

**H260
H261**

EUH014

PRODUCT FILE



**CHEMICALS WHICH REACT
VIOLENTLY WITH WATER**

MANAGEMENT OF CHEMICAL ACCIDENTS
HEALTH - ENVIRONMENT

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**H260
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EUH014

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CHEMICALS WHICH REACT VIOLENTLY WITH WATER

MANAGEMENT OF CHEMICAL ACCIDENTS HEALTH - ENVIRONMENT

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1. KEY POINTS

1.1. DEFINITIONS

Chemicals which react with water are considered as dangerous substances or mixtures. This danger represents an entirely separate class in the CLP¹ labelling system, from the moment that release of flammable gases results from the contact of said products with water.

The former European classification of chemicals (Directive 67/548/CE) included two risk phrases for substances and preparations which react with water:

- **The risk phrase “R 14 – Reacts violently with water”**, was assigned to substances which strongly react with water, by virtue of their physical-chemical properties, but without necessarily leading to the release of a flammable gas or an explosion.
- **The risk phrase “R15 – Contact with water liberates extremely flammable gases”** was assigned to substances and preparations when, during a test-assay (test method A12, regulation (EC) 440/2008 of the 30/05/2008) ignition occurred, or that the flow of flammable gas generated exceeded the limit value of 1l/kg/h.

In the CLP labelling system, the R14 phrase has been replaced by the phrase **“EUH014 – Reacts violently with water”**.

It applies “to substances and mixtures which react violently with water, such as acetyl chloride, alkaline metals, titanium tetrachloride”, according to the definition in CLP. This hazard statement, which does not exist in the GHS², has been added by the European Union.

The phrase R15 corresponds to the new hazard class “Substances and mixtures which, in contact with water, release flammable gases”, which is divided into 3 categories (hazard statements H260³ and H261⁴). These are “Liquid or solid substances or mixtures which, through reaction with water, are capable of igniting spontaneously or releasing flammable gases in dangerous quantities”, according to the CLP definition.

1 - CLP : Classification Labelling Packaging, European regulation N°1272/2008/EC

2 - GHS : Globally Harmonised System

3 - H260 : In contact with water releases flammable gases which may ignite spontaneously

4 - H261 : In contact with water releases flammable gases



The reaction must take place at ambient temperature. Then, different criteria are taken into account for a classification into 3 categories:

CATEGORY	CRITERIA
1	Vigorous reaction with water releasing a gas capable of igniting spontaneously OR Rather vigorous reaction with water releasing a flammable gas $> \text{ or } = 10 \text{ l/kg/min}$
2	Rather vigorous reaction with water releasing a flammable gas $> \text{ or } = 20 \text{ l/kg/h}$ and which does not meet the classification criteria in category 1
3	Slow reaction with water releasing a flammable gas $> \text{ or } = 1 \text{ l/kg/h}$ and which does not meet the classification criteria in categories 1 and 2

Furthermore, if a spontaneous ignition occurs (for example ignition of a solvent due to a temperature increase), the tested substance or mixture is then classified as a substance or mixture which on contact with water releases flammable gases.

1.2. USES

All these chemicals are used for their high reactivity:

- Organomagnesium compounds, or Grignard reagents, are very useful as synthesis intermediates in the pharmaceutical industry.
- Metal hydrides, such as lithium aluminium hydride (LiAlH_4), are also used in organic chemistry for their strong capacity to produce hydrides.
- Lithium is used in lithium batteries, installed as such to power, for example, mobile phones.
- Phosphoryl chloride (POCl_3) is used in the manufacture of photovoltaic panels.
- Titanium tetrachloride (TiCl_4) is used for the production of titanium, white titanium oxide pigment, artificial glass pearls, for the production of smoke screens or the surface treatment of glass bottles.

Given their reactivity and their frequent use, it is not uncommon that accidents occur with chemicals which react strongly with water. The problem is twofold:

- Achieve an optimal and active decontamination for exposed personnel in the event of splashes on the body, capable of limiting the consequences of the specific physical/chemical properties of these chemicals.
- Capable of absorbing this type of substance in the event of ground spillage, in order to preserve the environment⁵ and limit explosive and inflammable reactions.

2. LABELLING

Products reacting with water while releasing flammable gases will be labelled in the following manner, according to the previously cited test results:




CLASSIFICATION	CATEGORY 1	CATEGORY 2	CATEGORY 3
GHS pictograms			
Signal word	Danger	Danger	Danger
Hazard statement	H260: In contact with water releases flammable gases which may ignite spontaneously	H261: In contact with water releases flammable gases	H261: In contact with water releases flammable gases
Precautionary statement Prevention	P223 P231 + P232 P280	P223 P231 + P232 P280	P231 + P232 P280
Precautionary statement Response	P335 + P334 P370 + P378	P335 + P334 P370 + P378	P370 + P378
Precautionary statement Storage	P402 + P404	P402 + P404	P402 + P404
Precautionary statement Disposal	P501	P501	P501

Table 2.12.2 of the CLP regulations

Products which react violently with water will be labelled in Europe with the wording of the statement EUH14 – Reacts violently in contact with water.

There is no pictogram or associated signal word.

⁵ - Here this is taken to mean preservation of the environment and management of chemical spillages.



3. CHEMICAL CHARACTERISTICS

Chemicals which react strongly with water can be classified according to chemical families:

- Alkaline metals, such as lithium (Li), sodium (Na) or potassium (K)
- Chlorosilanes (chlorinated silicon compounds), such as trichloromethylsilane (CH_3SiCl_3)
- Metal alkyls such as aluminum, zinc, magnesium, or lithium alkyls (organometallics)
- Acid chlorides (of general formula R-COCl)
- Certain Lewis acids, such as titanium trichloride (TiCl_4) and phosphorous pentachloride (PCl_5)
- Metal phosphides such as aluminum phosphide (AlP) or magnesium phosphide (MgP)
- Phosphorus sulphides (such as P_4S_{10} dimer form of diphosphorus pentasulphide)
- Sulfonyl isocyanates ($\text{R-SO}_2\text{-NCO}$)
- Metal hydrides (LiAlH_4)

The chemical reactions on contact with water may be of different types:

- > It can be a hydrolysis with oxidation of alkaline metals:



A release of hydrogen gas (H_2) takes place and the residue is very alkaline, because of hydroxide ion OH^- presence.

> It can be a decomposition reaction of the substance in contact with water:



> It may involve hydration reactions, such as with oleum (SO_3) :



A more interesting classification may be proposed if the nature of the products derived from the decomposition by water is taken into account. Distinction needs to be made between reactions with water releasing:

- Hydrogen gas (H_2),
- Hydrogen chloride (HCl), or any other halogen hydride (HBr, HF, HI)
- Phosphine (PH_3)
- Alkanes (methane, ethane, etc.)
- Carbon dioxide (CO_2)
- Hydrogen sulphide (H_2S)

Releases following contact with water are violent. They are generally accompanied by a strong heat increase, leading in the worst cases to an explosion (such as with the release of phosphine – example of phosphorous fires) or to a fire. Gas emission, if it does not ignite, can carry along vapours of all reagents present with possible intoxications and/or depletion of ambient oxygen.



For example, in the decomposition reaction of titanium tetrachloride with water, a plume of hydrogen chloride and titanium compounds (TiO_2 , TiCl_4 that has not yet reacted) is formed.

As in nature, exceptions do exist and chemicals in other forms than gas can be released!

For example, calcium carbide reacts with water to form acetylene and solid lime:



$$\Delta H = -130 \text{ kJ/mol } (-31,1 \text{ kcal/mol})$$

Another example is methoxysilanes (e.g. vinyltrimethoxysilane), which release liquid methanol at ambient temperature.



Chemicals which react violently with water can be classified depending on hazards resulting from gas emissions.

Following contact with water, there can be release of:

- **Flammable gases** (sometimes spontaneously ignitable) such as hydrogen gas or alkanes, such as methane, ethane, etc...
- **Corrosive products** such as hydrochloric acid, bromic acid, phosphorous acid, sulphuric acid, propionic acid, etc...
- **Toxic gases** such as carbon dioxide, hydrogen sulphide, methanol, phosphine (gas which is also flammable) or hydrofluoric acid (corrosive and toxic gas).

4. CORROSIVITY

Cutaneous or ocular splashes which react violently with water can generate a double or even triple hazard:

- If the chemical is irritant/corrosive, a chemical injury can develop.
- Lesions caused may then be more severe due to the exothermic nature of the reaction with water. Heat can induce further thermal burns.
- Finally, a risk of toxicity may exist, depending on by-products released.

In addition, a physical risk of explosion or fire is not negligible (see the chapter on the management of associated risks).



Figure 1 : Illustration of a chemical and thermal lesion – source: Turbomeca

The corrosiveness of chemicals reacting with water will be linked to the nature of by-products released.

> When hydrogen chloride (HCl) is released, it can be responsible for skin, eyes and respiratory mucous membrane chemical lesions, on account of its acid character. On contact with moisture, it is transformed into hydrochloric acid. The induced injuries are due to contact with the H^+ proton which is released. Lesions concern the respiratory tracts, to a greater or lesser degree with, apart from the risk of corrosion, that of initial bronchospasm, which can be more or less severe. In addition, exists the possibility of secondary onset of Brooks syndrome⁶, even after a single exposure. Furthermore, the hydrochloric acid inhalation may lead to an acute pulmonary oedema, through a toxic alveolar mechanism, which can be more or less delayed in the hours following contact. It is therefore advisable to remain vigilant and to place the victim under observation for 24 hours to avoid a real fatal risk ; thus explaining the classification of hydrogen chloride as a toxic substance through inhalation.

6 - Asthma with a non-immunological mechanism, induced by irritants

> Hydrogen bromide and hydrogen iodide, HBr and HI, which can be released depending on the initial halogen (respectively Br or I), are also highly corrosive. HF, hydrofluoric acid, is known for its corrosive properties on one side, linked to the production of the H⁺ hydrogen ion, and its toxic properties on the other, linked to the production of the F⁻ fluoride ion.

During hydrolysis reaction of chlorinated phosphides, the release of hydrogen chloride is accompanied by a release of phosphoric acids:

> Phosphorous acid, H₃PO₃, corrosive diacid:



> Phosphoric acid, H₃PO₄, a triacid which is also corrosive but which is in solid form as soon as the temperature returns to ambient temperature:



> When the hydroxyl ion, OH⁻, is released, it can cause alkaline chemical lesions:



Precisely in this type of reaction with alkaline metals (such as potassium or sodium), the released dihydrogen (H₂) is an extremely flammable gas, which can lead to a deflagration on contact with air.

> **Phosphine (PH₃)** is a very toxic and corrosive gas and is used as a source of organophosphorous compounds. There is then formation of H[•] radicals, through an oxidation reaction with oxygen, capable of spontaneous ignition.

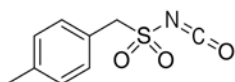
A massive dose of inhaled phosphine is necessary to be fatal (400 ppm for 30 minutes to 1 hour) but the first serious symptoms can occur as of an exposure of several hours at concentrations of 5/10 ppm.

> **Hydrogen sulphide (H₂S)** is a very toxic and highly flammable gas, without corrosive activity. It has the particularity of being highly odorous when it is at low concentration (fetid odour when it is at a concentration below 5 ppm) and becomes odourless when it is at a concentration above 10 ppm. Its toxicity threshold is 14 ppm. H₂S is thus non odorant when it is toxic. Specific H₂S detectors exist for indicating the presence of this gas.



> **Carbon dioxide (CO₂)** is mainly released when sulphonyl isocyanates, come into contact

with water.



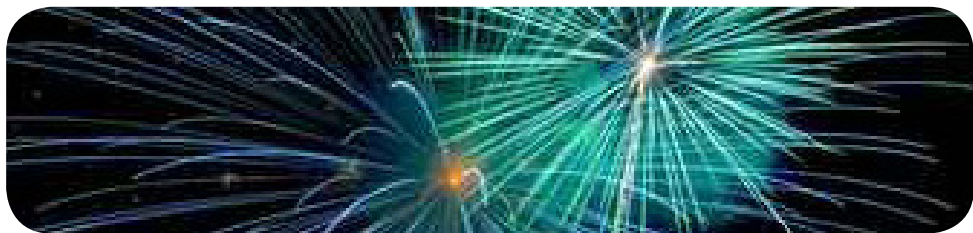
It does not present a corrosive danger. The corresponding carbamide acid, which is also released, will be responsible for certain corrosiveness, due to its more or less acid character.

Urea, which can also be a by-product of the hydrolysis, is non corrosive.

> **Alkanes** do not represent a corrosive danger. On the other hand, they can be flammable.

> **Hydrogen gas (H₂)** does not represent a corrosive hazard, but is likely to react with the ambient oxygen in a noticeable violent and exothermic combustion reaction, with only a little spark, or a small temperature rise.

FAMILY	TYPE OF REACTION	PRODUCT RELEASED	HAZARD OF PRODUCT RELEASED	EXAMPLE
Alkaline metals	Reductive	HO ⁻	Corrosive	$\text{Na} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$
Chlorosilanes	Electrophilic	HCl	Corrosive gas	$\text{ClSiMe}_3 + \text{H}_2\text{O} \longrightarrow \text{HOSiMe}_3 + \text{HCl}$
Acyl halogenides	Electrophilic	HX, X halogen	Corrosive gas	$\text{RCOCl} + \text{H}_2\text{O} \longrightarrow \text{RCOOH} + \text{HCl}$
Lewis acids (metal halogenides)	Electrophilic	HX, X halogen	Corrosive gas	$\text{TiCl}_4 + 2 \text{H}_2\text{O} \longrightarrow \text{TiO}_2 + 4 \text{HCl}$
Metal alkyls	Basic / nucleophilic	alkanes	Flammable liquids / gases	$\text{CH}_3\text{MgBr} + \text{H}_2\text{O} \longrightarrow \text{CH}_4 + \text{MgBr}^+ + \text{HO}^-$
Metal hydrides	Basic / reductive	H ₂	Flammable gas	$\text{NaH} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$
				$\text{LiAlH}_4 + 4 \text{H}_2\text{O} \longrightarrow \text{LiOH} + \text{Al(OH)}_3 + 4 \text{H}_2$
Metal phosphides	Basic / nucleophilic	PH ₃	Flammable, explosive, toxic gas	$\text{AlP} + 3 \text{H}_2\text{O} \longrightarrow \text{Al(OH)}_3 + \text{PH}_3$
Metal sulphides	Basic / nucleophilic	H ₂ S	Toxic gas	$\text{Al}_2\text{S}_3 + 6 \text{H}_2\text{O} \longrightarrow 2 \text{Al(OH)}_3 + 3 \text{H}_2\text{S}$



5. EXOTHERMICITY

By reacting more or less violently on contact with water, all of the chemicals studied in this file will lead to a more or less significant release of heat.

This heat release may be quantified in a theoretical manner, by calculating the enthalpy of reaction ΔH . This value represents the amount of energy involved. When this value is negative, this means that the reaction is exothermic and thus, releasing heat.

FOR EXAMPLE:



$$\Delta H^\circ = -323 \text{ kJ/mol}$$



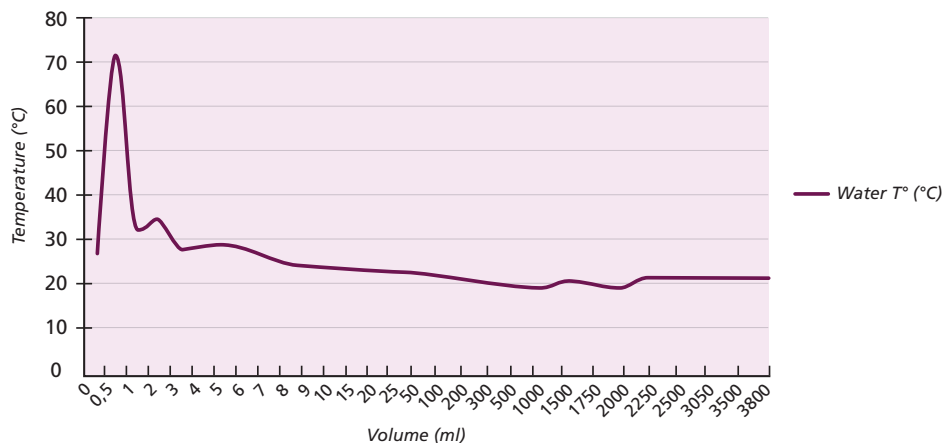
$$\Delta H^\circ = -237 \text{ kJ/mol}$$

The increase in temperature will vary according to the initial chemical substance and its capacity to react more or less quickly with water.

The associated maximum increase in temperature may be measured experimentally. Since titanium tetrachloride is one of the chemicals which react the most violently with water, its hydrolysis is monitored in a beaker, by adding a continuous volume of water.

For example, on an initial sample of 1 ml of 99% titanium chloride, when water is added to dilute it, the temperature reached at the start of the addition rises to 72°C, and then very quickly returns to a value below 30°C once the first 3 millilitres of water have been added.

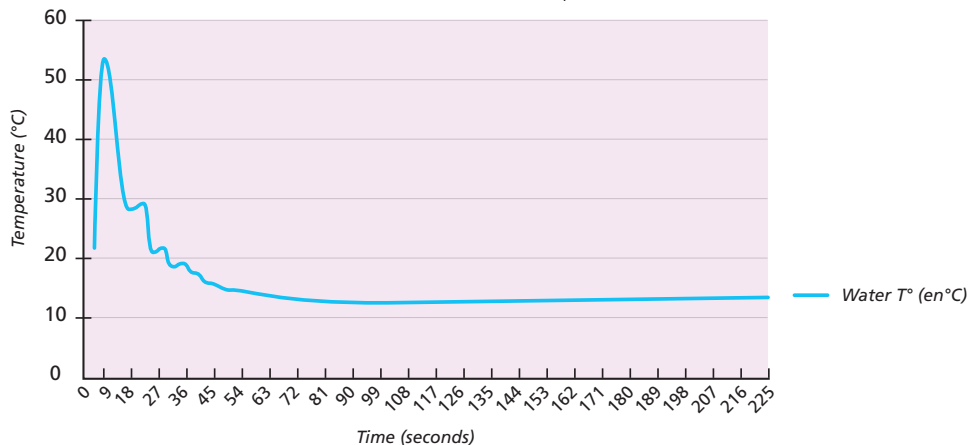
Temperature evolution during the addition of water to 1 ml of 99% TiCl_4 in a beaker



This experiment is carried out in a closed environment. It is thus less representative of a real washing simulation, where the wash-off effect is reproduced. When the same type of experiment is carried out in a dynamic washing situation, the rise in temperature is less important.

For example, by simulating the wash-off effect of washing a splash of titanium tetrachloride with water, it is then observed that the maximum temperature reached in the first few seconds does not exceed 55°C. After 20 seconds, the reaction temperature comes down to around 30°C.

Temperature evolution during washing with water with wash-off effect on 1 ml of 99% TiCl_4



6. MANAGEMENT OF ASSOCIATED RISKS

For chemicals releasing flammable gases on contact with water, the first risk is physical and precautionary measures must be taken in the same way as for highly flammable products.

6.1. COLLECTIVE PROTECTIVE MEASURES

- > First of all, the safest possible work processes should be designed: automation, self-contained work operations, planned organisation of maintenance and repair operations in the event of an incident, design of strict storage conditions.
- > Chemicals that react when coming into contact with water must be identified and stored independently of aqueous chemicals, to avoid the risk of any contact in the event of leaks.
- > Just as important the storage sites of these chemicals do not include any water pipes. These types of chemicals must be stored in such a way that any contact with water is impossible, even in the event of flooding.
- > Implement a system of use in isolation and provide for a suction system at work stations. While handling, avoid the proximity of water or other chemicals in order to limit further accidents in the event of flames or explosion⁸.
- > The chemicals must be kept away from moisture and, if possible, from air (INRS, 2011)

THESE CHEMICALS MUST NEVER BE Poured DOWN THE SINK.



- > Then, and failing this, set up a regular control of potentially emitted fumes suction.
- > It is also necessary to install a retention tank to recuperate liquids.
- > Firefighting measures: pressurized dry chemical and/or CO₂ extinguishers must be readily available. The use of specific extinguishing agents based on graphites or special dry powders for metal fires may also be justified, particularly for lithium and other mineral elements. Failing this, sand must be available to extinguish the flames and limit contact with air moisture (INRS FT 183, 2000).

6.2. INDIVIDUAL PROTECTIVE EQUIPMENTS:

- > **Protective clothing**
- > **Gloves resistant to chemicals used**
- > **Protective glasses or face screen**
- > **Safety shoes**
- > **Chemical cartridge respirator, for short operations, or supply-air respirator.**

Since some gases emitted may be toxic, it is advisable that fire fighting personnel is equipped with self-contained breathing apparatus with a full facepiece. Absorbents must also be available to collect any leaks and thus limit the risks of an explosion / fire.



7. EMERGENCY RESPONSE TO SPLASHES

7.1. EVALUATION OF WASHING METHODS

7.1.1. WASHING WITH WATER

We have thus seen previously that although these chemicals react violently with water, decontamination with water is however recommended within the context of first aid since a continuous washing enables a very rapid return to body surface ambient temperature.

Washing with water also makes it possible to remove a large part of the chemical from the surface of body tissues, by mechanical removal. **However, it will not have any action on by-products released.** This can lead to dangerous situations for first aid or emergency services personnel who will be faced with emanations of by-products from the reaction of the chemical with water while washing the injured person.

For example, R-methoxysilane type compounds generate methanol on contact with water. Methanol is a toxic substance through ingestion and inhalation. In addition to the victim, the persons present during the decontamination are going to be exposed (Lazzeri D, 2009). The responders must therefore be equipped with suitable personal protective equipment.

7.1.2. WASHING WITH AN ACTIVE SOLUTION

Setting up an active washing helps to keep the wash-off and dilution effects of washing with water, while optimising the decontamination process of the irritant chemicals.

Diphoterine® solution meets these efficiency requirements. Its hypertonicity limits the penetration of caustic substances in depth and helps to create an inverse flux from the interior towards the exterior, of skin or eye.

Its amphoteric and chelating properties will enable washing optimisation by acting on irritant and corrosive chemicals. Its effect is nevertheless limited with hydrofluoric acid and fluorides in acid medium.

Products which generate hydrofluoric acid (HF) on contact with water, such as boron trifluoride (BF₃), need to be identified. Washing with Hexafluorine® solution will respond to the twofold corrosive and toxic hazard of HF.

7.2. EXPERIMENTAL EVIDENCE

Experimentally, the efficiency of washing with an amphoteric and chelating solution such as Diphoterine® solution can be shown during an *in vitro* splash simulation, compared to washing with water.

If we return to the previous example of titanium tetrachloride (TiCl₄):

The chemical action of Diphoterine® solution on hydrochloric acid released is represented by a decrease of the pH in solution, whereas washing with water only results into a dilution:

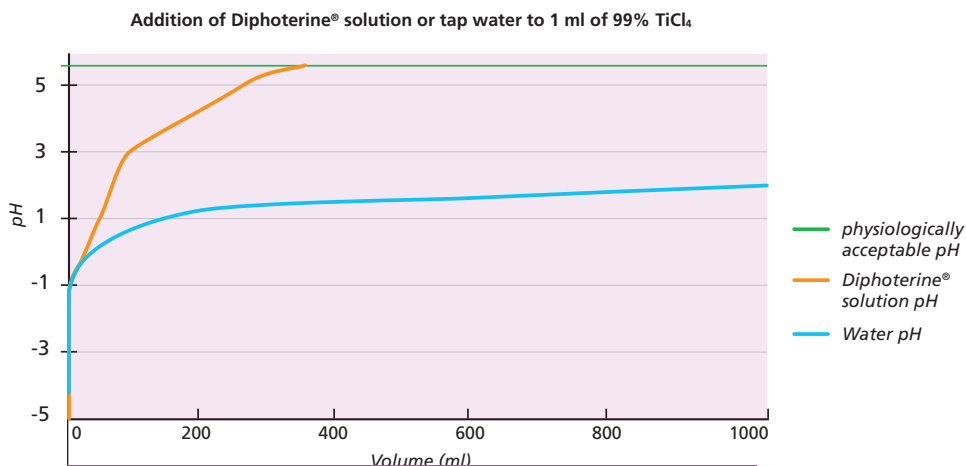


Figure 2 : *In vitro* simulation of static washing of a TiCl₄ splash with Diphoterine® solution compared with water.

This can also be verified with another substance which reacts strongly with water, such as boron tribromide.

On contact with water, the chemical reaction is as follows:





This reaction is exothermic and generates heat if it is carried out via static washing simulation (experimental temperature of 85°C during the addition of one millilitre of water to a millilitre of boron tribromide – Figure 3).

In dynamic washing situation, the temperature will not exceed 40°C, only for several seconds, and it will return very quickly to ambient temperature.

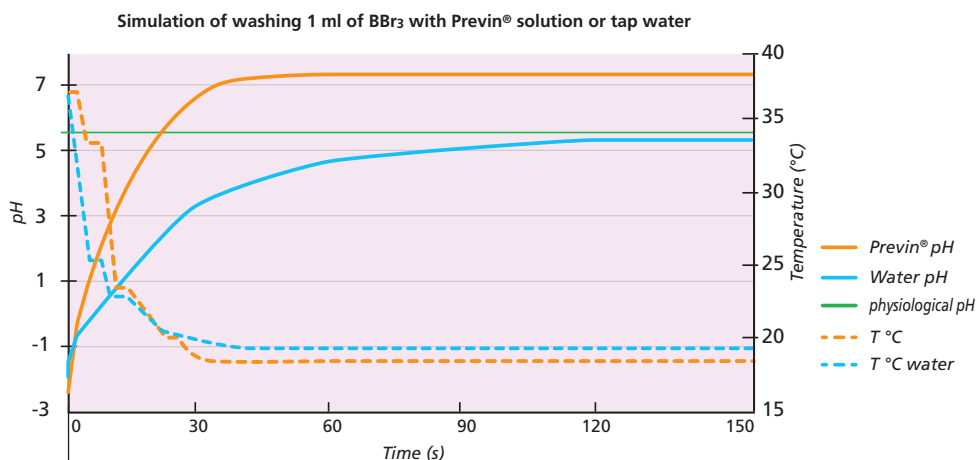
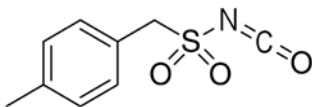


Figure 3 : *In vitro* simulation of dynamic washing of a splash of BBr_3 with Previn® solution (molecule similar to Diphoterine® solution commercialised in Germany), compared to water.

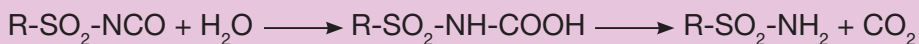
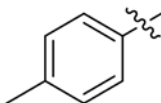
In Figure 3, the wash-off effect of the two washing solutions is identical and the action of washing will limit in both cases any additional heating. The action of Diphoterine® / Previn® solutions on bromic acid is illustrated by the pH value, which rapidly returns to a physiologically acceptable pH zone (in 20 s and after adding 60 ml) whereas for a same volume of added water, the pH remains at a corrosive value. A volume of water almost 10 times greater is necessary to reach the same physiological pH.

Without the dynamic effect of washing, the sole action of Diphoterine® solution on the corrosive character of a chemical which reacts with water can be monitored by pHmetry, according to the volume of the washing solutions added.

Take the example of 96% p-toluene sulphonyl isocyanate [CAS n°4083-64-1]:



Where "R" designates the group:



The gas emitted is carbon dioxide (CO₂), without specific danger.

Carbamide acid, R-SO₂-NH₂, which is also a reaction by-product, is corrosive.

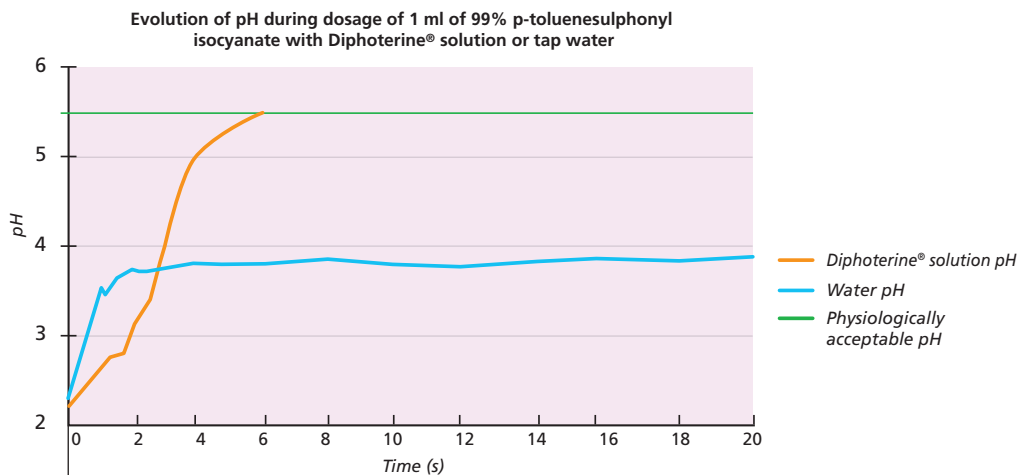


Figure 4 : *In vitro* simulation of static washing of a splash of 1 ml of p-toluene sulphonyl isocyanate with Diphoterine® solution or tap water.

Figure 4 shows that a volume of 6 ml of Diphoterine® solution is sufficient to reach the physiologically acceptable pH zone.



7.3. CLASSIFICATION OF SOLUTIONS

Diphoterine® solution thus appears as a first aid choice to wash chemical splashes reacting violently to water, and thereby generating corrosive products.

In the specific case where hydrofluoric acid is one of the acids coming from the reaction of a chemical with water, you are advised to use first aid Hexafluorine® solution, specific for splashes due to hydrofluoric acid, or fluorinated salts in acid medium.

CLASSIFICATION OF DIPHOTERINE® AND HEXAFLORINE® SOLUTIONS

- > Washing solutions of corrosive and irritant chemicals (Hexafluorine® solution is dedicated to emergency washing splashes of hydrofluoric acid and its derivatives)
- > Medical device of class IIa
- > CE 0459 marking, delivered by G-MED
- > Manufactured by PREVOR laboratory
- > Read carefully advice given on instructions for use, on labelling, or at the end of this document in section "9.1 washing instructions"

8. MANAGING SPILLAGES

8.1. EVALUATION OF SPILLAGE COLLECTION METHODS

8.1.1. CONVENTIONAL METHOD OF SPILLAGE COLLECTION

Conventionally, spillages are absorbed by natural or synthetic products. One can mention sand, sepiolite, diatomaceous earth or synthetic absorbents based on polypropylene. The absorption residue is then collected, temporarily stored and treated with hazardous solid waste.

Two problems can be linked to the collection of reactive chemicals by conventional absorbents:

- > First, during their absorption, chemicals which react violently with water can react with moisture in the air (there can then have release of dangerous gases). The absorption of chemical products which react with water, using a conventional absorbent, **does not reduce** the risks associated with the chemical.
- > Then, if the residue is stored with other solid humid wastes, there can be a delayed exothermic reaction with these other wastes, release of heat and dangerous gases. This delayed reaction can be even more dangerous as unexpected by operators.

In all cases, the absorption residues must be stored in appropriate sealed airtight containers. One may sometimes consider treating them with excess water so as to neutralize the hazard linked to the reactivity of the chemical with water (e.g: organometallic). **The addition of water will not however have any action on gases released.** This can lead to dangerous situations for the personnel who are going to be faced with emanations of products stemming from the reaction of the chemical with water. This delicate operation will have to be carried out with all necessary precautions.

For example, TiCl_4 generates gaseous HCl on contact with moisture in the air. HCl is a corrosive gas that will contaminate all persons present at the accident site (Kapias T, 2005). In case of spillage of this type of chemicals, the personnel present should therefore be evacuated rapidly and the responders should be equipped with appropriate individual protective material.

8.1.2. ABSORPTION WITH AN ABSORBENT/NEUTRALISING PRODUCT

Absorption of a chemical which reacts violently with water, with a neutralising absorbent, makes it possible to keep the solidification notion of a hazardous liquid derivative and to neutralise corrosive species that could form during the reaction of the chemical with water.

Trivorex® absorbent answers to these efficiency requirements.

Its amphoteric properties will help acting on a large majority of irritant and corrosive chemical by-products (HCl, HBr, HF, PH₃, NaOH, etc...). In addition, its absorption capacity enables the absorption of any flammable by-products that could form.

8.2. EXPERIMENTAL EVIDENCE

Experimentally, we have demonstrated the absorption efficiency of boron tribromide (BBr₃) by Trivorex® absorbent.

On contact with water, the chemical reaction is the following:



As we have seen previously, this reaction is exothermic and generates heat if it is carried out in an enclosed space. Furthermore, boron tribromide reacts with air moisture during simple exposure and bromic acid (HBr) is formed (see figure 5).



Figure 5 : BBr₃ before absorption

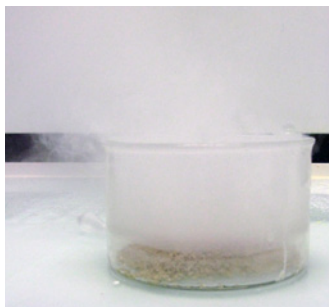


Figure 6 : 5ml BBr₃ absorption by 20g of sepiolite

If a spillage of boron tribromide is absorbed by a non-neutralising absorbent, one is faced with two problems. First, the absorption residue still contains boron tribromide. The later continues to react with moisture in the air through an exothermic reaction. Moreover, bromic acid can continue to be formed after absorption (sometimes visible in the form of white fumes, see figure 6). It will then be necessary to take all possible precautions to collect the residue, store it (protect from moisture, and limit any contact with other products/wastes), before treating it subsequently.

In the case of the absorption of boron tribromide by Trivorex® absorbent, several processes will take place. Part of the boron tribromide is going to be neutralised by the Trivorex® absorbent, which enables the residue containing boron tribromide not to be stored. Moreover, bromic acid, released by-product, will also be neutralised by Trivorex® absorbent, as soon as water is added. Finally, the presence of a coloured indicator helps to indicate if part of the chemical has not been neutralised and whether necessary precautions need to be taken when handling the residue.

In the case of boron tribromide, addition of water to the trivorexation residue is necessary in order to completely eliminate the corrosive hazard. A release of carbon dioxide (CO₂) is observed, product of the neutralisation reaction. There is then no longer a risk of emission of bromic acid, and the residue has a neutral pH.

Boron tribromide (5 ml)	Quantity of Trivorex® absorbent (g)	Quantity of water added (ml)	pH	Observations
Absorption	5	/	Not available	Pink residue BBr ₃ still reacts with moisture (white fumes) (Figure 7)
Neutralisation	15	4	> 5	Water favours the neutralisation with Trivorex® absorbent (disappearance of fumes and effervescence) (Figure 8)

PHOTOGRAPHS:



Figure 7 : absorption, less fumes:
(BBr₃+ Trivorex® absorbent, after 1 minute)



Figure 8 : absorption/neutralisation
BBr₃ + Trivorex® absorbent + water



Family	Example	Product released	Quantity of Trivorex® absorbent (Kg) to add for 1 l of product spilled	
			Absorption	Neutralisation*
Chlorosilanes	ClSiMe ₃	HCl	0.25	0.5
Acetyl chloride	Pivaloyl chloride	HCl	1	1.5
Lewis acids (metal halogenides)	BBr ₃	HBr	0.5	2
	TiCl ₄	HCl	1.5	4.5
	POCl ₃	HCl	1	10

* : With addition of water

In conclusion, Trivorex® absorbent enables easy collection of all types of chemical product, as well as an indication of hazard and neutralisation of part of spillage hazards.

8.3. FEEDBACK

The photovoltaic industry uses phosphoryl chloride (POCl₃) for doping cell emitters. POCl₃ is a liquid that reacts with water to form phosphoric acid and hydrogen chloride:



In the event of spillage, this means limiting contact with moisture. By using Trivorex® absorbent, the acids generated are neutralised, thus making collection safe.



> POCl_3 reacts with moisture in the air: a white fume is released from the poorly sealed bottle.



> Monitoring the neutralisation reaction using a coloured indicator.



> Absorption/neutralisation finished.

Parts of a video produced by the Air Liquide firm

9. WASHING AND COLLECTING ADVICE

9.1. WASHING ADVICE OF A CHEMICAL SPLASH

To decontaminate an ocular or cutaneous splash, we strongly recommend never delaying washing which, for maximum efficiency, must begin as soon as possible, in other words within seconds following the accident. Ideally, management of the incident should take place within one minute following the splash. In a similar vein, soiled clothing must be removed very quickly because with some chemicals of this class, the risk of ignition is very real. It is therefore advisable to remove clothing at the start of washing so that once again precious seconds are not wasted during which the chemical begins to react with the biochemical components of the body tissues with which it is in direct contact.

The mechanical effect of washing the surface of the skin or the eye makes it possible to eliminate a large quantity of the chemical received.

Chemicals which react with water can generate irritating, corrosive or toxic substances.

Generally speaking, the following protocol aims to optimise the way in which incidents are managed and to minimise chemical ocular or cutaneous-mucous membranes burn lesions.

WASHING PROTOCOL

- **Start washing within one minute** following the splash, beginning with the **uncovered areas**.
- **Remove clothes and/or contact lenses**.
- Rapidly continue washing the **unclothed areas**.
- Do not put back on clothing soiled by the washing or by the chemical.
- Consult a specialist.

GENERAL INSTRUCTIONS FOR WASHING

- Never delay washing.
- For optimal effectiveness, use Diphoterine® or Hexafluorine® solutions as first-line action.
- Use the entire contents of the container.
- Failing this, use water and wash as quickly as possible with Diphoterine® or Hexafluorine® solutions.
- In the case of a washing started after one minute, extend the washing of the affected surface from 3 to 5 times the contact time. It is not useful to continue washing for more than 15 minutes for a delayed ocular wash.
- Then seek medical advice urgently.

In the case of a cutaneous or ocular splash, we recommend carrying out very rapid and prolonged washing with Diphoterine® solution or with Hexafluorine® solution in the particular case of splashes with hydrofluoric acid or fluorinated salts in acid medium.

In case of ocular splashes:

- For a contact time less than 10 seconds, use the SIEW (sterilised individual eyewash).
- For a response time of 1 minute, use a 500 ml eyewash.
- Finally, in order to facilitate the return to a physiological osmolarity zone, we recommend ending washing with the use of Afterwash II® solution, isotonic to cornea.



In the case of cutaneous splashes (hand, forearm, neck, etc...) and a contact time less than a minute, use a Micro DAP. For extended splashes on the body and a contact time less than one minute, use a Portable Autonomous Shower (DAP containing 5 litres).

In the case of a skin splash of hydrofluoric acid, use a DAP of Hexafluorine® solution.

- > In the case of chemical and thermal lesions, the chemical burn injury must be treated first, then the thermal burn. Washing can then be continued, or a water gel compress may be used.
- > Given the reactive potential of these chemicals with water, in the event of abundant splashing or in the absence of possibility of rinsing within several seconds following the splash, the medical and safety supervisors may recommend, in their accidental protocol management on the place of the accident, an immediate wiping of the skin splashes before starting washing with water or with specific active decontamination solutions. This measure could thus contribute to removing an important quantity of product before it reacts, in contact with the skin, with sweat.
- > **Do note that INRS underlines the importance of prolonged washing. The pain feeling disappearance does not indicate washing's end. It is thus necessary to use all of the dispenser in accordance with the body surface to be decontaminated.**
- > If oral mucosa have been affected by the splash, rinse the victim's mouth with Diphoterine® solution **(or with Hexafluorine® solution when appropriated)** and then spit it out.

If the ear canal has been affected, rapidly wash with Diphoterine® solution **(or with Hexafluorine® solution when appropriated)** by instilling 500 ml in the ear canal, leaning the head to one side, to enable the flow of the liquid out of the ear. Ideally the solution is slightly warmed up to limit the triggering of dizziness. As with any unilateral ear bath with a liquid at ambient temperature, a dizzy feeling, can occur without any serious consequences. It will spontaneously disappear after a few minutes.

- > Diphoterine®, Hexafluorine® and Afterwash II® solutions are medical devices of class IIa. Do read carefully instructions for different dispensers which can be found on prevor.com website.

Protocol for Diphoterine® solution use

In cases of corrosive or irritant chemical splashes on skin or eyes*.

ACTION WITHIN THE FIRST MINUTE



Action within
the first 10 seconds

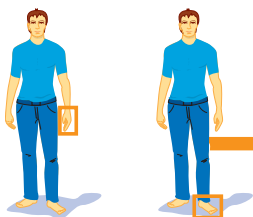


Use
1 LIS
50 ml

Intervention after
10 seconds



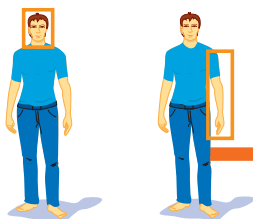
Use
1 LPM
500 ml



3% of body
surface



Use
1 MICRO DAP
100 ml



9% of body
surface



Use
1 MINI DAP
200 ml



+ de 9% of body
surface



Use
1 DAP
5 litres

* Limited efficacy on hydrofluoric acid or its derivatives in an acidic medium. Hexafluorine® solution is better adapted for this use.

In compliance with the law, this medical device is a regulated health product bearing the certified EC marking by LNE/G-MED accredited body by ANSM in France.

Protocol for Hexafluorine® solution use

In cases of hydrofluoric acid splashes or its derivatives in an acidic medium*

ACTION WITHIN THE FIRST MINUTE



To wash one eye



Use
1 LPM
500 ml



To wash a body



Use
1 DAP
5 litres

In all cases, washing must be followed by a medical examination.

Depending on the company's recommended medical protocol, apply locally a specific antidote such as calcium gluconate.

In the case of delayed washing, the application of an antidote is justified because of the systemic effect involved in this kind of situation.

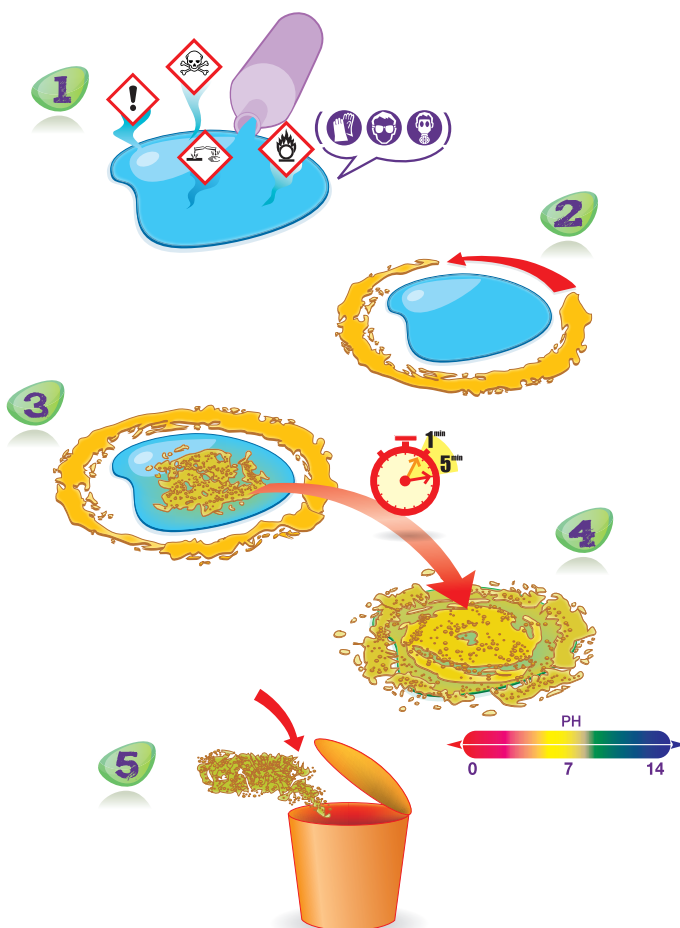
* Limited efficacy on alkaline chemicals. Diphoterine® solution is better adapted for this use.

9.2. COLLECTING ADVICE

Given the reactive potential of chemicals classified H260/261 with water, in the event of spillage, it is necessary to use a non-flammable absorbent. In all cases, absolutely avoid the use of absorbent paper which risks catching fire on contact with these chemicals.

Non-neutralising absorbents do not make it possible to limit the reaction of the spilled product classified H260/261 with moisture in the air. Corrosive (or toxic) gases can be emitted or a significant rise in temperature can occur, once the product has been absorbed, creating a new danger. It is therefore advisable to neutralize the residue with a suitable product.

A neutralising absorbent, such as Trivorex®, makes it possible to both absorb the chemical that reacts violently with water and to neutralize its corrosiveness.



We strongly recommend **absorbing-solidifying and neutralising spillages of chemicals which react violently with water using TRIVOREX® absorbent in a well-ventilated area**. Ensure that the appropriate respiratory apparatus is used when dealing with the fumes of the spilled chemical.

The absorption-solidification is carried out at the site of the spill. **To rapidly absorb-solidify the liquid (within a minute)**, it is necessary to add from 0.5 to 1.5 times the quantity by weight of TRIVOREX® absorbent with respect to the quantity of spilled liquid.

Neutralisation can be carried out either, at the site of the spill or, in another area, better suited to waste treatment. It is sometimes necessary to add water to the Trivorexation residue in order to totally eliminate the corrosiveness of the residue.

10. DOCUMENTARY REFERENCES

- Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, Toxicological profile for titanium tetrachloride, September 1997
- Clare Robert A. and Krenzelok Edward P., Chemical burns secondary to elemental metal exposure: Two case reports, The American Journal of Emergency Medicine, Volume 6, Issue 4, July 1988, 355-357
- Eldad A, Chaouat M, Weinberg A, Neuman A, Ben Meir P, Rotem M, Wexler MR., Phosphorous pentachloride chemical burn--a slowly healing injury, Burns. 1992 Aug; 18(4):340-1.
- L. Fernie, P. Wright, T. Kapias, Water Reactive Materials: Incorporation into Safety and Environmental Risk Assessments, Process Safety and Environmental Protection, Volume 85, Issue 2, 2007, Pages 162-168
- T. Kapias, R.F. Griffiths, Accidental releases of titanium tetrachloride (TiCl₄) in the context of major hazards--spill behaviour using REACTPOOL, Journal of Hazardous Materials, Volume 119, Issues 1-3, 17 March 2005, 41-52
- INRS, Fiche toxicologique FT5, méthanol, Edition 2009 [French]
- INRS, Fiche toxicologique FT13, chlorure d'hydrogène et solutions aqueuses, Edition 2010 [French]
- INRS, Fiche toxicologique FT32, sulfure d'hydrogène, Edition 2009 [French]
- INRS, Fiche toxicologique FT179, phosphine, Edition 2008 [French]
- INRS, Fiche toxicologique FT183, lithium, Edition 2000 [French]
- INRS, Stockage des produits chimiques, Edition 2011 [French]
- Lazzeri D., Pieri M, Lazzeri S, Colizzi L, Giannotti G, Pagnini D, Stabile M, Gatti GL, Massei A., Silane coupling agent chemical burns: a risk for medical personnel too, Burns 35 (2009), 600-605
- Thanabalasingham T, Beckett MW, Murray V., Hospital response to a chemical incident: report on casualties of an ethyldichlorosilane spill, BMJ. 1991 Jan 12;302(6768):101-102



HAZARD AND PRECAUTIONARY STATEMENTS

- H260 : In contact with water releases flammable gases which may ignite spontaneously
- H261: In contact with water releases flammable gases
- EUH 014: Reacts violently with water
- P223: Keep away from any possible contact with water, because of violent reaction and possible flash fire
- P231: Handle under inert gas
- P232: Protect from moisture
- P280: Wear protective gloves / protective clothing / eye protection / face protection
- P334: Immerse in cool water / wrap in wet bandages
- P335: Brush off loose particles from skin
- P370/378: In case of fire: Use... for extinction
- P402: Store in a dry place
- P404: Store in a closed container
- P501: Dispose of contents/container to ...



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