

7.0 Transportation of Phosgene

7.1 General

Caution - Information contained in this section of the Manual is based upon United States Department of Transportation (USDOT) regulations in effect in 2006. Refer to the actual USDOT regulations (49 CFR Parts 100 –185) to review the regulations in their entirety and to see the most recent requirements.

Phosgene is classified by USDOT as follows: Phosgene, 2.3, (8), UN1076, RQ (Phosgene), poison inhalation hazard, hazard zone A. It is the responsibility of each person shipping, transporting or using phosgene to know and to comply with all applicable regulations pertaining to shipping, labeling and placarding.

Shipments originating within the United States must comply with the current issue of the Code of Federal Regulations (CFR), Title 49, Parts 100 to 185, inclusive.

Furthermore, many states and some municipalities have adopted these Federal and other regulations to govern the transportation of hazardous materials within their jurisdiction.

7.2 Shipping Containers

General

Phosgene shipping containers must comply with authorized specifications. See 49 CFR Section 173.192 (non-bulk containers) and Section 173.314 (bulk containers).

Phosgene is authorized to be shipped by highway using private or common carriers (49 CFR Section 177.840) or by rail (49 CFR Part 174). Phosgene however is not typically shipped by rail in the United States.

Non-bulk containers

The only non-bulk containers approved by USDOT for phosgene shipments are carbon steel cylinders ranging from 7.5 pounds to 95 pounds. Steel cylinders are used that conform to applicable USDOT specifications (49 CFR Part 178). Specification 8, 8AL and 39 cylinders are not authorized by USDOT. The type of cylinders used are typically DOT 3AA seamless high pressure cylinders with a service pressure rating

of 1800 psig. These may come with or without a full length dip tube. In the United States, containers available along these lines are 7.5-pound cylinders, 95-pound containers, and 1-ton tanks.

Packaging of cylinders must comply with 49 CFR Section 173.40. These requirements include:

Sec. 173.40 General packaging requirements for toxic materials packaged in cylinders. When this section is referenced for a Hazard Zone A or B hazardous material elsewhere in this subchapter, the requirements in this section are applicable to cylinders used for that material.

(a) Authorized cylinders.

(a)(1) A cylinder must conform to a DOT specification or a UN standard prescribed in subpart C of part 178 of this subchapter, except that acetylene cylinders and non-refillable cylinders are not authorized. The use of UN tubes and MEGCs is prohibited for Hazard Zone A materials.

(a)(2) The use of a specification 3AL cylinder made of aluminum alloy 6351-T6 is prohibited for a Division 2.3 Hazard Zone A material or a Division 6.1 Hazard Zone A material.

(a)(3) A UN composite cylinder certified to ISO-11119-3 is not authorized for a Division 2.3 Hazard Zone A or B material.

(a)(4) For UN seamless cylinders used for Hazard Zone A materials, the maximum water capacity is 85 L.

(b) Outage and pressure requirements. For DOT specification cylinders, the pressure at 55°C (131°F) of Hazard Zone A and Hazard Zone B materials may not exceed the service pressure of the cylinder. Sufficient outage must be provided so that the cylinder will not be liquid full at 55°C (131°F).

(c) Closures. Each cylinder containing a Hazard Zone A material must be closed with a plug or valve conforming to the following:

(c)(1) Each plug or valve must have a taper-threaded connection directly to the cylinder and be capable of withstanding the test pressure of the cylinder without damage or leakage.

(c)(2) Each valve must be of the packless type with non-perforated diaphragm, except that, for corrosive materials, a valve may be of the packed type with an assembly made gas-tight by means of a seal cap with gasketed joint attached to the valve body or the cylinder to prevent loss of material through or past the packing.

(c)(3) Each valve outlet must be sealed by a threaded cap or threaded solid plug and inert gasketing material.

(c)(4) The materials of construction for the cylinder, valves, plugs, outlet caps, luting, and gaskets must be compatible with each other and with the lading.

(d) Additional handling protection. Each cylinder or cylinder overpack combination offered for transportation containing a Division 2.3 or 6.1 Hazard Zone A or B material must conform to the valve damage protection performance requirements of this section. In addition to the requirements of this section, overpacks must conform to the overpack provisions of §173.25.

(d)(1) DOT specification cylinders must conform to the following:

(d)(1)(i) Each cylinder with a wall thickness at any point of less than 2.03 mm (0.08 inch) and each cylinder that does not have fitted valve protection must be overpacked in a box. The box must conform to overpack provisions in §173.25. Box and valve protection must be of sufficient strength to protect all parts of the cylinder and valve, if any, from deformation and breakage resulting from a drop of 2.0 m (7 ft) or more onto a non-yielding surface, such as concrete or steel, impacting at an orientation most likely to cause damage. "Deformation" means a cylinder or valve that is bent, distorted, mangled, misshapen, twisted, warped, or in a similar condition.

(d)(1)(ii) Each cylinder with a valve must be equipped with a protective metal cap, other valve protection device, or an overpack which is sufficient to protect the valve from breakage or leakage resulting from a drop of 2.0 m (7 ft) onto a non-yielding surface, such as concrete or steel. Impact must be at an orientation most likely to cause damage.

(d)(2) Each UN cylinder containing a Hazard Zone A or Hazard Zone B material must have a minimum test pressure

in accordance with P200 of the UN Recommendations (IBR, see §171.7 of this subchapter). For Hazard Zone A gases, the cylinder must have a minimum wall thickness of 3.5 mm if made of aluminum alloy or 2 mm if made of steel or, alternatively, cylinders may be packed in a rigid outer packaging that meets the Packing Group I performance level when tested as prepared for transport, and that is designed and constructed to protect the cylinder and valve from puncture or damage that may result in release of the gas.

(e) Interconnection. Cylinders may not be manifolded or connected. This provision does not apply to MEGCs containing Hazard Zone B materials in accordance with §173.312.

Phosgene cylinders that are shipped must be tested according to 49 CFR Section 173.192(c) which reads as follows:

(c) For cylinders used for phosgene:

(c)(1) The filling density may not exceed 125 percent;

(c)(2) A cylinder may not contain more than 68 kg (150 lb) of phosgene; and

(c)(3) Each cylinder containing phosgene must be tested for leakage before it is offered for transportation or transported and must show no leakage. The leakage test must consist of immersing the cylinder and valve, without the protective cap attached, in a bath of water at a temperature of approximately 66°C (150°F) for at least 30 minutes, during which time frequent examinations must be made to note any escape of gas. The valve of the cylinder may not be loosened after this test. Suitable safeguards must be provided to protect personnel and facilities should failure occur during the test. As an alternative, each cylinder containing phosgene may be tested for leakage by a method approved in writing by the Associate Administrator.

DOT further requires that each used cylinder returned to the manufacturer “must be” tested according to the above-referenced procedure prior to being released for shipment. This mandate includes empty, full, or partial cylinders. The requirements for testing apply to all cylinders of phosgene in any size (1- to 95-pound cylinders). One-ton phosgene containers “are not considered” cylinders and are not

required by DOT to undergo the testing described in this section.

Per DOT requirements, outlet threads on phosgene cylinder valves are not standard pipe threads, but are special straight threads (designated at 1.030"-14NGO-RH-EXT). Compressed Gas Association (CGA) Publication V-1 provides information on phosgene container connections. See connection number CGA 660. These cylinder valves are not equipped with a fusible metal type safety relief device.

Bulk containers, - Ton Containers - 2,000 lbs. Capacity

As described in 49 CFR Part 179, DOT specification 106 A tank car tanks, these tank car tanks are filled to a maximum of 2000 pounds. The containers are commonly referred to as "ton containers." Ton containers are carbon steel with loaded weights up to 3700 lbs. These DOT specification 106 A containers are designed, built, maintained, marked, used, filled and shipped according to DOT specifications. These containers are 500 pounds per square inch gauge rated containers containing a maximum of 2000 pounds of phosgene. The container is approximately 87% full when shipped. Each valve connects with an internal education pipe. The valves are protected by a gas-tight removable steel valve protection bonnet designed to withstand the hydrostatic test pressure of the container. The containers and the valves are not equipped with fusible metal type safety relief devices.

Multi-Unit Tank Cars (TMU Cars)

Multi-unit tank cars, designed to carry up to **15** one-ton containers are authorized for transportation by rail according to 49 CFR Part 174.

Other Containers

No other containers are authorized by USDOT.

Compliance with Shipping Regulations

DOT provides that shippers who supply containers are responsible for determining that containers provided for transportation of hazardous materials are made, assembled, marked, etc., in compliance with applicable regulations. Users are responsible for determining that containers comply with shipping regulations before returning to shipper.

7.3 Shipping requirements

DOT Shipping Requirements: 49 CFR Parts 171-179 provides shipping requirements for transportation of phosgene in the United States.

Shipping Name: Phosgene

Technical Name: Phosgene

Hazard Class: 2.3

UN/NA Number: UN1076

Packing Group: None

Label(s): Inhalation Hazardous Gas (2), Corrosive (8)

Placard(s): Inhalation Hazardous Gas (2) UN1076

Markings: UN1076

Hazardous Substance: Yes

RQ: 10#

Poison / Inhalation hazard: Yes, containers must be marked "poison inhalation hazard."

Marine Pollutant: No

Packaging Requirements: Bulk - 173.314, Non-bulk 173.192

Exemption Number: None

Bill of Lading Description: UN1076, Phosgene, 2.3, (8), RQ(Phosgene), Poison inhalation hazard, Hazard Zone A, (List Container Size here), Inhalation Hazardous gas and Corrosive labels affixed, Current USDOT Emergency Response Guide for phosgene attached.

Other information: Special provisions: 1, B7, B46, §172.102 Quantity Limitations: Passenger aircraft or railcar: Forbidden. Cargo aircraft only: Forbidden. Vessel Stowage Requirements: Vessel stowage: Category D. Other stowage provisions: 40 §176.84

Precautionary Labeling

In preparing a label for containers of phosgene, there are a variety of items for consideration. Some items are presented below; the discussion focuses on product as shipped for industrial use. This information is for consideration, in addition to or in combination with any specific wording required by law. Individual statutes, regulations, or ordinances may require that particular information be included in the label, that certain information be displayed in a particular manner, or that a specific label be affixed to a container. Review of the information below will not necessarily ensure compliance with such laws. In the United States, such laws include the Federal Hazardous Substances Labeling Act; Federal Insecticide, Fungicide and Rodenticide Act, Occupational Safety and Health

Administration hazard communication standard, and similar state and municipal legislation.

Items for consideration during precautionary labeling development:

- Physical and Chemical Hazards
 - Nature of liquid and gas under pressure
 - Potential health risks
 - Ventilation or engineering controls to meet Occupational Safety and Health Administration permissible exposure limit
 - Availability of emergency self-contained breathing apparatus or full-face air-line respirator
 - Evacuation procedures, personnel, equipment, etc.
 - Fire-related information (e.g., container removal and/or cooling)

- First Aid
 - Procedures for inhalation exposure
 - Procedures for contact with phosgene

- Handling and Storage
 - Storage conditions
 - Temperature limits
 - Training for personnel handling phosgene
 - Reference to Material Safety Data Sheet or product bulletin
 - Ventilation or engineering controls to meet Occupational Safety and Health Administration permissible exposure limit
 - Use of approved connections for unloading phosgene
 - Maintenance of dry and clean piping conditions
 - Procedures for returning empty containers

Treating all containers, whether empty or filled, according to the specifications for handling and labeling until the containers are completely purged and tests have verified that they are decontaminated reduces potential risks.

7.4 Loading and Unloading

All persons involved in loading or unloading of phosgene must be properly trained. 49 CFR Section 172.704 provides United States training requirements.

Tank Car Tanks (Ton containers):

See 49 CFR Parts 100-185 for details. When tanks are loaded and prior to shipping, items for shippers to evaluate include determining to the extent practicable that the tank, safety appurtenances, fittings, labels and markings are in proper condition for safe transportation.

The United States Department of Transportation requires that ton containers loaded onto a trailer shall meet the following requirements:

- Loaded on a flat floor or platform of a motor vehicle or onto a suitable frame of a motor vehicle.
- In either such case, such containers shall be safely and securely blocked or held down to prevent movement relative to each other when in transit.

Rail cars are equipped with approved metal clamps securely bolted to the car frame.

Cylinders

Department of Transportation regulations require that cylinders be securely lashed in an upright position in racks securely attached to the motor vehicle or packed in boxes or crates of such dimensions as to prevent their overturning; or loaded and secured in a horizontal position.

Shipments should be properly loaded. Unless adequately designed, ends, sidewalls or doors of truck bodies or trailers may not prevent the shifting of heavy loads.

7.5 Transportation Security

With regard to transportation of phosgene containers, strict security procedures, including the use of detailed security assessments and the implementation of strict measures, have been designed to help prevent

and minimize risks of terrorism. Guidance entitled “Transportation Security Guidelines for the U.S. Chemical Industry” is available from the American Chemistry Council and provide general information on this subject.

7.6 Retesting

Tanks (one-ton containers) and cylinders must be periodically tested according to DOT regulations at an authorized testing facility.

7.7 Moving and Handling Cylinders and Ton Containers

Phosgene is a hazardous substance; containers must be handled with appropriate care. When moving containers, consider whether valve protection hoods have been used. Dropping a container, or allowing any object to a container with force, can result in container damage and associated risks.

Containers may be loaded onto and removed from trucks to a dock at truckbed height. If a hydraulic tailgate is used, apply appropriate action to prevent containers from falling off.

A properly balanced hand truck with a clamp or chain on the cylinder can be used to move single cylinders. It is important that the clamp or chain is placed on the cylinder at an appropriate location on the cylinder to reduce potential damage. When cylinders must be lifted and an elevator is not available, a crane or hoist equipped with a special cradle or carrier represents a useful option. Use of a sling or magnetic device raises concerns. Lifting a cylinder by the valve protection hood also raises concerns if the neckring to which the hood is attached is not designed to carry the weight of the cylinder.

Ton containers have been handled with a suitable lifting beam in combination with a hoist, crane, or towmotor of at least two tons capacity. To help prevent shifting and rolling, ton containers being trucked can be carefully chocked or clamped down on cradles.

7.8 Storing Containers

Containers may be stored in properly designed outdoor or indoor storage locations. Consider whether the storage area is well marked, secured for unauthorized access, and monitored for the presence of phosgene with appropriate monitoring/detection devices. Keeping the storage area clean reduces fire hazards associated with accumulated trash. Storing

containers near elevators or ventilating systems increases risk that dangerous concentrations of gas could spread rapidly if a leak develops. Indoor storage areas can be vented to a phosgene scrubbing system to help prevent accidental releases of phosgene to the atmosphere.

Consider whether the containers have been stored in a manner to minimize external corrosion. If standing water can collect, suitable platforms or supports can be provided. Steps can be taken to permit inspection and to facilitate prompt removal if a leak occurs. Hazards can be created if containers are stored in places where containers can drop, where heavy objects can fall on the containers, or where vehicles can strike the containers. Subsurface storage areas can cause difficulties and are not used by a number of companies. Procedures can be established to discourage access by unauthorized persons.

Evaluate actions to help prevent the exposure of containers to flame, intense radiant heat or to high temperature steam lines.

To reduce potential risks, full and empty containers can be stored separately. Even though the container is empty, consider whether valve outlet caps and valve protection hoods are in place. Generally, cylinders are stored in an upright position, and ton containers on their sides above the ground or floor on steel, concrete, or wooden supports.

7.9 Using Containers

General

Using cylinders and ton containers in the order in which they are received offers benefits.

Modifying, altering, repairing or using containers and valves in any manner except as authorized and without prior consultation with the supplier can raise significant concerns.

Gas Discharge

Most cylinders have a dip pipe as well as a top valve so that either liquid or gas can be discharged with the cylinder in a vertical position. Some cylinders need to be inverted to obtain liquid discharge. Ton containers in a horizontal position and with the valves in a vertical line deliver gas from the upper, and liquid from the lower, valve.

The flow of phosgene gas from a container depends on the internal pressure which, in turn, depends on the temperature of the liquid

phosgene. In order to withdraw gas, liquid must be vaporized. This tends to reduce its temperature and thereby its vapor pressure. At low discharge rates, sufficient heat can usually be obtained from the surrounding air so the pressure in the container will remain constant and uniform flow can be maintained. At high discharge rates, however, the temperature and pressure within the container will fall due to the cooling effect of vaporization; the rate of flow will gradually diminish. At excessive discharge rates, the liquid will be cooled to such an extent that frost will form on the outside of the container. The insulating effect of the frost causes a further decrease in the rate of discharge. Discharge rates may be increased by circulating room temperature air around the container with a fan.. Care should be taken to avoid exposing the container to excess heat, which can weaken the container due to over pressurization.

Liquid Discharge

To obtain liquid phosgene from cylinders having a dip pipe, connect to the appropriate valve with the cylinder in an upright position. To obtain liquid from a cylinder which does not have a dip pipe, one approach has been to invert the cylinder and clamp it securely on a rack set at an angle of about 60° to the horizontal. Liquid phosgene is discharged from the lower valve of a ton container. When discharging liquid, very high withdrawal rates may be obtained. The rate depends on the temperature of the phosgene in the container and on the back pressure. Users should consider an appropriate discharge rate as part of their liquid discharge procedures.

Connection of containers discharging liquid to a manifold can be problematic because differences in pressure among the containers (due to temperature or noncondensable gases, or due to difference in elevation head) will cause liquid phosgene to flow to the container under the lowest pressure. Then, when the container valve is closed, and the temperature subsequently allowed to rise, the liquid expansion may generate an increase in hydrostatic pressure which could rupture the container.

Weighing

The quantity of container contents can be determined by a weighing process. The weight of the full container is recorded and the net weight of the contents determined by subtracting the tare weight of the container.

Connections

A flexible connection between the container and the piping system has been used; common connections include:

- Copper or stainless steel tubing; and
- Polytetrafluorethylene lined kynar braided transfer hose with carbon steel fittings.

Note – All connections must be evaluated for proper pressure, temperature, and compatibility specific to the process prior to use.

Inspecting the connection before each use and replacing the connection annually (or sooner especially if there is evidence of deterioration) reduces potential risk.

Connections approved by DOT for use with phosgene cylinders are found in the current edition of the CGA Standard V-1, Compressed Gas Cylinder Valve Outlet and Inlet Connections. The currently approved connection is the cylinder valve outlet connection CGA 660. (CGA V-1 1997). Consider use of a new gasket each time a connection is made.

The container valve is opened by turning the valve stem in a counter-clockwise direction. Special square box wrenches are available for turning the valve stem from the manufacturer. Any other type of wrench or device can result in serious damage to the valve. Usually the valve can be opened by striking the end of the wrench with the heel of the hand. One complete turn of the valve permits maximum discharge. There is no need to open the valve further.

After the connections are tight, consider cautious application of phosgene pressure and testing the system for leaks. See section 6.1.2 of this Guideline.

NOTE: The use of Ammonia solutions for leak detection can damage the metallurgy of the cylinder valves which can cause stress corrosion cracking.

Disconnecting Containers

As soon as a container is empty, steps can be taken to remove it from service, apply the outlet cap, and promptly attach the valve protection hood. A procedure for deactivating the container can be developed that

will both prevent liquid phosgene from becoming trapped in connection lines and keep atmospheric moisture out of the system.

One example procedure for disconnecting a container is:

1. Shut off the valve on the process side of the connection line.
2. Heat the connection line with steam to vaporize any liquid phosgene and force it back into the container. Then close the container valve.
3. Purge the connection line with either dry air or nitrogen, forcing the contents into a caustic scrubber or other absorption system.
4. Disconnect the connection line from the container and cap it immediately.

It is important that only experienced personnel who are using proper personal protective equipment perform this work.