

EMERGENCY RESPONSE WHEN ADDRESSING INCIDENTS INVOLVING METHYL CHLOROFORMATE (MCF) AND ETHYL CHLOROFORMATE (ECF)

CFSG 002

Edition 1

September 2023

chloroformates
A sector group of Cefic 

A Chloroformates Sector Group publication

A sector group of Cefic 

This document can be obtained from:

Chloroformates Sector Group – Rue Belliard 40, Box 15 - B-1040 BRUSSELS

E-mail: chloroformates@cefic.be

Chloroformates Sector Group

The Chloroformates Sector Group (a Sector Group of Cefic; CFSG) is the European group which represents European producers of Methyl Chloroformate (MCF) and Ethyl Chloroformate (ECF).

CFSG is working to:

- Promote the safe production, handling, transport and storage of Chloroformates;
- Foster science and innovation around Chloroformate safety;

This document is provided to share CFSG experience to assist downstream operations. When applied, it should help to prevent/ manage incidents and improve procedures. Anyone involved in handling Chloroformates or empty Chloroformate containers can benefit from the information presented here.

Questions on the content of this document should initially be raised with your provider of Chloroformates but can also be sent to the contacts on the final page of this guidance.

.....

This document has been produced by the members of CFSG and should not be reproduced in whole or in part without the prior written consent of CFSG.

It is intended to give only guidelines and recommendations. The information is provided in good faith and was based on the best information available at the time of publication. Although CFSG makes every effort to ensure the completeness of the information provided, the information may not be sufficient or appropriate in all cases to take the needed measures. This information is not intended to replace a specific case-by-case assessment done by a specialist. The information is to be relied upon at the user's own risk. CFSG, Cefic and its members make no guarantee and assume no liability whatsoever for the use and the interpretation of or the reliance on any of the information provided.

This document was originally prepared in English by our technical experts. For our members' convenience, it may have been translated into other EU languages by translators / CFSG members. Although every effort was made to ensure that the translations were accurate, CFSG, Cefic and its members shall not be liable for any damages or losses of accuracy/ information due to the translation process.

RESPONSIBLE CARE IN ACTION

This document is part of a series which European producers, acting through their Chloroformate Sector Group (CFSG), have drawn up to promote continuous improvement in the general standards of health, safety and the environment associated with Chloroformate manufacture and handling in the spirit of *Responsible Care*[®].

The voluntary recommendations, techniques and standards presented in these documents are based on the experiences and best practices adopted by member companies of the CFSG at their date of issue. They can be considered, in full or partly, whenever individual companies review their operation of existing processes and in the design of new installations. They are in no way intended as a substitute for the relevant applicable national or international regulations, nor to replace a specific case-by-case assessment done by a specialist.

It has been assumed in the preparation of these publications that the users will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance these publications have been prepared. The contents are based on the best available information at the time of writing and on good engineering, medical or technical practice but it is essential to take account of appropriate subsequent developments or legislation. As a result, the text may be modified in the future to incorporate evolution of these and other factors.

This edition of the document has been drawn up by a team of experts from the CFSG to whom all welcome suggestions concerning possible revision should be addressed through the CFSG secretariat (cover page).

MAIN MODIFICATIONS IN THIS EDITION

EDITION	Section	Nature
1	-	None in this edition

TABLE OF CONTENTS

1. INTRODUCTION	5
2. LEAKAGES AND SPILLS	7
3. PERSONNEL HEALTH AND SAFETY	10
4. HANDLING AND TRANSPORTATION INCIDENTS	14
5. FIRE RESPONSE	18

1. INTRODUCTION

The following reflects the way that some European Chloroformate producing companies approach emergency response. Whilst the reader should never neglect the requirements and advice of authorities, their suppliers and emergency responders in their respective country, this document provides general information on how to deal with emergencies involving Chloroformates. It is based on the experiences of European Chloroformate producers and should be read in its entirety, in collaboration with the Safety Data Sheets (SDS), before activities involving these products take place.

This document may apply for all Chloroformates but as MCF/ ECF are the most common, most toxic and most commercially relevant, focus will be on the specific measures involving incidents that concern them. Whilst relevant for global audiences, it is written with the European reader in mind due to local, specific requirements.

All employees, site emergency personnel, transporters or forwarders who handle Chloroformates should be thoroughly trained and informed about the potential hazards, exposure and incident techniques, emergency response plans, personal protective equipment and environmental protection aspects. Possible safety incidents involve or include (but are not limited to) the following:

- Spillages (irrespective of location and volume)
- Personnel exposure (including inhalation and skin contact)
- Handling and Transport incidents involving
 - Drums – overpressure/ bulging/ leakage due to damage
 - Bulk containers – overpressure, possibly with blown pressure safety valves/ leakage/ road accidents/ temperature rise/ maritime incidents/ lifting and craning incidents/ rail tank car incidents
 - Box containers (with drums) – road accidents/ lifting and craning incidents
- Fire

Written emergency response plans are also recommended for potential release, fires and unintended reactions. These plans should be regularly consulted and reviewed and be part of the training programme of plant operators. Documented, regular drills (including emergency personnel) should also take place alongside the use of checklists to confirm that everything has been covered in practice.

Emergency personnel should always check the supplier SDS (which include 24/7 supplier emergency contact information) and other excellent additional sources of information such as the following:

- Annexes to this document; single page summaries of some of the information in this document
- [Cefic Emergency Response Intervention Cards](#) (URL checked August 2023)
- [ILO](#) website (URL checked August 2023)
- TUIS/ ICE/ ChemTrec (US) information sources
- Poison Control Centres

2. LEAKAGES AND SPILLS

Users of Chloroformates should develop emergency plans for implementation during a spill. These plans should focus on what would classify as an emergency spill, measures to secure the site in case of such a spill and immediate actions to mitigate any hazards. Depending on local requirements, notification of a spill to authorities should be a key initial part of such an emergency spill plan alongside any necessary training and drill procedures.

In the event of a spill, the primary concern is for the safety of all personnel impacted. Personnel who are not protected by breathing equipment must leave to a safe distance (considering the wind direction) and not approach the spill. An early action should be for a team of qualified and Personal Protective Equipment (PPE) equipped personnel to evaluate the situation and determine the response.

Water curtains can be used to contain the product vapours to a certain area (see next paragraph for considerations when using water). Any further activities should be performed by qualified personnel equipped with appropriate safety equipment (as detailed in section 3). Should danger to local communities or water/ sewage be a possibility, local authorities should be informed.

As (some) Chloroformates (e.g. MCF/ ECF etc.) are very volatile, immediate measures should be taken to hinder any toxic evaporation. The surface area of an evaporation pool should be kept as small as possible and be carefully (i.e. to avoid agitating any liquid) covered by suitable means (e.g. light paraffin oils). Alcohol Stable Aqueous Film Forming Foams (AS-AFFF) or even water can be used if no paraffin oil is available, but a potential, exothermic chemical reaction with water must be considered. This reaction at the interface between Chloroformate and water phase is delayed and slow so responders may have time to stabilise the situation.

If emergency responders can safely approach the spill, commercially available spill absorbents (e.g. Vermiculite) may be used by placing it over the liquid and gently agitating (e.g. with a broom) until all of the liquid is absorbed. The loaded absorbent should then be placed into a suitable plastic container and labelled accordingly. Attention should be paid to the potential reaction between humidity of the absorbent and the chloroformate (i.e. gas formation). Never place concentrated mixtures of these products and water or other reactive chemicals into sealed/ closed containers as they could be over-pressured since a vigorous reaction is highly likely.

Larger spills should be contained within a dike area. For clean (i.e. free of water/ alkaline) spills, the chemical may be recoverable into suitable containers. Spills may be destroyed by water but the reaction can take several days and checks whether all spilled Chloroformate has been destroyed may be needed. The use of a diluted alkaline solution (e.g. sodium bicarbonate/ ammonia) has an associated risk of an uncontrolled/ highly exothermic reaction so should be carefully considered. The resulting material may also be hazardous (e.g. flammable/ toxic).

Due to many Chloroformates being heavier than water, there may be a layer of Chloroformate beneath any sluicing water which should be considered. Attention should be paid when pumping/ mixing as an exothermic reaction is likely.

As part of any clean-up process, response personnel should put all waste materials in appropriate sealed containers, after ensuring that there is no risk of reaction, which may lead to pressure build-up. Consider constant pressure release during treatment in a container and only seal a container if there is no risk of reaction (see later in this section). This behaviour may include materials such as product, by-products of chemical treatment, cleaning solutions and cleaning supplies. Consultation with product experts is highly recommended.

Transferring spilled products into a container.

If emergency responders can safely approach the spill, they may ideally use an explosion-proof double-diaphragm air-driven pump or electric pump to transfer most of the spilled product into containers. Fluid transfer equipment and containers must always be grounded before making transfers.

Before pumping Chloroformates into a container, especially if you expect them to be contaminated with other reactive chemicals (including water), consult a product expert first. Chloroformates may decompose to hydrochloric acid and carbon dioxide with heat development and pressure build up. Dissolved iron and elevated temperatures can catalyse the decomposition of Chloroformates.

Pumping mixtures of Chloroformates in the presence of water might accelerate any decomposition. Mixtures of Chloroformates and water can be separated into two phases before pumping in a container as Chloroformates are usually heavier than water. As a consequence, all equipment used for pumping (hoses, pumps, containers etc.) should be clean, dry and made of a suitable material. Containers made of a suitable plastic can be used for temporary storage. However 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- and resin-lined vessels are well suited for these products.

Disposal of spilled products.

Chloroformates must, if discarded, be disposed of in accordance with appropriate local regulations and standards. The resulting wastewater may then be sent to an approved biological wastewater treatment facility if applicable local requirements allow. An alternative is to burn Chloroformates in an approved chemical incineration plant.

Where Chloroformates are disposed of as waste, they should be considered ignitable, corrosive and reactive. They should be treated/ handled in the same manner as the product itself.

Final Decontamination of spill area and tools.

Clean the spill area and any contaminated tools with a dilute alkaline solution (e.g. ammonium or sodium bicarbonate) to remove residual product. Place cleaning supplies and spent cleaning solution into a labelled plastic container and seal. Thoroughly rinse the area with water and then decontaminate any potentially contaminated PPE. Contaminated clothing and PPE may also be placed into the labelled plastic containers for disposal.

3. PERSONNEL HEALTH AND SAFETY

Toxicology.

Detailed information on the toxic properties of Chloroformates are described in the associated SDS of the specific compound. Typically, these substances are toxic by inhalation, flammable and are highly corrosive.

Chloroformates (especially their vapours) can burn mucous membranes causing severe damage to the eyes, lungs and airways, potentially damaging the underlying tissues, particularly if they are inhaled or if Chloroformates are swallowed. The vapour associated with pungent odour can cause stinging of the eyes and/ or nose (a 'warning signal' of exposure) so impacted personnel should immediately leave the area. Exposed persons might lose orientation due to tearing eyes. Exposure by skin contact can result in severe burns, particularly to the lower layers of the skin due to high penetration of these substances.

Exposure by inhalation can result in severe lung damage and even death by toxic lung (pulmonary) oedema. The effect is largely dependent on the concentration/ time of exposure. Exposure can be indicated via phosgene detection 'badges' that also react with Chloroformate vapours (and hydrochloric acid) but the exact dose of inhaled Chloroformate cannot be quantified by these badges. Delayed toxic lung (pulmonary) oedema has been observed by people who have been exposed to certain doses of Chloroformates. Even if exposed people do not feel unwell to begin with, these people require immediate hospitalisation, remaining there for at least 24 hours after exposure. The earlier (potentially) required medical treatment starts the better the chance of survival.

First Aid and Initial Treatment.

Rescuers should always take care to avoid intoxicating themselves (e.g. avoiding direct mouth-to-mouth resuscitation) and protect themselves with appropriate PPE (e.g. filter masks).

First-aid teams need adequate training, equipment, transport facilities for accident victims and a control room or other safe location with fresh air supply where casualties can be taken to. Medical oxygen supplies and communication facilities with immediate access to local ambulance and hospital services should be available in the control room/ safe location. These local services should be aware of the specific requirements for the transport and follow-up treatment of victims of Chloroformates.

It is useful to regularly review the protocols with the staff of the local hospital and also considering the latest information from national poison information centres.

In any accident, the victim should be transported to a medical treatment unit as quickly as possible.

Personnel who are suitably trained, and have been given the responsibility to do so, may also administer medication depending on local regulations and at their own discretion. Such medications that could be used may be found in publicly available publications, such as in the [BASF advice document](#) on Chloroformates (URL checked August 2023).

On specific First Aid measures, the following advice is given:

In case of inhalation:

- The casualty should be evacuated to the nearest well-ventilated area.
- Always seek medical attention.
- The casualty will need monitoring for at least 24 hours after exposure as intoxication symptoms could appear later. Further monitoring/ treatment should always be decided by a physician.
- Physicians may administer corticosteroids as soon as possible to suppress inflammations at their own discretion.
- Site ambulances/ local first aid kits may also have inhalers of corticosteroids available for instant medication at their own discretion.
- Details on any medication (treatment) administered should accompany the casualty in case of hospitalisation.

In case of contact with eyes:

- The casualty should immediately flush both eyes with running water for at least 15 minutes at the nearest eye wash station.
- Eyelids should be held open (assistance may be necessary to hold the eyes open) and away from the eyes during the flushing time and contact lenses should be removed.
- Always seek medical attention (with additional consultation from an ophthalmologist).
- Where such medical support is not available, the casualty should continue flushing for a second 15-minute period.

In case of contact with skin:

- The casualty should be evacuated to a safety shower to immediately rinse off the chemical for at least 15 minutes.
- Beneath the shower, remove contaminated clothing leaving eye protection/ respiratory protection in place until the last possible moment to ensure the absence of product.
- Place contaminated clothing in a sealed container/ bag.

- Always seek medical attention as some Chloroformates can penetrate deep into the skin causing (permanent) damage even some time after exposure.
- Do not apply any medicines or burn ointments without specific instruction from a physician.

In case of ingestion:

- Do not induce vomiting.
- Always seek medical attention (in consultation with the local poison control centre).
- If conscious, immediately rinse the mouth but do not swallow this water. The casualty may drink a small amount of fresh water.
- The casualty may need to be placed in the recovery position (i.e. lying on their side with their airway extended) as appropriate.

If the casualty has become unconscious:

- Use individual protective equipment to rescue casualties.
- Remove casualty to fresh air, if possible to a quiet area.
- Carefully remove contaminated clothing (this may need to be carefully cut away using medical scissors and ensuring that the rescuers are also protected with appropriate PPE).
- If breathing has ceased, start artificial respiration, avoiding self-contamination. Direct mouth-to-mouth resuscitation should be avoided at any time.
- Let the patient sit in a half-seated position or let them lie down comfortably.
- Administer oxygen as soon as possible.
- In case of skin and/ or eye contamination, irrigate the impacted area with water for at least 15 minutes.
- Keep the casualty warm and seek medical attention.

Personal Protective Equipment (PPE).

For PPE during standard handling/ maintenance, please refer to the SDS. There should be facilities/ training to enable decontamination and replacement of PPE. PPE may include, but is not limited to:

- Breathing protection for normal operations, including availability of a filter mask if no SCBA (Self Contained Breathing Apparatus) is available.

- Independent air supply (SCBA) for work involving potential contact with the products.
- Adequate face/ eye protection (e.g. goggles, face shields etc.).
- Skin coverings should be of a material that is adequately impervious to Chloroformates (e.g. butyl rubber gloves, chemical suits). Gas/ liquid-tight suits may be necessary.
- Rubber boots.

All PPE should be thoroughly rinsed prior to removal if they have been involved in an incident. As clothing could be contaminated during incident response, the final piece of PPE that should be removed is the breathing protection.

4. HANDLING AND TRANSPORTATION INCIDENTS

In case of road accidents or incidents in port/ ship area/ container storage areas, manufacturers may be consulted as they have the most knowledge of dealing with such incidents (e.g. container with blown valves). They may also be able to provide information in case of warehouse handling incidents (e.g. drum damage from forklifts/ bulged drums) which may require specific information. More information on drum handling under normal conditions can be found in document CFSG 001 (available via <http://www.chloroformates.org>, URL checked August 2023).

Professional, general advice on managing emergency response for transport incidents is available from sources such as ICE/ TUIS and summarised in ERICards (see section 1).

For any handling or transport incidents involving Chloroformates, the product vapour pressure and current wind direction should be considered for initial, safe intervention but also to help estimate risk to the local population and environment to assist in taking appropriate measures. Authorities and local intervention organisations need to be informed according to the expected risk.

In case of leakages, it should also be determined how the spill will be contained and which appropriate measures can be used to prevent further spread of liquids and toxic vapours (e.g. by firefighting foams; see section 5).

Drum Incidents.

For larger spills, this typically involves the puncturing of a drum with a fork lift blade. In such situations, the forks should be left in the drum to seal the leakage and the contents of the drum should then be pumped into another suitable container for recovery and disposal. At the same time, suitable containment should be built around the punctured drum (e.g. a spill pallet/ absorbent spill pads/ flexible spill barriers etc.) to avoid a larger spill area that may result in larger toxic clouds. Any spills can then be cleaned up as per the recommendations in section 2.

In case of potentially damaged or bulged drums without visible spill (e.g. in accidents involving a box container/ closed truck), refer first to any information on the outside of the container concerning opening (e.g. warning sign/ text). Carefully open the container with suitable PPE (at least a full face filter mask) as a toxic atmosphere will exist if the drums inside have been compromised. In case of *leaking* drums, proceed as described previously. *Damaged* drums should preferably be placed into a sleeve/ overpack followed by transfer into a suitable container or drum (that carries the correct UN Packaging code) at a chemical site with suitable equipment and safety installations. If no sleeve/ overpacks are available then pumping into a suitable container should be carefully done at the accident site.

Any contamination of surfaces/ box container/ truck bed should be decontaminated as per section 2.

Container/ rail car incidents.

In case of any accidents with containers, the immediate area should be evacuated and authorities informed. Ensure that all response personnel in the immediate area are safe and protected (everyone else should be evacuated to a safe distance). Local emergency services should be alerted. The containers should then be secured against further incident, with contact being made to ICE/ TUIS call centres for advice if needed. Once the container is adequately protected, check to ensure that there are no leakages from it. A surveyor can then fully assess the integrity of the container for transport to the closest, safe location.

For incidents involving tanker flipping, determine whether it is not leaking and can be flipped back over without further damage.

Exposure should be minimised and, where safe and possible, undamaged valves should be closed (employing appropriate PPE). However pressure increase may be expected. As such, pressure build up in any closed containers should be monitored and vented only when appropriate safety measures (such as mobile scrubbers, described later) are available. Safety valves should never be blocked off.

Should a damaged container be leaking, spills can be treated as per the directions in section 2. Caution should be exercised here though to avoid water ingress into any ruptured container/ valve from a water curtain (see advice in section 2). Experts outside of the company may be needed here (particularly from suppliers). The content of any leaking container should be transferred to other suitable tanks/ containers as described above.

It may be that a damaged container is not able to be transported. As containers holding chloroformates typically have a dip tube and no bottom outlet, an (electrically driven membrane) pump is necessary. Any remaining product can be pumped to another suitable container for further recovery or disposal. For this transfer, the product lines (via the dip tube) of both containers can be connected as shown in Figure 1.

As part of this recovery, mobile scrubbers may be used. This refers to an IBC filled with dilute sodium hydroxide that Chloroformate can vent to, with appropriate back- and overflow protection, to destroy any toxic vapours. A constant nitrogen flow can protect the product from moisture and possible further reaction. This is detailed in Figure 1.

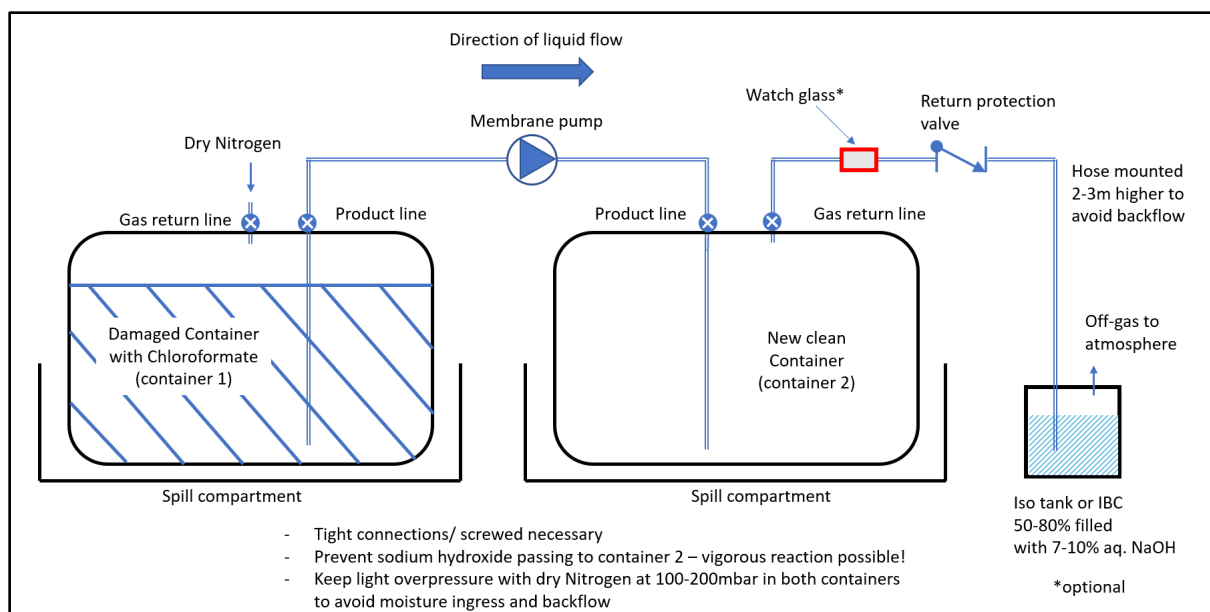


Figure 1. Transfer of Chloroformate from a broken container into a new one.

As Chloroformates may build up pressure, or even vent through safety valves if transported under unfavourable conditions, a second problem may be foreseen in the need to stabilise this via safe pressure release. Vented Chloroformate vapours also contain hydrochloric acid gas so should also be treated using a mobile alkaline scrubber. It should be ensured that the flow direction is always from the ‘decomposing’ Chloroformate into the sodium hydroxide (e.g. by maintaining positive pressure in the Chloroformate tank and appropriate back/ overfill protection such as a catch vessel). This scrubber is connected to the gas return line (not the discharging/ product line with the dip tube; red ‘X’ in Figure 2) and that there is a clear filling level so that any connectors do not enter the liquid Chloroformate. Expert advice on such activities should be sought from the suppliers before starting.

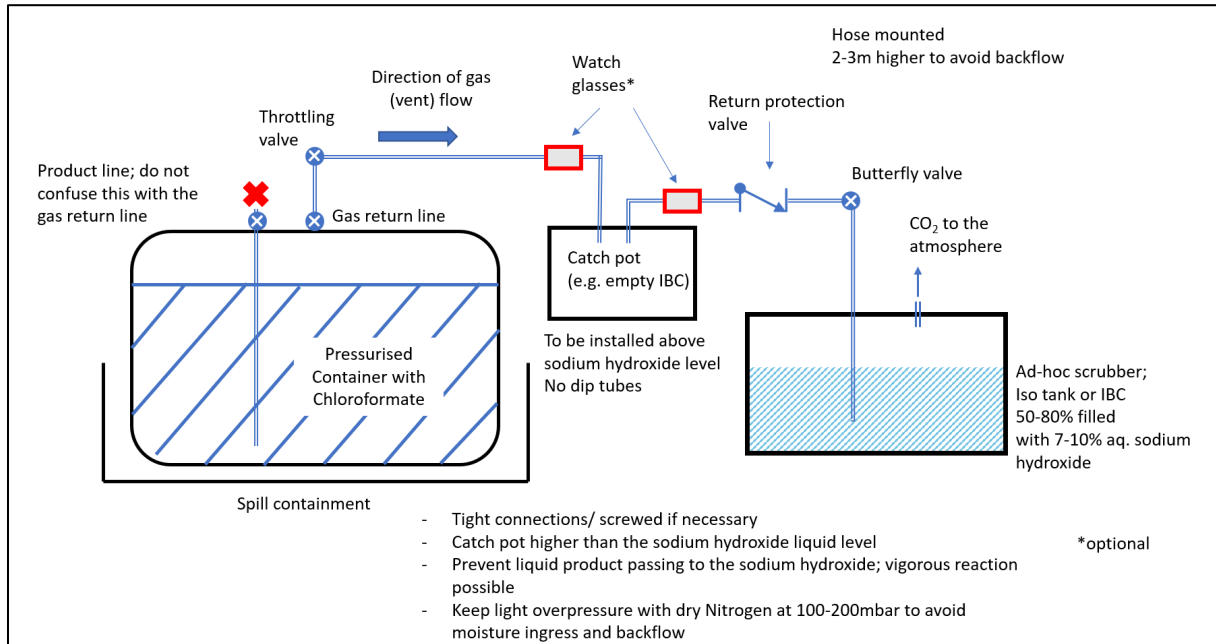


Figure 2: Example set up of a mobile scrubber for Chloroformates to address decomposing (unstable) product

5. FIRE RESPONSE

All emergency responders should be made aware of the potential hazards of Chloroformates, the necessary PPE, the availability of local firefighting equipment, monitoring, decontamination procedures and first aid information. Emergency responders should also be made aware that Chloroformates are highly corrosive to most metals and typically stored and handled in glass- or plastic-lined equipment (N.B. lower heat transfer rates are expected in glass-lined equipment). At elevated temperatures, decomposition of a Chloroformate may initiate and generate heat and high pressures. For further advice, please contact your supplier.

Some (liquid) Chloroformates and their vapours are highly flammable (flash point <23°C, initial boiling point >35°C). Such vapours, even after the fire is extinguished, can be fatal if inhaled or can reignite. Upon discovery of a fire, emergency responders should be immediately alerted, and personnel in the area evacuated to a safe distance. Vapour curtains may be needed to prevent spread of these chemicals.

When making an initial assessment of the fire, responders should use appropriate PPE including a full-face mask with independent air supply on top of appropriate skin protection. If local communities may be impacted, the local authorities should be immediately informed. Information on wind direction and velocity may be needed as this will determine the authorities' public information and evacuation plans. If there is risk that Chloroformates may enter a local sewer system or if there is a potential for explosion/ inhalation, this should also be relayed to authorities.

The source of any fuel should be isolated by stopping pumps and closing valves.

Applying a Foam Blanket to Extinguish a Fire.

Chloroformate pool fires in open areas can be extinguished by blanketing with an alcohol-resistant foam (e.g. Alcohol Stable Aqueous Film Forming Foam; AS-AFFF). A foam blanket may also help prevent flashback and suppress toxic emissions. It should be noted though that the water in the foam can be expected to hydrolyse these products generating some heat and hydrochloric acid. This includes the use of water in a 'water curtain' which is common on many sites. Additionally, placing foam directly into closed tanks, vessels and fluid-transfer systems containing Chloroformates can cause over-pressurisation so should *never* be done.

As highly toxic atmospheres must be considered, even after the fire has been extinguished, any cleaning or removal of product residues has to be done by wearing appropriate PPE. Once any pool of Chloroformate has been carefully covered (e.g. with any AS-AFFF to avoid agitating any liquid) and any fire risk prevented, the pooled material can be carefully destroyed as per previous guidance in section 2.

All above measures should only be carried out after consultation with product experts.

ABBREVIATIONS AND ACRONYMS

AS-AFFF	Alcohol Stable Aqueous Film Forming Foam
ATEX	Explosive Atmospheres
CFSG	Chloroformate Sector Group
ECF	Ethyl Chloroformate
GPS	Global Positioning System
IBC	Intermediate Bulk Container
ICE	Intervention in Chemical Transport Emergencies
ILO	International Labour Organisation
MCF	Methyl Chloroformate
NaOH	Sodium hydroxide
PPE	Personal Protective Equipment
PTFE	Polytetrafluoroethylene
SCBA	Self-contained breathing apparatus
SDS	Safety Data Sheet
TUIS	Transport Accident Information and Emergency Response System
URL	Uniform Resource Locator

Industrial consumers of Chloroformates, engineering and equipment supply companies worldwide and chlorine producers outside Europe may establish a permanent relationship with CFSG or comment on this document by contacting:

Chloroformates Sector Group (CFSG)

Cefic

Rue Belliard 40

Box 15

B-1040 Brussels

Belgium

Tel: +32 2 436 9300

Fax: +32 2 436 9550

Email: chloroformates@cefic.be