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Acid Chlorides and Chloroformates Safety and Handling

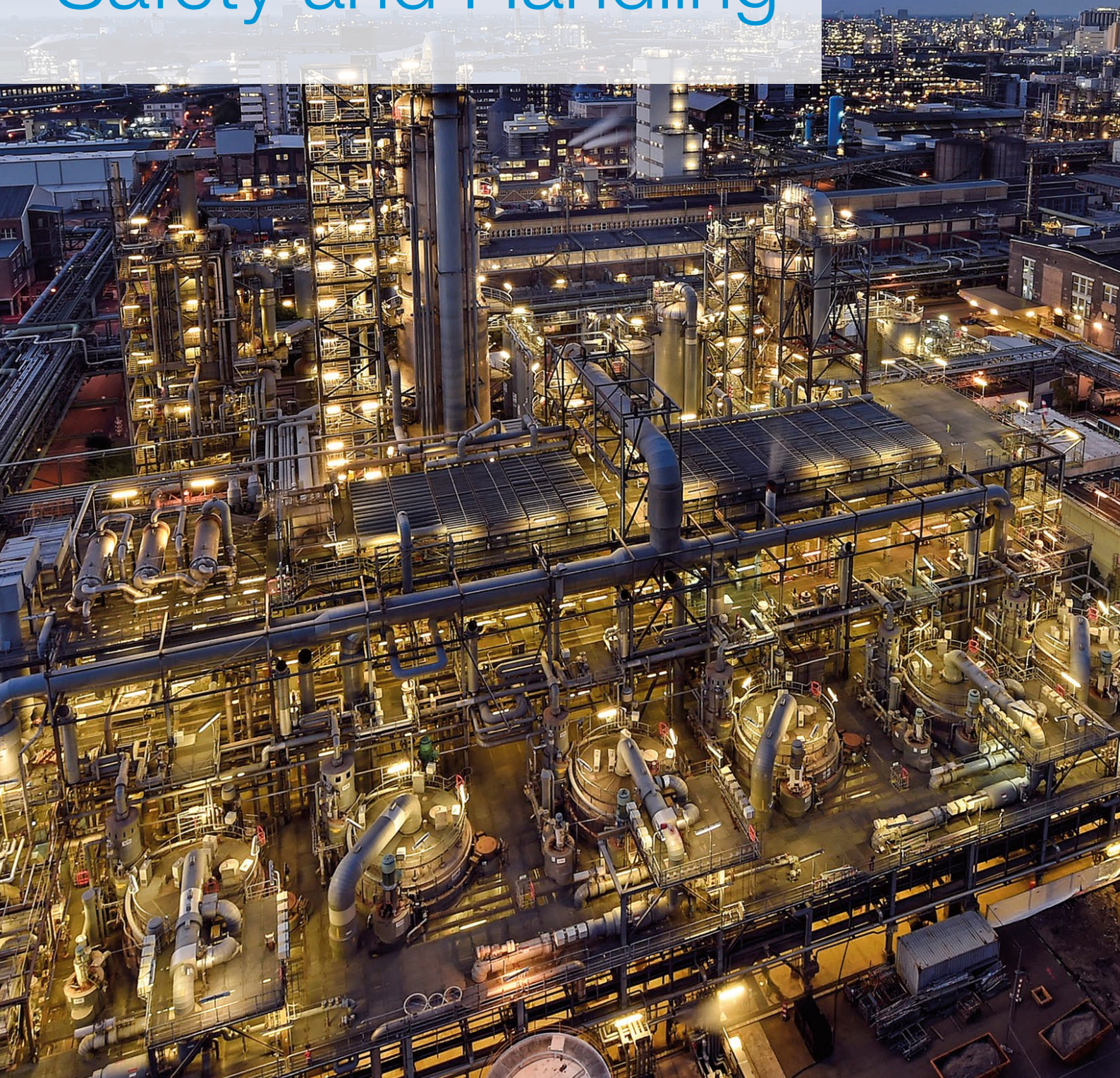


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Abbreviations

CPS _____	Chemical protective suit
CCD _____	Chloro carbonyl derivatives
ECF _____	Ethyl chloroformate
ICE _____	International Chemical Environment
MCF _____	Methyl chloroformate
MSDS _____	Material safety data sheet
PCF _____	Propyl chloroformate
PFA _____	Per fluoro alkoxy polymer
PPE _____	Personal protective equipment
PTFE _____	Poly tetra fluoro ethylene polymer
SCBA _____	Self-contained breathing equipment

01

Introduction

Introduction

BASF - A responsible and reliable supplier

BASF began manufacturing phosgene derivatives such as acid chlorides and chloroformates more than 40 years ago. Today, BASF is one of the leading global suppliers of phosgene derivatives. Our acid chlorides, chloroformates and alkyl chlorides are produced in state-of-the-art chemical processing facilities that are based on an in-depth knowledge of hazards and the continuous development of advanced technology.

BASF aims for safety along the whole value chain especially for the highly toxic phosgene derivatives like methyl or ethyl chloroformate.

Introduction

The purpose of this brochure is to provide general information on the safe handling and storage of acid chlorides and chloroformates.

Our intention is to share BASF's safety and handling experience as part of our Responsible Care® commitment. It is suggested that this entire document, along with the safety data sheet (MSDS) should be read before using any of these products. In addition, you are strongly encouraged to call your BASF representative with any further questions you may have.

These recommendations are valid for all acid chlorides and chloroformates, but specific concerns have been taken regarding the high toxic substances Methyl- and Ethyl chloroformate, which will be covered by specific paragraphs in the different chapters in this brochure.

Disclaimer and limitation of liability

While the information and data contained herein are presented in good faith and believed to be reliable, it is provided as part of our continuing Responsible Care® commitment and is offered for guidance only. Because many factors may affect processing, applications, or use, we suggest that further tests and/or analysis be pursued to determine suitability of the information.

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BASF Portfolio

BASF Portfolio

C Chain length	Acid Chloride			Chloroformate	
	Linear	Branched	Functionalized	Linear	Branched
C1				Methyl-	
C2	•		2-Chloroacetyl-chloride	Ethyl-	
C3	Propionic-	•	3-Chloropropionyl-chloride	Propyl-	•
C4	Butyric-	Iso-butyric-	4-Chlorobutyroyl-chloride	Butyl-	sec-Butyl-
C5	n-Valeric-	Pivalic-	5-Chlorovaleroyl-chloride	•	•
C6	Hexanoic-	•	•	Hexyl-	•
C7	Heptanoic-	•	•	•	Benzyl-
C8	Octanoic-	2-Ethylhexanoyl-	•	•	2-Ethylhexyl-
C9	•	Iso-Nonanoic-	•	•	•
C10	•	Neo-Decanoic-	•	•	p-tert.- Butyl-cyclohexyl-
C12	Lauroyl-	•	•	•	•
C14	Cocoyl-	•	•	Myristyl-	•
C16	Palmitoyl-	•	•	Cetyl-	•
C18	Stearyl-	iso-Stearoyl-	•	•	•

03

**Safety and
Handling**

Safety and Handling

3.1 General Considerations

All employees and contractors, who handle acid chlorides and chloroformates should be thoroughly trained and informed about the shall potential hazards, exposure/incident prevention techniques, emergency response plans, personal protective equipment and environmental protection aspects of chloroformates and acid chlorides.

3.2 Safety, Health and Environmental Reviews

Risk assessments or safety reviews must be conducted as part of the engineering and construction project for new or modified storage, handling and unloading facilities.

3.3 Operating Procedures

It is recommended to have written operating procedures in place, which shall give stepwise directions to employees and contractors involved in handling acid chlorides and chloroformates.

suggested, that involved personnel receives trainings on the operating procedures, which are documented.

All personnel handling methyl or ethyl chloroformate shall be annually trained on the hazardous potentials and safe handling of these substances.

3.4 Emergency Response Plans

Written emergency response plans are recommended for potential releases, fires and dangerous reactions/decompositions.

These emergency response plans should be covered in safety, health and environmental reviews and made part of the documented training program.

Documented drills are suggested as part of the emergency training program. Corrective action and communication should always be addressed in the written emergency response plans.

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**Health and
Safety Factors**

Health and Safety Factors

4.1 Toxicology

General

The toxic properties of acid chlorides and chloroformates are described in detail in the MSDS of the specific compound. In general, the following properties shall be considered:

The vapor of acid chlorides and chloroformates can burn mucous membranes and possibly damage the underlying tissues when inhaled, swallowed or contacted with the eyes, even at low concentrations.

Exposure by inhalation can result in permanent injury or death. Acid chloride and chloroformate vapors can form hydrochloric acid when exposed to moisture in the air or in the respiratory system.

Contact with acid chloride or chloroformates in liquid form can cause severe burns of the skin and/or eyes and possibly cause permanent eye damage. For detailed toxicity data, please refer to the individual MSDS of each compound.

Acute Exposure

Inhalation of vapors or mists of acid chlorides or chloroformates, even in low concentrations, can cause death due to formation of a pulmonary edema. The toxic effects depend on the degree (concentration and time) of exposure.

Exposure to mists, vapor or decomposition products such as hydrochloric acid can produce eye, nose, skin, or lung irritation and injury, even at low concentrations.

Vapors of acid chlorides and chloroformates are corrosive and may form hydrochloric acid upon contact with moisture in the air. Eye exposure may result in permanent injury, including loss of vision. In case of contact to skin, severe burns have been observed.

Chronic Exposure

The main routes of exposure to acid chlorides and chloroformates are by inhalation of vapor or by liquid and/or vapor contact on the skin or eyes. There are no known chronic effects associated with these materials.

Potential Sequelae

If the patient survives the initial 48 hours after exposure, recovery is likely. Sensitivity to irritants may persist, causing bronchospasm and chronic inflammation of the bronchi.

Pulmonary tissue destruction and scarring may lead to chronic dilation of the bronchi and increased susceptibility to infection.

Health and Safety Factors

4.2 Industrial Hygiene

General

A program should be implemented to minimize the risk of exposure by utilizing suitable engineering controls and safe work procedures. Suitable personnel protective equipment should always be worn in situations where engineering controls and safe work procedures do not adequately eliminate the risk of exposure.

In general, it is recommended to handle and store these products in a closed environment. Emission control devices should be considered for all vent lines. Personnel protective equipment for skin, eyes and respiratory protection must be used whenever closed systems have to be opened. The selection and use of personnel protective equipment is covered in Section 3.4.

4.3 First Aid

General

The location of all emergency eyewash stations and showers must be known to the employees for all relevant places using chloroformates and acid chlorides (e.g. warehouses). The phone number(s) to call for emergency medical services and all workplace specific emergency procedures should be readily accessible, including the poison control center.

Contact with Eyes

In case of eye exposure, the affected person should immediately flush both eyes with running water at the nearest eyewash station for at least 15 minutes while holding eyelids open and away from the eyes. A physician should be contacted immediately for further medical attention. If a physician is not immediately available, the process of flushing the eyes with water should be continued for a second 15-minute period.

MCF & ECF specific

Stinging of the eyes and/or nose is a sign of possible overexposure and personnel should immediately leave the area. Exposed persons might lose orientation due to tearing eyes.



Contact with Skin

In case of contact of acid chloride or chloroformate the individual should immediately use the nearest safety shower to rinse off the material. All contaminated clothing and shoes should be removed. The affected area(s) should be washed continuously with large quantities of water for at least 15 minutes or longer if odor persists. A physician or emergency medical services should be contacted for further assistance. No ointments or medications should be applied to the skin without specific instruction from a physician. All contaminated clothing should be properly disposed of.

Inhalation

In case of inhalation the contaminated area shall be left and the affected employee shall be directed to a well-ventilated area. Emergency assistance and medical attention should be immediately requested. Since the symptoms of intoxication may show a latency time of up to 24-48 hours, it is strongly recommended to extend medical observation for a minimum of 48 hours.

Health and Safety Factors



MCF, ECF & PCF specific

Inhalation of ECF or MCF could lead to severe inflammations in the lung followed by lung edema which could finally lead to death within 48h.

A critical fact of MCF & ECF is the delayed corrosion due to their low water solubility. They reach the lower respiratory tract (alveoli) and release hydrochlorid acid at this most sensitive lung tissue. The consecutive corrosion of alveoli may be lethal as of suffocation caused by toxic lung edema. The toxic lung edema may appear with a delay of 24 – 48 h.

In case of inhalation of these volatile chloroformates, apply corticosteroids such as betamethasone dipropionate as soon as possible to suppress inflammations. Site ambulance or local first aid kit should have inhaler of corticosteroid available for instant medication.

BASF Cooperate Health Management issues medical guidelines for first aiders, paramedics, physicians and patients. These guidelines are freely available under following internet link:

<https://collaboration.basf.com>

Ingestion

Do not induce vomiting. Immediately contact local emergency medical services or the local poison control center for assistance. If conscious, immediately rinse mouth and then drink plenty of water.

4.4 Personal Protective Equipment

General

Personal protective equipment (PPE) should be selected based on the potential for exposure to the particular chemicals. When PPE is provided to employees or contractors, they must be trained in using the equipment and for which situation which PPE is applicable. The facility must also have provisions for decontaminating and replacing such equipment as necessary.

Eye Protection

Minimum eye protection in the form of chemical splash goggles should be worn. Goggles should be non-vented and designed specifically to protect against a chemical splash.

The vapors of the short chain chloroformates are lachrymatory. If vapor concentrations warrant, a properly fitted facemask is recommended. The vapors of acid chlorides and chloroformates are corrosive. Exposure even to low concentration of these vapors can cause a stinging sensation in the eyes and can cause permanent eye damage.

Skin Protection

Skin protection must be made of a material adequately impervious to acid chlorides or chloroformates. Personal protective equipment should be selected on the basis of potential exposure, e.g., gloves may be required for handling small samples in the laboratory while full-body clothing including gloves (e.g. Butoject), boot covers and head covering may be necessary for unloading transport containers.

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Instability Hazards

Instability Hazards

5.1 Reactions / Decomposition

Acid chlorides and chloroformates are stable, provided the recommendations given in the MSDS are strictly followed. The recommended storage conditions include:

- storing at proper temperature
- preventing contact with moisture
- avoiding contamination

Some chloroformates are instable at room temperature, so they will be delivered under temperature controlled conditions (e.g. reefer container).

Heat

Acid chlorides and chloroformates might decompose exothermically under emission of gaseous products like hydrochloric acid and carbon dioxide. The tendency to decompose depends strongly on the individual chemical structure. In general, compounds with a chloroformate group attached to a secondary carbon or a benzylic carbon atom undergo slow decomposition even at ambient temperatures. Such thermolabile compounds must therefore be shipped, handled and stored permanently under strictly controlled temperature conditions.

Water / Moisture

Acid chlorides react readily with water to form hydrochloric acid and the respective carboxylic acid. The reaction is strongly exothermic and very vigorous. Due to the limited mutual solubility of acid chlorides and water a time lag between bringing in contact and start of reaction may occur.

The reaction of chloroformates with water yields the corresponding alcohol and the gaseous products, hydrochloric acid and carbon dioxide. Compared with the reaction of acid chlorides and water the reaction rate is slower.

The controlled reaction of acid chlorides and chloroformates with water or alkaline solutions of ammonia or caustic can be used for destroying product vapors in scrubber towers.

Moisture is easily absorbed by acid chlorides and chloroformates resulting in generation of hydrochloric acid which in turn leads to pressure build up and to corrosion if improper materials were used for construction of tanks, vessels, piping or instrumentation.

Contamination

Acid chlorides and chloroformates can react with a variety of other chemicals.

Reactions with compounds possessing active hydrogen atoms like alcohols and amines are strongly exothermic and very vigorous. A time lag between contamination and the start of the exothermic reaction was observed in certain cases.

Metal ions (e. g. iron) may catalyze the thermal decomposition described above. Contamination with metal ions easily happens if moisture enters the product and corrosion occurs.

Instability Hazards

5.2 Flammability

Bulk quantities of acid chlorides and chloroformates are stored and transported under a nitrogen blanket to reduce the risk of ignition. Electrical grounding of all liquid transfer systems and storage vessels is essential to reduce the risk of ignition. Acid chlorides and chloroformates have a low conductivity and static electrical charges can buildup during liquid transfers if the entire system is not properly grounded. All transport vessels and containers must be grounded before transfers are made.

The need for flame-stopping devices, constructed of a suitable material, should be considered during the design of acid chloride and chloroformate facilities. For increased safety, flame arresters may be installed in any vapor (vent) line that can be opened directly to the atmosphere except for the emergency vent. When using closed circuit unloading, an additional flame arrester can be considered for the vapor return line.

06

**Bulk Storage and
Unloading Facilities**

Bulk Storage and Unloading Facilities

6.1 General overview

Storage Tanks

A program should be implemented to minimize the risk of exposure by utilizing suitable engineering controls and safe work procedures. Suitable personnel protective equipment should always be worn in situations where engineering controls and safe work procedures do not adequately eliminate the risk of exposure.

In general, it is recommended to handle and store these products in a closed environment. Emission control devices should be considered for all vent lines. Personnel protective equipment for skin, eyes and respiratory protection must be used whenever closed systems have to be opened. The selection and use of personnel protective equipment is covered in Section 3.4.

All acid chlorides and most chloroformates can be safely stored at ambient temperatures. Thermolabile chloroformates must be stored in cooled tanks or cooled warehouses according to the recommendations given in the MSDS. Storage tanks should be glass lined. Tanks may be set on a concrete pad within a concrete dike, although the tanks may be also placed on pedestals or saddles within a dike. The storage tank must also be designed to allow for complete drainage of the tank.

It is imperative, that a spill of acid chloride or chloroformate can be adequately contained. The dike volume must be adequate to contain the contents of the tank and satisfy regulatory requirements for such systems. Concrete dike walls and flooring are recommended. The durability of concrete surfaces should be improved by applying a suitable coating (e.g. Rheoponol O.R.G.). The containment area should drain to a sump, that will allow for the discharge of collected water.

Redundant instrumentation is suggested to protect against overfilling tanks and vessels. A level-high alarm, followed by a high-high shutdown interlock of the transfer is suggested. Radar tank level indicators have been successfully used in acid chloride and chloroformate service along with a high-high level switch based on a tuning fork.

Tanks used in acid chloride or chloroformate service should be well-grounded electrically.

Bulk storage and unloading systems should be closed, all components electrically grounded, and blanketed with nitrogen. Typically, a 10 percent minimum void volume in bulk storage vessels is used as a buffer against tank overflow. The system should be designed to exclude moisture. Cleaning solution lines should not be connected to the storage system to avoid the accidental introduction of incompatible chemicals, such as steam and water. The accidental introduction of incompatible chemicals may lead to dangerous conditions such as overpressurization and/or excessive venting.

Fluid Transfer Systems

Glass-lined piping and equipment is preferred for acid chloride and chloroformate service. Fluid-transfer equipment and instruments such as pumps, valves, flanges, swivel joints, flow meters, level indicators, etc., can be lined with antistatic plastics such as PTFE, PFA, and PVDF or constructed of Hastelloy® B or C. BASF has positive experience with Hastelloy B3. Commercially available gaskets of PTFE are suggested for sealing flanges.

Self-priming centrifugal magnetic drive pumps with a suitable plastic liner (fluoropolymers, e.g. PTFE or PFA) are recommended for unloading acid chlorides or chloroformates from bulk transport vessels. Instrument protection to guard against running magnetic drive pumps dry is suggested.

For some applications, it may be acceptable to transfer acid chlorides and chloroformates using nitrogen pressure.

For thermolabile chloroformates (e.g. sec.-butyl chloroformate) keep the fluid transfer as short as possible and empty all pipes and pumps immediately after finishing the transfer process.

Residual liquid in pipes and pumps may reach ambient temperature soon and subsequent exothermic decomposition with rapid pressure build up may occur.



Bulk Storage and Unloading Facilities

Emissions Control

A suitable emission control device, such as a caustic scrubber tower, should be used to remove acid chloride and/or chloroformate vapors before venting to the atmosphere. The scrubber solution is typically maintained at pH 9 to 12. Safeguards must be in place to prevent liquid acid chlorides or chloroformates from entering the scrubber tower. A properly designed and well-maintained emission control device is essential for the safe storage and handling of these products.

Unloading Stations

BASF supplies acid chlorides and chloroformates in specific equipment (e.g. phenolic-resin-lined ISO-containers) equipped for closed loop top unloading. Safe access equipment is recommended to help prevent falls and an emergency safety shower and eye bath station should be readily accessible. All applicable codes and regulations for the geographic location of the facility should be met with respect to fall protection and emergency safety shower and eye bath stations. It is suggested that PTFE-lined flexible hoses be supported by an unloading arm and that a low-volume coupling system, such as a flange-to-flange or dry-break coupler, is used to connect the flexible hose to the ISO-container. A weather-protection canopy located above the unloading rack may help provide additional safety during bad weather and reduce the risk of moisture entering the system.

Fire Prevention and Control

Fire protection of bulk acid chloride and chloroformate storage tanks should be considered in the initial design. Overheating an acid chloride or chloroformate bulk storage tank may result in a major release of toxic vapors including hydrochloric acid.

6.2 Design Considerations

Design features of an acid chloride or chloroformate storage facility are given as an example in Figure 5.1 (key to symbols are found in Table 5.1).

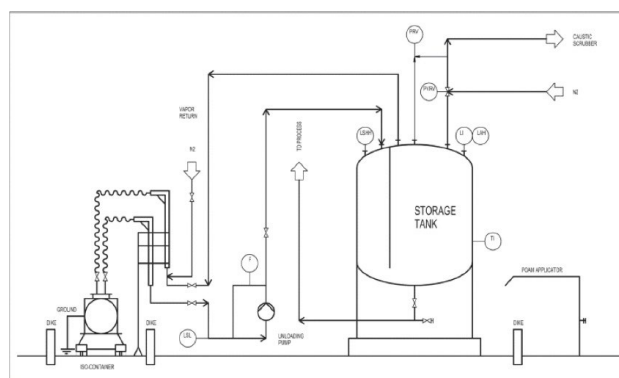


Figure 5.1: Example of an Acid Chloride or Chloroformate Storage Facility

Table 5.1: Key to Symbols in Figures 5.1 and 7.2

Symbol	Definition
LAH	Level alarm – high
LI	Level indicator
LSHH	Level switch – high-high (shuts down unloading pump)
PVRV	Pressure and vacuum-relief valve
TE	Temperature element
TR	Temperature recorder
LSL	Level Switch – Low
PRV	Pressure relief valve

Bulk Storage and Unloading Facilities

Materials for Construction and Sealing in Acid Chloride and Chloroformate Service

Proper choice for materials of construction is important for safety, health and protection of the environment. Some specific guidance for acid chlorides and chloroformates service is given below. Depending on the setup, materials with antistatic properties should be used.

- Glass-lined steel storage tanks are recommended.
- When practical, glass-lined steel piping and equipment is recommended.
- PTFE-based gaskets are recommended for flanges of glass-lined piping and equipment.
- Glass or PTFE-lined flange couplings are recommended.
- Phenolic-resin-lined (e.g. Procoemail®) steel is commonly used for transport vessels.
- Stainless steel flexible hoses with PTFE or PFA liners are recommended.
- Magnetic-drive centrifugal pumps with PTFE or PFA liners are suggested.
- Teflon® (or equivalent) gaskets are suitable for most applications.
- Kalrez® (or equivalent) and Viton® O-rings are used in a variety of applications.
- Certain special metal alloys, such as Hastelloy® B-3, may be suited for certain applications. Traces of water and oxidative conditions might lead to corrosion even if special steels are used.

Engineering Considerations for Temperature Control of Bulk Storage Tanks and Accessories

Acid chloride and most chloroformate tanks and piping systems may be maintained at ambient temperatures, heat traced or cooled, depending on the physical and chemical properties of the products.

The entire storage and handling system should be designed to prevent accidental exposure to high-temperature heat sources such as steam, deadheaded pumps and fires. Exposure to high-temperature heat sources can result in decomposition and/or the release of toxic vapors, including hydrochloric acid. The entire system should also be designed to prevent the accidental introduction of water or other chemicals as liquids or vapor. The addition of water can generate heat and produce by-products such as hydrochloric acid and carbon dioxide leading to over pressurization and/or the release of toxic vapors.

The heat introduced by the pump should be considered for all storage tanks that can be circulated. Heat dissipates slowly from glass-lined equipment and tanks.

Prolonged circulation may overheat the storage tank. Engineering safeguards and operating procedures should be employed to ensure that excessive temperatures do not occur during the circulation of a tank.

Engineering Considerations for Pumps and the Protection of Pumps

Centrifugal magnetic-drive pumps that have a suitable plastic liner have proven successful for acid chloride and chloroformate service. These seal-less pumps help reduce the risk of a release. Magnetic-drive pumps can quickly overheat if operated dry or dead-headed. It is recommended that safeguards be provided to prevent accidental overheating of acid chloride and chloroformate pumps. Deadheading (blocking in) a centrifugal pump usually causes a rapid temperature rise inside the pump. Operating a magnetic-drive centrifugal pump dry quickly eliminates all lubrication/



Chloroformates decompose in presence of iron ions or other metal ions. Any sources of metal ions have to be avoided and corrosion stable materials are mandatory.

Bulk Storage and Unloading Facilities

cooling and damages the pump. Some options to help protect pumps from damage are given below. Choice of method or methods of pump protection may vary from case to case and should be based on a safety analysis.

- A liquid-level sensor can be placed in the suction line that activates an alarm and shutdown switch if liquid is not detected. A tuning-fork type of liquid-level sensor installed in the suction line of acid chloride and chloroformate pumps has been used with good results. A five-second time delay is typical to allow starting the pump.
- A power monitor that senses a low power consumption and activates an alarm and shutdown switch can be installed. Deadheading a centrifugal pump usually results in an immediate reduction in power consumption. A time delay may be necessary for startup situations.
- A flow detection element on the discharge line that activates an alarm and shutdown switch when a low flow is detected can provide protection. A time delay may be necessary for startup situations.
- A temperature sensor placed inside the pump or close to the discharge/suction which activates the alarm and shutdown switches if a high temperature is detected.
- The point of disconnection should always be isolated before opening the system. All disconnected hoses and nozzles should be quickly capped to minimize emissions.
- Supporting the flexible hose from a loading arm may help reduce the risk of leaks developing at the couplers.
- Allowing the pump to run until the liquid level approaches the suction of the pump is suggested. A level switch in the pump suction line, such as a tuning-fork probe, can be used to shut the pump down before the vapor space reaches the pump.
- If justified, cleanout systems can be used to minimize residual product vapor and liquid in the transfer lines before disconnecting. A properly designed cleanout system may reduce the quantity of product released when the system is first opened.
- Vapor return lines are an option for bulk acid chloride and chloroformate unloading facilities for reducing emissions without generating additional caustic scrubber tower wastewater.
- A caustic scrubber tower is suggested for removing acid chloride and/or chloroformate vapors from vents. The scrubber solution is typically maintained at a pH of >11. Safeguards must be in place to prevent liquid acid chlorides or chloroformates from entering the scrubber tower. The accidental overflow of a storage tank into a caustic scrubber tower can cause overheating, high pressures, and the release of hazardous chemicals such as caustic.

Engineering Features for Environmental Protection

All environmental regulations applicable to the geographic location of the facility must be met. All systems must be designed, operated and maintained to minimize the risk of releases. Below is a list of engineering safeguards to help protect the environment.

- Adequate concrete spill containment around storage tanks.
- Instrumentation to monitor liquid level in bulk storage tanks. An independent high-high level switch that activates an alarm and stops the unloading process gives additional protection.
- Condensed acid chlorides and/or chloroformates may accumulate in low points of the scrubber inlet line. The scrubber line should be such that large quantities of these condensed products will not suddenly enter the scrubber tower and should be designed in a way, that high temperatures and pressures. Installation of a low point drain is recommended.
- It must be decided, whether the caustic scrubber should be sized for normal emissions or for an emergency situation such as a pool fire.
- Magnetic-drive pumps can reduce fugitive emissions

Bulk Storage and Unloading Facilities

and the risk of spills.

- The number of flange fittings should be minimized to reduce fugitive emissions and the risk of leaks.



Any MCF & ECF emissions to the environment have to be avoided. The use of a caustic scrubber or other means to destroy these vapors is mandatory.

Venting of Bulk Storage Tanks

It is recommended, that acid chloride and chloroformate vapors are normally vented to a caustic scrubber or other suitable emissions control device. It is also recommended that a vacuum relief valve be installed that is connected to a nitrogen gas header. A pressure-relief valve can be installed on the vent line to the caustic scrubber to help maintain a suitable nitrogen blanket in the storage tank and help minimize emissions from the tank. A combination pressure/vacuum-relief valve, sometimes referred to as a conservation vent valve, is frequently employed to help minimize the multiplicity of equipment and nozzles.

It is suggested that vapor return lines be installed to significantly reduce emissions during unloading or loading of bulk transport vessels such as ISO-containers. These lines should be kept free of residue and the vent conservation valves correctly adjusted to contain most of the vapors during unloading. It is essential that incompatible chemicals, such as water, alcohols, amines or ammonia not be able to enter an acid chloride or chloroformate storage tank through the vent system.

Emergency Venting of Bulk Storage Tanks

Standard practice is to design storage tank emergency venting capacity for the vapor generation rate resulting from a pool fire around the tank. However, this type of device may not provide adequate relief in the event of an uncontrolled reaction or decomposition.

The emergency venting should be directed through the caustic scrubber system. The efficiency of the scrubber could be increased during an emergency by adding ammonia.

Emergency vent devices must be inspected at a frequency that ensures operability and allows for maintenance.

07

**Equipment Preparation
and Cleaning**

Equipment Preparation and Cleaning

7.1 Cleaning Acid Chloride and Chloroformate Bulk Storage Facilities

- Typical steps for cleaning acid chloride and chloroformate bulk storage facilities are given below. All workers shall wear proper PPE when there is a risk of exposure to hazardous liquids and/or vapors. This includes potential exposure to hazardous cleaning solutions and rinse water.
- Blow all product residues from pipes and accessories back into tank using nitrogen.
- Fill product residues from the tank into a suitable container. Properly handle, store and dispose of all collected product.
- Methanol could be used to further clean the emptied tank.

Attention: potential residues might react with the Methanol in an exothermic reaction forming gaseous hydrochloric acid.

- Further cleaning could be done by flushing all lines and accessories with a diluted aqueous caustic and/or ammonia solution. Collect, treat and properly dispose of all wastewater.

- Circulate a caustic and/or ammonia solution to convert the acid chloride or chloroformate into less hazardous materials. Remove alkaline solution and rinse thoroughly with water.
- Flush with nitrogen to a suitable emission-control device (e.g. caustic scrubber or thermal oxidizer).
- Repeat some or all of the above steps as needed to thoroughly clean the system and eliminate all hazardous chemicals.
- Remove any solid residue (.e.g salts) that is found.
- Decontaminate and dispose of any residual product, residue, cleaning solutions/supplies and rinse solutions by following approved guideline.



Salts may be formed, potentially contaminating the piping systems.

One or all of the following steps may be needed to thoroughly remove all hazardous vapors:

- Steam all lines and accessories until clean. Take precautions not to damage any sensitive equipment or seals.

08

**Safe Transport and
Unloading of Acid Chlorides
and Chloroformates**

Safe Transport and Unloading of Acid Chlorides and Chloroformates

8.1 Transportation of CF

Depending on their hazardous potential, BASF sells chloroformates in drums, IBC or bulk and strives to take door to door responsibility for the supply chain of chloroformates to enable a safe and secure transport to the customer.

MCF and ECF transports have to follow ADR 10.1 security regulation and only forwarder with according capabilities may carry out these transports. BASF transports these materials segregated, so no other chemicals shall be loaded during the transport.

In case of a transport incident, e.g. traffic accident during the transportation, please contact BASF ICE center (International Chemical and Environmental Initiative) by +49-621-43333.

MCF and ECF Bulk

BASF uses bulk iso container with specific coating for MCF & ECF, that are constructed without bottom outlet. These containers are equipped with a dip tube for safe unloading (T20 or T22 container). **BASF iso container shall not be cleaned by third parties and opening of manhole is not allowed by unauthorized parties.**

MCF and ECF drums

Drums are transported either in closed trucks or in box container in a single layer. No other chemicals may be transported together with such hazardous goods transport.

The truck or box container may only be opened wearing appropriate PPE. Before unloading the drums, the truck or container shall be vented for at least 1 hour to reduce the risk of a potential toxic atmosphere.

8.2 Personal Protective Equipment for Unloading and Handling

Full-protective clothing should be considered as follows: a chemical-resistant splash suit, gloves, boots, eye protection, and respiratory protection (ideally independent air supply). See Section 4.4 for further guidance.

Safe Transport and Unloading of Acid Chlorides and Chloroformates

8.3 General Considerations

The following are general considerations for transporting and unloading -hazardous acid chlorides and chloroformates.

- Acid chlorides and chloroformates are blanketed with nitrogen when transported in bulk containers to reduce the fire hazard risk.
- Bulk containers should be top unloaded by pumping, remembering that the vapor space is always filled with nitrogen.
- After unloading, any excess nitrogen pressure should be vented to a suitable emission-control device (e.g. caustic scrubber or thermal oxidizer). During transport, an excessive positive pressure can increase the risk associated with accidental releases.
- Do not use air for sparging, blowing lines, or blanketing. Air could create a fire hazard.
- All equipment must be free of contamination, including water.
- Acid chlorides and chloroformates should not be heated besides of those delivered as melt. High product temperatures or high-temperature heat sources may compromise product stability, leading to hazardous decomposition products.
- All acid chlorides and chloroformates transport containers, transfer systems and storage tanks must be electrically grounded. Without electric grounding, static charges may develop and discharge creating a potential source of ignition.



8.4 Transportation Incidents - Immediate Actions

In the event of a spill, fire or suspected reaction, immediately call appropriate hazardous materials authorities.

Phone numbers for your region are given in Appendix A and the respective MSDS.

In the event a shipping container or vessel becomes damaged so that delivery to destination cannot proceed safely, every effort should be made to place the vehicle where it will not endanger people or property. The local hazardous material authorities (for example, police and fire departments) should be notified and the public should be restricted from the area. Follow precautions stipulated in the MSDS for acid chlorides or chloroformates.

Bulk Cargo Temperatures

Acid chlorides and chloroformates are shipped in bulk at elevated temperature, ambient temperature or

Safe Transport and Unloading of Acid Chlorides and Chloroformates

cooled, depending on the physical and chemical properties. An abnormally high temperature is an important indicator of a reacting cargo. If a cargo starts to self-heat, immediately notify local emergency response personnel.

High temperatures can be a warning sign or indicator of a possible contamination with incompatible materials such as water. High temperatures can cause over-pressure and venting and must be taken seriously.

8.5 Delivery in ISO-Container

ISO-Containers

BASF supplies acid chlorides and chloroformates in ISO-containers. See Figure 8.1. These ISO-containers are lined with a protective coating e.g. a phenolic resin, are designed for top unloading, have a capacity of about 20,000 liters, and are designed to accommodate closed system unloading. Both the liquid discharge and vapor return lines have flange connections. Typically, the liquid inductor tube nozzle is 50 mm (DN 50) and the vent nozzle is 40 mm (DN 40).

The containers may have additional facilities for heating or cooling depending on the product properties.

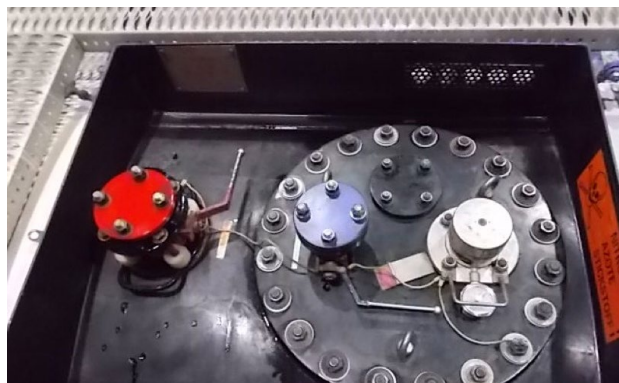


Figure 8.1: Views of ISO-Containers Used by BASF to Transport Acid Chlorides and Chloroformates

Unloading ISO-Containers

The contents of the ISO-containers must be positively identified before they are transferred. If sampling is required, refer to site-specific procedures. Continuous monitoring of the unloading process is appropriate.

1. An emergency shower and eyewash station should be directly accessible from and within the unloading spot. The emergency shower and eyewash stations should be tested periodically to ensure that they work properly. Personal protective equipment should be worn while performing tasks that require opening the system such as sampling, making connections, or breaking connections. Proper equipment should be used to protect against spills and splashes.

Safe Transport and Unloading of Acid Chlorides and Chloroformates

- The recommended method for unloading an ISO-container is by pumping with a closed loop (vapor return) system in which displaces the equivalent volume of vapors which are returned to the ISO-container or by sending them to a caustic scrubber. The example unloading procedures given below refers to the closed loop (vapor return) system illustrated by Figure 8.2.
- Spot the trailer and set wheel chocks. The engine must be stopped, and the emergency breaks applied during unloading.
- Connect ISO-container grounding. Verify that the receiving vessel will hold the entire contents of the ISO-container.
- Remove caps from the ISO-container dip pipe nozzle and the ISO-container vent nozzle.
- Couple the liquid discharge line to the ISO-container inductor pipe nozzle and couple the vapor return line to the ISO-container vent nozzle.
- Open the hand-operated isolation valves on the liquid discharge and vapor return systems.
- Open the remote-actuated Valves 2 and 3.
- Confirm that all appropriate valves on the liquid discharge and vapor return lines are in the correct position.
- Start pump and open Valve 1. Once flow has started, continue to monitor the storage tank level. Confirm that the pressure equalization system is preventing a vacuum from forming in the ISO-container.
- The level switch low switches off the pump when the container is empty.
- Empty contents of product line by flushing with nitrogen to the tank, close Valves 2 and 3.
- Close the hand-operated isolation valve on the ISO-container dip pipe.
- Close the hand-operated isolation valve on the liquid discharge line, the hand-operated isolation valve on the vapor return line, the hand-operated isolation valve on the vent nozzle, and Valve 1.
- Confirm that all valves are in the proper position.
- Disconnect the ISO-container from the unloading system and install the caps on the ISO-container nozzles.
- Quickly clean up any liquid released when disconnecting the ISO-container. Place all used cleaning supplies and solution in labeled, sealed containers.
- Close and secure housings. Leave placards in place. Follow site guidelines for securing truck before shipment.
- Disconnect ground and remove wheel chocks.
- Verify that truck is empty. If truck cannot be emptied, notify shipper before returning the truck.

Do not clean out the ISO-Container! The addition of water and/or other reactive substances can be dangerous.

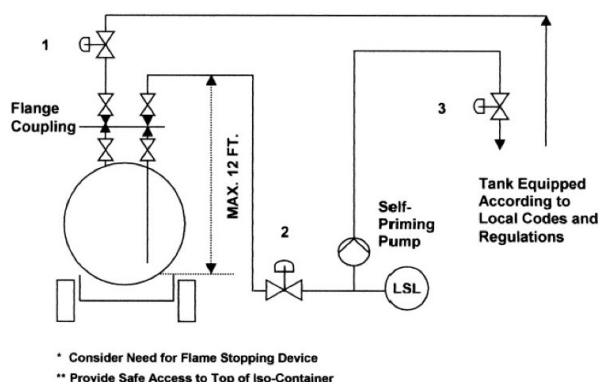


Figure 8.2: Example of an Acid Chloride or Chloroformate Unloading Station

Safe Transport and Unloading of Acid Chlorides and Chloroformates

8.6 Delivery in Drums or IBCs

BASF supplies acid chlorides and chloroformates in plastic-lined steel drums or special Intermediate Bulk Containers (IBC). Before transporting, storing or handling acid chlorides or chloroformates, the current product labeling information and the MSDS (available from BASF) should be obtained, read and understood. Neither the plastic-lined steel drums nor IBCs should be re-used.

Handling Procedure

Acid chlorides and chloroformates are toxic and flammable liquids and should be handled accordingly. The contents of the drums should be positively identified before they are transferred. The procedures outlined below are suggested to reduce risks during the handling of acid chlorides and chloroformates.

Receipt

When a truckload of drums is received, it is recommended to leave the door open for 1 h to ensure proper ventilation. The use of a filter mask is strongly recommended when opening the door of the truck or isocontainer. A persistent odor and/or stinging sensation in the eyes may indicate a damaged container.

The truck driver is instructed by BASF to follow the procedure above.

Moving MCF & ECF drums:



When using forklifter for internal site transport the risk of puncturing a drum of MCF or ECF has to be considered. A major spill will create a toxic atmosphere in the warehouse within minutes.

BASF requirements on the use of forklifters are as following:

- Preferable use of electrically powered fork lifters only
- Speed limit of 6 km/h when handling MCF or ECF drums
- Use of fork blade protectors to increase the impact area and to minimize the risk of puncturing a drum or
- Forks with thickness of a least 2cm without sharp edges or other suitable constructions to prevent damage.

Safe Transport and Unloading of Acid Chlorides and Chloroformates



Example of a fork blade protector.



Storage of methyl- or ethyl chloroformate and propionic acid chloride drums

Though BASF drums are specially designed for chloroformates or acid chlorides, the low molecular and more volatile substances like methyl- / ethyl- chloroformate or propionic acid chloride are suspected to migrate through the plastic in-liner of the drums and could create a local corrosive atmosphere. This could lead to corrosion of the metal drum, especially around the bung holes. Therefore, BASF recommends the following storage conditions:

- Single layer storage
- Designated area in the warehouse
- Biweekly check of drums
- Vented warehouse
- If ambient temperatures exceed 25°C for a longer time, an active cooling of the warehouse should be considered

Emptying Drums

The following steps outline procedures for safely emptying drums. This procedure is also applicable for IBCs unless otherwise noted. Drums must be electrically grounded during transfer operations. Use a static-free dip pipe or flexible hose to drain the acid chloride or chloroformate. To minimize emissions, drums should only be opened for a short period of time and quickly closed once the transfer operation is completed. All equipment coming in contact with products, such as pumps and suction lances, should be quickly decontaminated. All used cleaning supplies and solutions should be quickly placed in labeled, sealed containers and properly disposed.

1. Drums and fittings should never be struck with tools or other hard objects which may cause sparking.
2. Before removing plugs from drums, locate the nearest emergency safety shower and eyewash station and put on personal protective equipment.
3. Open and empty drums only in a work area with good ventilation and spill containment.
4. The safe method for emptying drums is by pumping or by using a suction lance. Do not apply pressure to the drum to displace contents. Use a drum pump made of a suitable plastic. Insert the pump dip pipe through the larger opening and extend down a very short distance from the drum bottom.
5. Provide adequate vacuum breaking to prevent collapse of the drums during emptying.
6. The emptied drum should contain less than 100 ml of residual product.
7. The drum-emptying station should include sufficient local exhaust ventilation to remove product vapor. Collected vapors should be routed to an emission control device.
8. Quickly clean up the work area and equipment. Seal the empty drum and place all cleaning supplies and solution in labeled, sealed containers.

Safe Transport and Unloading of Acid Chlorides and Chloroformates

Disposal of Emptied Drums

Empty acid chloride and chloroformates drums shall be disposed and not reused.

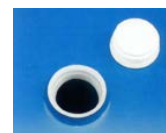
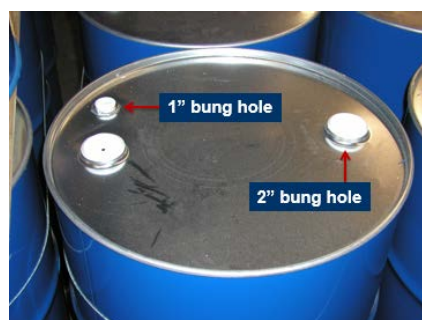
Short chain acid chlorides and chloroformates tend to chloroformates and acid chlorides like methyl chloroformate, ethyl chloroformate, propionic acid chloride and 3-chloropropionic acid chloride tend to permeate through the liner. The tendency of permeation depends on storage conditions like temperature and time. In a worst case up to 100 ml of product may have entered the space between liner and steel drum. For proper disposal a complete decontamination of the drum is necessary.

The drum type with the third bung hole gives access to the space between drum and liner and thus opportunity to remove any dangerous product which may have entered.

The recommended procedure for decontaminating, e.g. ECF or MCF drums is as follows:

1. Wear proper PPE, move the drum to good ventilation area and spill containment
2. Open 2" bung hole and drain any liquid into a suitable container, then close the bung hole
3. Open the small (1") bung hole, then repeat step 2
4. Open all bung holes
5. Fill drums through one 2" bung hole with aqueous diluted NaOH solution, ~ 5% - 7%. Ensure that the organic MCF / ECF layer is covered by an aqueous phase above (MCF / ECF is below the aqueous phase) - no MCF / ECF emissions is possible. Caution: an exothermic reaction may take place
6. Fill the space between liner and drum (small bung hole) with aqueous diluted NaOH solution, ~ 5% - 7%. Caution: an exothermic reaction may take place
7. Do not close the bung holes and soak for about 24 hours

8. Empty the drum from both 2" bung hole and 1" bung hole
9. Rinse the drum with plenty of water
10. All decontaminated water and rinse water should be collected and properly disposed off.
11. The drums may be crushed or shredded before final disposal.
12. Note for the third party disposal company if the drum will be cut: ensure the absence of an explosive atmosphere



09

**Environmental Information
for Acid Chlorides and
Chloroformates**

Environmental Information for Acid Chlorides and Chloroformates

9.1 Environmental Fate

Because of their reactivity, acid chlorides and chloroformates are generally not persistent in the environment. These products are unstable in water and can hydrolyze into the respective acids, alcohols, carbon dioxide, and hydrochloric acid.

They disperse via a combination of mechanisms, including hydrolysis, biodegradation and volatilization. The environmental impact of the respective decomposition products have to be regarded separately.

9.2 Discharges

General Information

The physical and chemical properties of acid chlorides and chloroformates indicate that, if the product is disposed of as waste, it could likely be classified as an ignitable, corrosive or reactive waste. Consult site waste disposal requirements.

Discharges to Navigable Waters or Municipal Publicly Owned Treatment Works (POTW)

Acid chlorides and chloroformates should not be discharged directly to navigable waters or POTW. Consult applicable local regulations and your site-specific water discharge permits.

Emissions to Air

Atmospheric emissions of acid chlorides and chloroformates and their decomposition products may be subject to various regulations and standards. Final vent streams should be routed through a caustic tower scrubber to control emissions. Regulatory authorities may also require a fugitive emission monitoring program which involves inspection and maintenance of valves, pumps and compressors associated with the transfer of acid chlorides and chloroformates.

The disposal of wastes residues from control devices may also be regulated. Consult your local regulatory agencies for guidance.

Removal of Acid Chlorides and Chloroformates Vapors from Exhaust Streams

Vapors of acid chlorides and chloroformates can be removed from exhaust by scrubbing with a caustic solution, combustion, venting to a flare, incineration or a combination of these methods.

- Scrubbing with a Caustic Solution

Caustic scrubbing at a pH of about 9 to 12 is the emission control device of choice for these chlorinated organic products. Air streams contaminated with acid chloride or chloroformate can be purified by absorbing the vapors in aqueous sodium hydroxide solution. Once absorbed, the products are neutralized and destroyed. Sodium chloride is a by-product. During emergency venting, the efficiency of the scrubber tower can be increased by adding ammonia. Note that disposal of the spent scrubbing solution may be regulated.

- Incineration

Acid chloride and chloroformate vapors in exhaust air can be burned using flare stacks, thermal incinerators or catalytic incinerators. In this case, close attention to the by-products of the combustion of chlorinated compounds is necessary. The choice of equipment is dependent upon the properties of the stream being treated and environmental regulations. Consult the suppliers of the combustion equipment for design assistance.

10

**Emergency Response
to a Spill**

Emergency Response to a Spill

10.1 General Consideration for Emergency Response

Users of acid chlorides and/or chloroformates should develop written emergency plans for spills, fires, and inadvertent reactions. These plans should focus on clearly identifying the features that categorize an event as an emergency, measures to secure the emergency site and immediate actions to mitigate the hazards. A very important feature of the plan should be early notification of appropriate local emergency response or hazardous materials authorities.

Emergency response plans should also address the training requirements established under the appropriate local standards.

Regulated acid chlorides and chloroformates are toxic by inhalation. Vapors from these liquid products can burn human tissue including the eyes, lungs and skin. The respiratory system and eyes are particularly susceptible to permanent damage by exposure to these vapors. At ambient temperatures, many acid chlorides and chloroformates can form a flammable and toxic mixture in air. See the MSDS for specific information on a product. Stinging or irritation in the eyes or respiratory system indicates an overexposure that may quickly lead to incapacitation, permanent injury or death.

10.2 Spill and Leak Control General Information

In any event of a spill, the primary concern is the safety of personnel. A team of qualified personnel should quickly evaluate the overall situation and determine the appropriate response.

Emphasis should be placed on the prevention of releases through careful design of equipment and sound operating procedures. Even a small spill of acid chlorides or chloroformates may create an immediate hazard.

Any obligation to report a spill to authorities depends its size and on the local requirements.

An important consideration is that some acid chlorides and chloroformates are heavier than water and may form a separate layer underneath the water that is difficult to detect. When chemical treating these products in aqueous systems, it is important to provide adequate time for reaction.

When a spill is detected, unprotected personnel (breathing protection) in the area should immediately evacuate to a safe distance and not approach the spill. The spill cleanup should be done by qualified emergency response personnel using suitable PPE and breathing protection (e.g. SCBA, or CPS). Emergency response personnel must quickly determine if there is a potential danger to the community and if so, contact the appropriate local authorities. After considering the wind direction and velocity, emergency response personnel must also determine what areas should be evacuated and when these areas can be re-entered. If acid chloride or chloroformate enters a sewer system, there is a potential explosion and inhalation hazard throughout the contaminated system.

If an emergency develops, immediately call appropriate local emergency response or hazardous materials authorities. Phone numbers for your region are given in Appendix A and the respective MSDS.

10.3 Specific Emergency Response to Spills

Small Spills

Response personnel should apply a suitable absorbent to the acid chloride or chloroformate and then transfer the contaminated absorbent into sealed plastic containers. Only seal a container if there is not a risk of reaction. Commercially available absorbents sold for the cleanup of chemical spills can be used, e.g. Vermiculite.

Emergency Response to a Spill

Emergency response personnel should also place all contaminated cleaning supplies and solutions into suitable sealed containers. Properly dispose of the contaminated absorbent, any contaminated soil, and any supplies or personal protective equipment.

If desired, contaminated materials can be converted into non-hazardous waste before final disposal by soaking in dilute solutions of ammonia. Contaminated absorptive materials may be treated by sodium bicarbonate powder followed by rinsing with water. It is imperative that personnel performing the decontamination of materials wear suitable PPE including breathing protection (e.g. SCBA, CPS) and avoid any potential pressure buildup inside of closed containers.

Large Spills

In the event of a spill, the primary concern is the safety of personnel. A team of qualified personnel should quickly evaluate the overall situation and determine the appropriate response. In many cases, the spill clean up may need to be done by qualified emergency response personnel.

If possible, response personnel should contain the spill within a dike area. If the products are clean, free of water and alkaline an option for cleanup may include recovery of product into suitable containers. Another option is applying light mineral oil or an alcohol-resistant, aqueous film-forming foam (AR-AFFF) to blanket the product and avoid evaporation of toxic gases (see infobox below; MCF, ECF & PCF specific).

In the event of accidental spill of acid chloride or chloroformate to surface waters or to a municipal sewer system, the appropriate pollution control and water supply agencies must be notified. As part of the cleanup process, response personnel should put all waste materials in appropriate sealed containers, after ensuring that there is no risk of reaction. This may include materials such as product, by-products of chemical treatment, cleaning solutions and cleaning supplies

MCF, ECF & PCF specific



These chloroformates are very volatile and immediate measures should be done to hinder any toxic evaporation. The surface area of an evaporation pool shall be kept as small as possible and covered by suitable means. Light paraffine oils like “white oil” or “gargoyle oil” are recommended to cover a spill and to hinder their evaporation.

Alcohol stable foam or even water can be used if no paraffin oil is available, but a potential, exothermic chemical reaction with water has to be considered. This reaction is slow and you have a while to stabilize the situation.

Cleaning up a Spill by Absorption

If emergency responders can safely approach the spill, apply a commercially available spill absorbent over the liquid and gently agitate until all of the liquid is absorbed. Place the contaminated absorbent into a suitable plastic container and then seal and label the container. Never place concentrated mixtures of these products and water or other reactive chemicals into sealed containers. The container could be overpressured if a vigorous reaction occurs. Consider releasing pressure during treatment in a container. Only seal a container if there is not a risk of reaction. Clean the spill area and any contaminated tools with a dilute ammonium or sodium bicarbonate solution to remove residual product. Ammonia solution has a faster reaction with these products than sodium bicarbonate. Place cleaning supplies and spent cleaning solution into a labeled plastic container and seal. As needed, rinse the area with water and then decontaminate any potentially contaminated PPE before removing.

Emergency Response to a Spill

Cleaning up a spill by Transferring spilled Product into Containers

For larger spills that are contained in a suitable dry area, it may be desirable to pump the spilled product into suitable containers. Do not transfer acid chlorides or chloroformate into a container if you expect them to be contaminated with other chemicals or even with water. Chloroformates may decompose to hydrochloride acid and carbon dioxide with heat development and the consequences of pressure build up. Pumping mixtures of chloroformates in presence of water might accelerate this decomposition. Mixture of chloroformate and water separate into two phases which you may separate carefully before pumping in a container. Typically, chloroformates are heavier than water.

If emergency responders can safely approach the spill, a double-diaphragm air-driven pump made of a suitable plastic material such as PTFE can be used to transfer most of the spilled product into containers. For emergency service, these pumps offer several advantages including self-priming, can be operated dry for extended periods of time, do not overheat if dead-headed, and are not a sparking device. Fluid transfer equipment and containers must always be grounded before making transfers.

Containers made of a suitable plastic can be used for temporary storage. However, acid chlorides and chloroformates can very slowly penetrate through many plastics so long-term storage in plastic containers is generally not recommended. If available, plastic-lined steel drums are preferred over self-supporting plastic drums. Glass-lined vessels and phenolic-lined vessels are well suited for these products.

Acid Chlorides and chloroformates contaminated with water should not be placed in closed systems. Hydrolysis can generate heat and pressure that may overpressure the container. It is recommended that only water-free products which are not contaminated with reactive chemicals are loaded into closed containers. Dissolved iron and elevated temperatures can catalyze the decomposition of acid chlorides and chloroformates.

Chemically Treating the Spill with Dilute Alkalis Solution

Destruction of large volumes of acid chlorides and chloroformates requires knowledge of their chemical reactions and experienced personnel trained in removing chemical.

Contact BASF (see emergency numbers, Appendix A) if you consider to destroy a large spill in an uncontrolled, open area!



10.4 Disposal of Wastes

All acid chlorides and chloroformates must, if discarded, be disposed in accordance with appropriate local regulations and standards. Contact with acid chlorides and chloroformates should be avoided by the implementation of good operating procedures, engineering safeguards, and the use of PPE. Suitable materials of construction should always be considered when handling or storing corrosive chemicals. A preferred disposal route is to pretreat with ammonium or sodium carbonate solution to neutralize and destroy the acid chloride or chloroformate. The resulting wastewater may then be sent to an approved biological wastewater treatment facility, if applicable local requirements allow. An alternative is to burn acid chlorides and chloroformates in an approved incinerator.

11

**Emergency response
to a Fire or Heat Formation**

Emergency Response to a Fire or Heat Formation

11.1 Specific Response to a Fire

First responder should always consider high flammability and life- or health-threatening toxic vapors from the products and hydrochloric acid when approaching a fire. When making an initial evaluation, emergency responders should use appropriate PPE including a full-face mask with independent air supply (CPS, SCBA) and appropriate skin protection.

When a fire is detected in or around equipment and/or vessels containing acid chloride or chloroformate, an atmosphere that contains significant levels of vapor may be present, if product or hydrochloric acid is in the air. Personnel in the area should immediately evacuate to a safe distance if there is a risk of toxic and flammable vapors. Firefighting that involves or may involve acid chloride or chloroformate should be done by qualified personnel only.

Emergency response personnel first on the scene must determine if there is a potential danger to the community and if so, contact the appropriate local authorities. After considering the wind direction and velocity, emergency response personnel must also determine what areas should be evacuated and when these areas can be re-entered. If acid chloride or chloroformate enters a sewer system, there is a potential explosion and inhalation hazard throughout the contaminated system. A large fire may cause vigorous venting of toxic vapors from emission control devices such as a caustic scrubber tower or directly from storage tanks and vessels.

Emergency responders should be made aware of the potential hazards, the PPE available, the firefighting equipment and supplies available, methods to monitor product concentration in air, decontamination procedures, and first-aid information. Emergency responders should also be made aware that acid chlorides and chloroformates are highly corrosive to most metals and typically stored and handled in glass-lined or plastic-lined equipment and lower heat transfer rate can be expected in glass-lined equipment. At elevated temperatures, decomposition of an acid chloride or chloroformate may initiate and generate heat.

Highly toxic atmospheres have to be considered even if the fire has been extinguished. Any cleaning or removal of product residues has to be done by wearing appropriate PPE.

Chemical reaction of acid chloride and chloroformates with the extinguishing water results into further toxic vapors.

Allowing the Fire to Burn

For fires that are considered dangerous to control, the best option may be to evacuate the area and allow the fire to burn. As possible, the source of fuel should be isolated by stopping pumps and closing valves.

Applying a Foam Blanket to Extinguish a Fire

In many cases, a pool fire of acid chloride or chloroformate in an open area can be quickly extinguished by blanketing with an alcohol-resistant (AR-AFFF) foam. A foam blanket may also help prevent flash back and suppress toxic emissions. The water in the foam can be expected to hydrolyze these products generating some heat and hydrochloric acid.

The addition of foam to closed tanks, vessels and fluid-transfer systems containing acid chloride or chloroformate can cause overpressurization.



Emergency response to a Fire or Heat Formation

Applying Water Spray and/or Water fog to Control a Fire

Applying a water fog over such a fire may help to control the fire and absorb toxic vapors from the atmosphere. The addition of water to closed tanks, vessels and fluid transfer systems containing acid chloride or chloroformate can cause overpressurization and is not recommended. Do not spray water on a pool fire of acid chloride or chloroformates when the density of the acid chloride or chloroformate is less than that of water.

Decontamination and Cleanup after Extinguishing a Fire

After a fire is extinguished and equipment is cooled, the emergency situation is similar to a spill. See Section 10 - Removing a spill

11.2 Specific Response to an Inadvertent Reaction

An emergency situation can be caused by reactions with incompatible material such as water, amines, alkalis and products containing amines. At elevated temperatures, decomposition of an acid chloride or chloroformate may initiate and generate significant heat. The liberation of heat and formation of gaseous by-product such as hydrogen chloride and carbon dioxide may lead to overpressure inside of closed systems and the release of large quantities of potentially toxic and flammable vapors.

See also chapter 6.1, storage tank.

12

Appendix A

Appendix A

Phone Numbers for Emergency Response

Global

International Chemical Environment (ICE)

Phone: +49-621-60-43333

US

Chemtec: +1 (800) 424 9300

BASF Hotline: 1-800-832-HELP (4357)

BASF Corporation Specialty Intermediates

Phone: +1 973 245-5228

EU

BASF SE Fire Brigade Ludwigshafen

Phone: +49-621-60-43333

Fax number: +49-621-60-92664

BASF SE Division Intermediates

Phone: +49-621-60-43241

Asia-Pacific

BASF Company Ltd.

CCD Production Team

Phone: +82 61 680 7121

Mobile: +82 11 612 7121

BASF East Asia Intermediates & Inorganics

Phone: +852-2731-0103

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