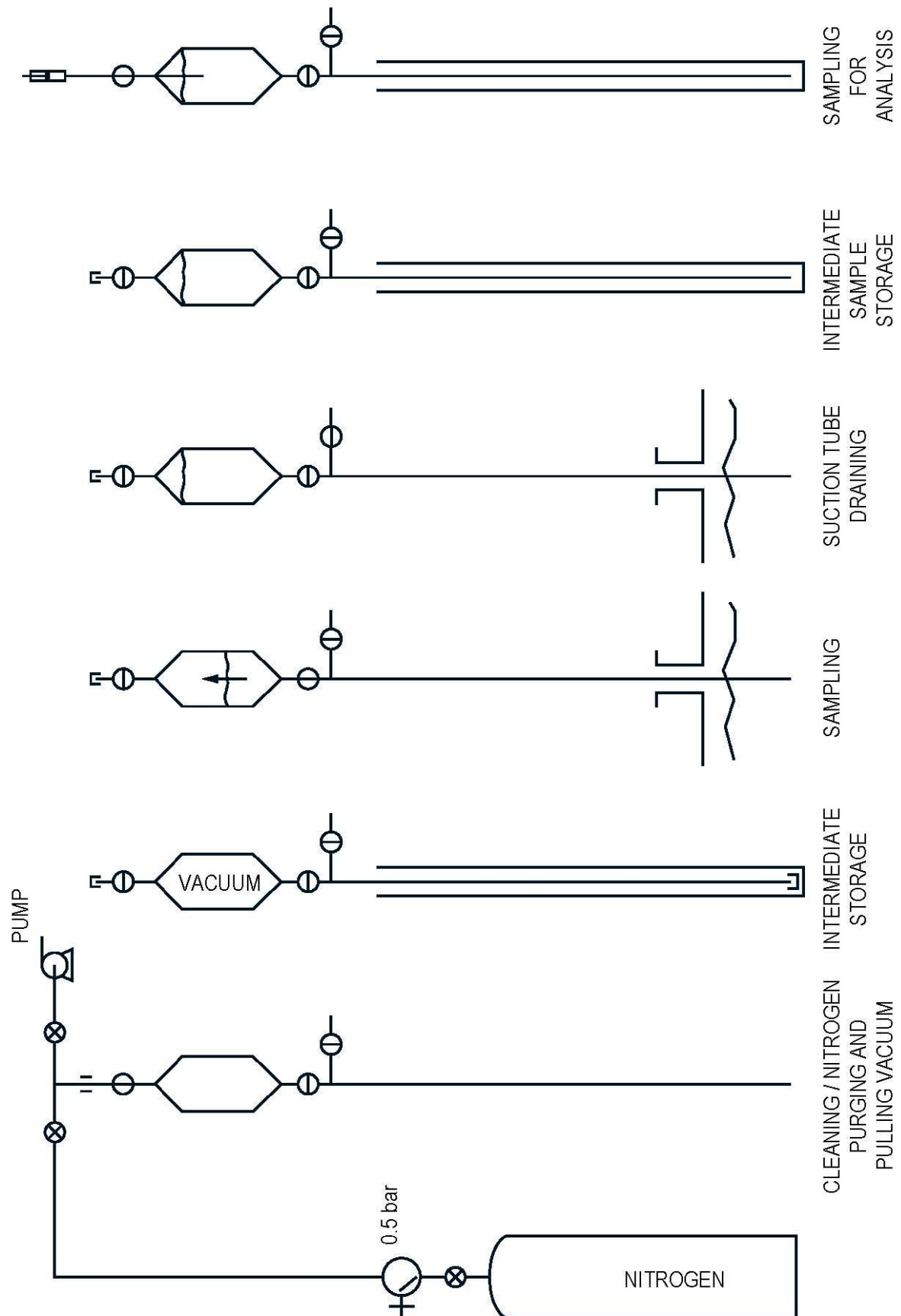
When solvent vapours are exposed to extreme heat, they decompose yielding hydrogen chloride (HCl), other chlorinated hydrocarbon compounds and possibly chlorine (Cl₂). If decomposition takes place in air (e.g. substances are burnt in a fire) phosgene (COCl₂) and carbon monoxide (CO) develop in small amounts, too. These thermal breakdown products are more hazardous than the solvents itself, as they are toxic, and for HCl, also highly corrosive to metals in the workplace and to the human body.

Therefore no operation with welding arc or cutting torch should be allowed in an area where chlorinated solvent vapours may be present.

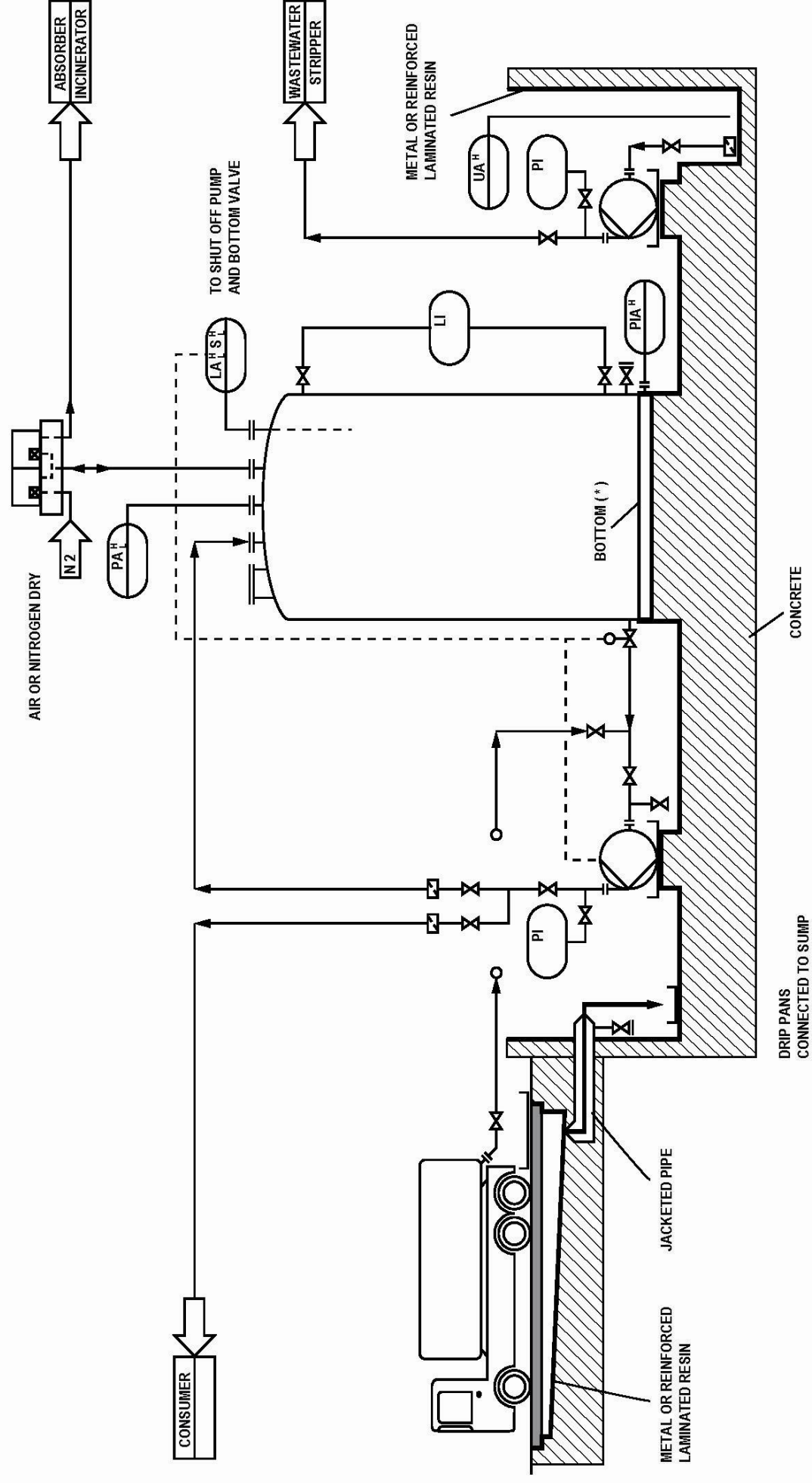
A.2. TYPICAL PROPERTIES OF CHLORINATED SOLVENTS

Properties	Unit	Methylene Chloride	Trichloroethylene	Perchloroethylene
Chemical Formula		CH ₂ Cl ₂	C ₂ HCl ₃	C ₂ Cl ₄
Vapour pressure at 20 °C	mbar (kPa)	476 (47.6)	99 (9.9)	25 (2.5)
Boiling Point at 1013 mbar	°C (°F)	39.7 (103.5)	87 (189)	121.1 (250)
Freezing Point	°C (°F)	-95 (-139)	-87.6 (-124)	-22.8 (-9)
Specific Gravity at 25/25 °C		1.32	1.456	1.619
Vapor Density at 20 °C (air = 1.00)		2.93	4.53	5.76
Heat of Vaporization at Boiling Point	kJ/kg cal/g BTU/lb	330 78.9 142	240 56.4 101.6	210 50.1
Viscosity at 25°C	mPa s	0.41	0.54	0.75
Solubility at 25°C H ₂ O in solvent Solvent in H ₂ O	g/kg g/kg	1.7 17.0	0.2-0.3 1.0	0.07 0.15

A.3. Sampling Method (Schematically)



A.4. EXAMPLE OF BULK UNLOADING AND STORAGE SYSTEM





ECSA – The European Chlorinated Solvent Association

ECSA represents the interests of the producers of chlorinated solvents in the EU that are organized under Euro Chlor.

Euro Chlor is the Brussels based business association representing chlor-alkali producers in the EU and EFTA regions, employing 39,000 people at nearly 70 manufacturing sites. Almost 2,000,000 jobs in Europe are related to chlorine and its co-product caustic soda. These two key chemical building blocks underpin 55% of the European chemical industry turnover. More than 90% of the European drinking water is made safe with chlorine and about 85 % of all medicines are synthesized using chlorine chemistry.

Euro Chlor is an affiliate of Cefic – the European Chemical Industry Council.

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