PRODUCT FILE

HYDROFLUORIC ACID

CAS n° 7664-39-3

MANAGEMENT OF EYE AND SKIN CHEMICAL SPLASHES

2010 Edition

PREVOR
ANTICIPATE AND SAVE
Toxicology Laboratory & Chemical Risk Management
www.prevor.com

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HYDROFLUORIC ACID

MANAGEMENT OF EYE AND SKIN CHEMICAL SPLASHES

1. KEY-POINTS

1.1. Background

The history of hydrofluoric acid is linked to the history of fluorine because hydrogen fluoride was synthesized for the first time by C.W. Scheele from fluoride and concentrated acid, while trying to isolate the fluorine atom.

On the industrial level, hydrofluoric acid results from the following reaction between calcium fluoride (molecular formula CaF_2) and concentrated sulfuric acid, at 250 °C:

$$CaF_2 + H_2SO_4 \rightarrow 2\ HF + CaSO_4$$

1.2. Names

- Hydrogen fluoride (gaseous state)
- Anhydrous hydrofluoric acid (other name of the gaseous state)
- Hydrofluoric acid (name of aqueous solutions)
- Fluorhydric acid
- Fluoric acid
- HF (using the molecular formula to name the substance)

HYDROFLUORHYDRIC ACID	
Molecular formula	HF
Molar mass	20,006 $g.mol^{-1}$
CAS number	7664-39-3
EINECS[1] number	231-634-8
ICSC[2] number	0283

1.3. Uses

It is used in the production of organic or inorganic fluorine compounds, in the treatment of metals (aluminum, steel) and of glass and crystal (etching and polishing), in the petroleum industry (refining), in the electronic industry for the surface treatment of electronic components as well as in the treatment of uranium in the nuclear industry, in the production of photovoltaic cells or in the chemical industry (particularly in laboratories).

1 - European Inventory of Existing Commercial chemical Substances
2 - International Chemical Safety Sheets

2. LABELLING

2.1. Hazard levels according to concentration

- **EC classification in force until end of December 2010** for substances (June 2015 for mixtures):

Chemical introduced in the 19th ATP[3].

HYDROFLUORIC ACID	HAZARD SYMBOL	RISK PHRASES
Anhydrous (hydrogen fluoride)	T^+ C	R26/27/28/R35
Concentration > or = 7%	T^+ C	R26/27/28/R35
Concentration from 1 to 7%	T^+ C	R23/24/25/R34
Concentration from 0.1 to 0.99%	Xn	R20/21/22/R36/37/38
Concentration from 0 to 0.09%	-	-

Risk phrases are given at the end of the document

- **New labelling, according to the CLP[4] regulation, with mandatory application from December 2010** for substances (end of June 2015 for mixtures):

Danger !

H300 Fatal if swallowed
H310 Fatal in contact with skin
H330 Fatal if inhaled

Danger !
Category 1A

H314 Causes severe skin burns and eye damage

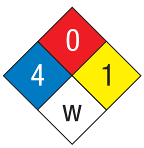
3 - Adaptation to Technical Progress annex 1 of the directive 67/548/EEC –included in table 3.2 of annex 6 of CLP
4 - Classification Labelling Packaging – Regulation 1272/2008/EC

HYDROFLUORIC ACID	CLASSIFICATION	HAZARD STATEMENTS
In general: The manufacturers adapt the acute toxicity according to the concentration in their preparation	Acute tox. 2* Acute toxicity level 2 Acute tox. 1 Acute toxicity level 1 Acute tox. 2* Acute toxicity level 2	**H300** Fatal if swallowed **H310** Fatal in contact with skin **H330** Fatal if inhaled
Regulation applying to corrosion:		
Concentration > or = to 7%	Skin Corr 1A Skin corrosion/irritation level 1A	**H314** Causes severe skin burns and eye damage
Concentration from 1 to 7%	Skin Corr 1B Skin corrosion/irritation level 1B	**H314** Causes severe skin burns and eye damage
Concentration from 0.1 to 1%	Skin Irrit 2 Skin corrosion/irritation level 2 Eye Irrit level 2	**H315** Causes severe skin burns **H319** Causes serious eye irritation

** indicates that the entry undergoes specific limits of concentration for acute toxicity in accordance with the European directive 67/548/CEE (previous table). These limits of concentration cannot be « converted » to limits of concentration as in CLP, particularly in the case of a minimal classification. However, when (*) is mentioned, the classification of acute toxicity of this entry may require special attention.*

2.2. Other classification

US Classification NFPA 704 :



- Rouge 0 – Flammability: non-flammable/will not burn.
- Bleu 4 – Health hazard: very short exposure could cause death or major residual injury (liquid and gas)
- Jaune 1 – Instability/Reactivity: Normally stable, but can become unstable at elevated temperatures and pressures

3. CHEMICAL PROPERTIES

The hydrofluoric acid is a colorless, liquid, mineral acid, with an irritating odor. When concentrated (in aqueous solutions above 40% at room temperature), it fumes when in contact with air. Because of the high electronegativity of fluor, this acid has a low potential of dissociation in water (pKa = 3.20). Then the 3 following chemical species may be found in solution: HF, H^+, F^-.

$$HF \rightleftharpoons H^+ + F^-$$

The measurement of pH must be taken carefully because it only measures the concentration in released acid and not the acid potential as is the case for HCl or H_2SO_4.
The actual acid potential of HF is therefore higher.
Its concentration potential gives hydrofluoric acid a very high acid activity, in the form of HF monomer, then in the polymer form of $(HF)_n$.

Molar mass	20,006 $g.mol^{-1}$
Boiling point	112,2°C
Melting point	-83,36°C
Vapor pressure	13,3 kPa at -28,2°C 53,3 kPa at 2,5°C 150 kPa at 30°C
VME[5]	1,8 ppm (1.5 mg/m^3)
PEL (TWA)[6]	3 ppm (2,5 mg/m^3)
STEL (TWA)[7]	6 ppm (5 mg/m^3)
Density at 0°C	1,002

Source : FT n°6 – INRS, 2006 edition.

4. CORROSIVITY OF HYDROFLUORIC ACID

4.1 - Chemical mechanisms

The mechanism of HF burns is linked to the dual corrosive and toxic effects of the hydrofluoric acid.

4.1.1 Corrosive effect

The corrosivity of HF is mainly due to its capacity to release an acid proton H+, which has the ability to damage the tissues of the eye and the skin.

4.1.2 Toxic effect

The toxic effect of HF is due to the presence of fluoride ions F^-. The superficial injuries, caused by the acid, allow the penetration of fluoride ions into the depth of tissues. Therefore they will generate a greater destruction of tissues (cellular necrosis) and some biological disorders, because of their capacity to chelate the calcium and magnesium of the cells. A systemic risk may arise because of a high concentration of HF or/and an extended time of contact. The table in Figure 1 reports, in relation with the body surface area, the minimal concentration of HF able to generate a lethal risk, for the different exposure routes.

TYPE OF CONTACT	BODY SURFACE AREA	HF CONCENTRATION
Skin	1 %	Anhydre
	5 %	> 70 %
	7 %	50-70 %
	10 %	20-50 %
	20 %	< 20 %
Ingestion		> 5 %
Inhalation		

Figure 1: Fatal systemic risk in relation to the HF concentration and the damaged body area (Dünser, 2004)

5 - Average Exposure Value in France
6 - Permissible Exposure Limit on a 8 hour working day as authorized by the Occupational Safety Health Administration – OSHA)
7 - Short-Term Exposure Limit for an exposure time of less than 15 minutes, as allowed by OSHA

The risk of respiratory penetration may be predominant in cases of exposure to HF in its gaseous state or by evaporation of aqueous solutions. Such situations are not dealt with in the present brochure.

Because of its high reactivity in acute exposure, there is little chronic risk due to HF. By way of contrast, the fluorinated salts such as NaF, SnF_2 or Na_2FPO_3 may generate skeletal and dental fluorosis.

4.2 - Chemical injuries due to hydrofluoric acid

4.2.1 Cutaneous exposure

The contact of concentrated solutions of HF (from 49%) with skin immediately causes severe and painful lesions. Then the damaged area of skin, which is initially erythematous and slightly oedematous, discolors and becomes whitish or grayish at the centre, surrounded by a purplish crown. If the time of contact increases, the damaged skin turns to red then to grayish purple/black purple, with a significant oedema and intense pain (see following photograph). Cutaneous exposure to HF vapors may cause similar lesions.

Source: Dünser and Rieder, NEJM 356 (6): e5, Figure 1, February 8, 2007

Compared to cutaneous lesions due to other mineral acids, the damage to tissues caused by HF are deeper and more severe. An *ex vivo* experimental study on human skin explants has permitted the histological observation of the development of the cutaneous lesions after exposure to 70% HF in real time *(Burgher, 2009 – fig. 2)*. Within 5 minutes, the deep dermis is reached.

TIME OF EXPOSURE	MICROSCOPIC LESIONS
1 min	Start of the penetration into the high section of the epidermis.
2 min	Attack of the basal layer (the deepest layer) of the epidermis.
3 min	The epidermis is completely damaged. Appearance of the first lesions in the papillary dermis (the most superficial part of the dermis).
4 min	The epidermis is completely damaged. The papillary dermis is clearly damaged.
5 min	The epidermis is completely damaged. Start of damage to the reticular dermis (the deepest layer of dermis).

Figure 2: Chronology of the appearance of lesions on human skin during a 70% HF burn

With the same type of model, a non-washed 20 seconds exposure to 70% HF shows that it only takes 5 minutes for all skin layers to be altered. After 10 minutes to 4 hours of exposure, the epidermis and the dermis are severely damaged.

After 24 hours, there is a complete necrosis of the epidermis and very marked lesions in all the layers of the dermis. *(Mathieu, 2008- fig. 3)*.

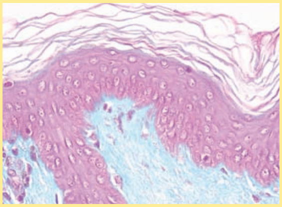
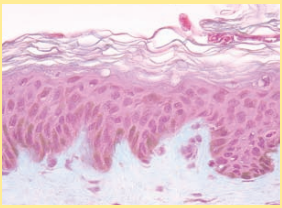
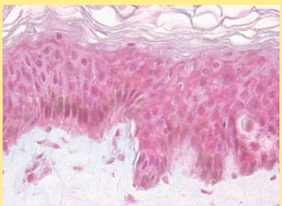
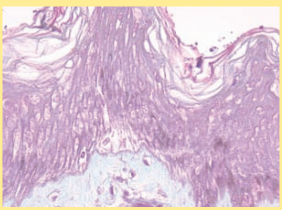
EXPLANT EXPOSURE	HISTOLOGICAL ASPECT	COMMENTS
Non exposed		The cellular structures of all the superficial layers of the skin (epidermis and dermis) show good morphology.
Exposure to 70% HF for 20 s after 5 minutes		The epidermis is clearly damaged. Same kind of lesions in the upper layer of dermis. Emergent and less marked lesions in the deepest layer of the dermis.
Exposure to 70% HF for 20 s after 1 hour		The epidermis is clearly damaged. There are lesions in all layers of the dermis.
Exposure to 70% HF for 20 s after 24 hours		The epidermis is necrotic (grey cytoplasm). All the layers of the dermis are clearly damaged.

Figure 3 : Chronologic observation of a 20 seconds exposure to 70% HF without treatment (model= human skin explants)

With lower concentrations, the lesions due to HF may be delayed up to 48 hours. The skin becomes red and oedematous then whitish to blackish with development of phlyctens. There is still a lethal risk, depending on the extent of the damaged body area.

The Industrial Hygiene department of the American National Institute for Occupational Safety and Health has proved a correlation between the concentration of HF, pain and observed symptoms (fig. 4).

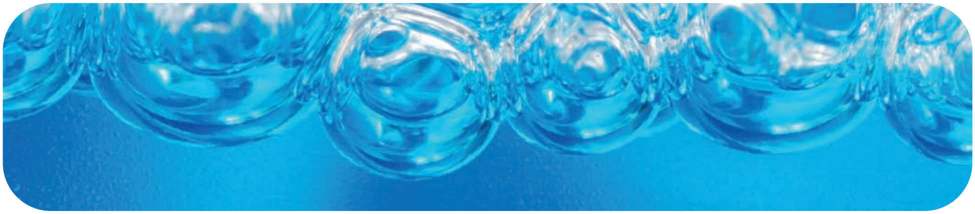
CONCENTRATION	PAIN
50% and more	Immediate, associated with a rapidly visible destruction of tissues
From 20 to 50%	Delayed by 1 to 8 hours after contact (with erythema developing with same delay)
Less than 20%	Delayed by 24 hours or more (with erythema developing with same time)

Figure 4 : Time course for pain after contact with HF, in relation with concentration

4.2.2 Ocular exposure

At the ocular level, exposure to HF will generate a severe burn with corneal opacification that may lead to necrosis of the structures of the anterior chamber of the eye.

Figure 5 presents the penetration of a 2.5% HF solution into an *ex vivo* rabbit cornea (EVEIT model), followed by HR-OCT (High Resolution-Optical Coherence Tomography). Within only 240 seconds (or 4 minutes), the acid has penetrated the cornea's entire thickness *(Spöler, 2008)*.



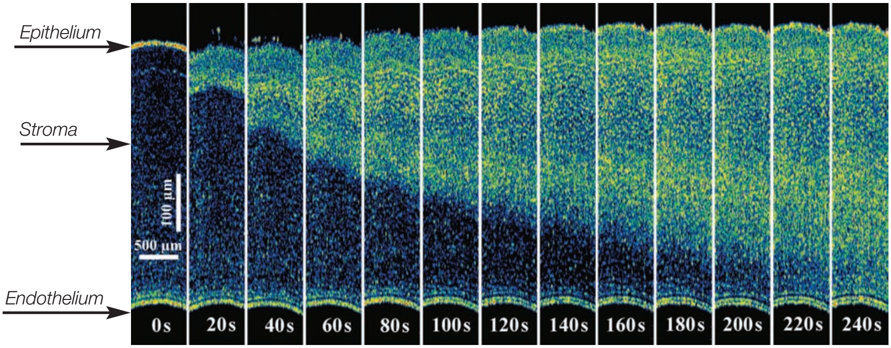


Figure 5 : Penetration of 2.5% HF into an ex vivo rabbit cornea within 240 s

Macroscopically, there is an opacification of the entire cornea (fig. 6).

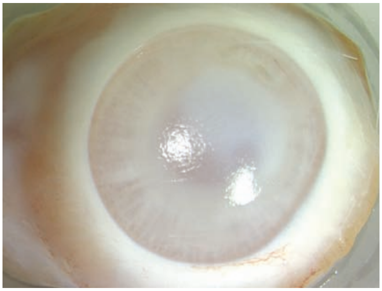


Figure 6 : Rabbit cornea exposed for 20 seconds to 2.5% HF, observation after 75 minutes without washing

5.MANAGING ASSOCIATED RISKS[8]

Collective and personal protection

Collective protection	Work in a sealed environment Capture emissions at their source
Personal protection	Waterproof glasses, a facial screen, a lab coat or an apron, neoprene gloves. In addition, forearm protections, long trousers and closed-in shoes or even boots.

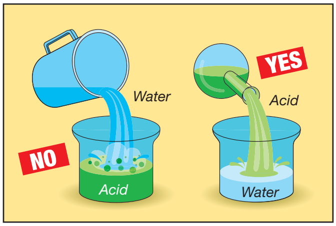
8 - See complete description in INRS Toxicological Sheet #6 (Fiche Toxicologique INRS #6) and OSHA guideline

Glove compatibility table:

	LATEX	NEOPRENE	NITRILE	VYNIL
Concentrated hydrofluoric acid (30-70%)	+ 1-4h	+ 1-4h	-	-
Diluted hydrofluoric acid	++	++	++	++

Specific recommandations:

- Availability of decontamination materials at all workstations.
- Anhydrous hydrofluoric acid reacts strongly with water and its dilution in water is associated with the emission of white fumes and a significant heat release. Therefore, the acid must be slowly poured in while stirring the mixture.



6. EMERGENCY RESPONSE TO HYDROFLUORIC ACID SPLASHES

6.1. Evaluation of washing methods

6.1.1. Washing with tap water followed by the application of calcium gluconate

Given the toxic danger of HF, numerous studies have aimed at finding an appropriate protocol, with an antidote specific to the toxic risk of this chemical. The « washing with water followed by the application of calcium gluconate » protocol is still the most widely used method.

Washing with tap water can remove a big part of the chemical from the surface of the tissue, by the mechanical effect.

Applied as a gel on skin, calcium gluconate chelates the diffused fluoride ions. During care management in hospital, the application of calcium gluconate will be repeated according to the pain felt by the patient (locally, in subcutaneous injection, in intravenous injection or intra-arterial injection – for fingers or hands).

Some cases of decontamination with the “water followed by calcium gluconate” protocol, as described in the literature, show its efficacy for low or average concentrations *(Barbier, 1987 – Beaudoin, 1989 – Henry, 1992 - Kono, 1992 – Lheureux, 1991)*. However, using it for high concentrations does not always prevent the appearance of severe burns, or even the death of patients *(Mayer, 1985 – Mullet, 1987 - Teppermann, 1980)*.

The benefits and limits of the « water followed by calcium gluconate » method can be summed up as in figure 7.

PROTOCOL	ADVANTAGES	LIMITS
WASHING WITH WATER	• External washing by mechanical effect • Dilution effect	• Risk of hypothermia for extended lesions • Hypotonic washing facilitating the penetration flow of the fluoride ions from the outside towards the inside of the tissues
APPLICATION OF CALCIUM GLUCONATE	• Chelation of the fluoride ions during their migration into the deep layers	• Limited action on acidity (H^+ ion) • Requires several applications • Factor depends on the injured person’s pain • Reversibility of chelation between the calcium from the gluconate and the cellular calcium

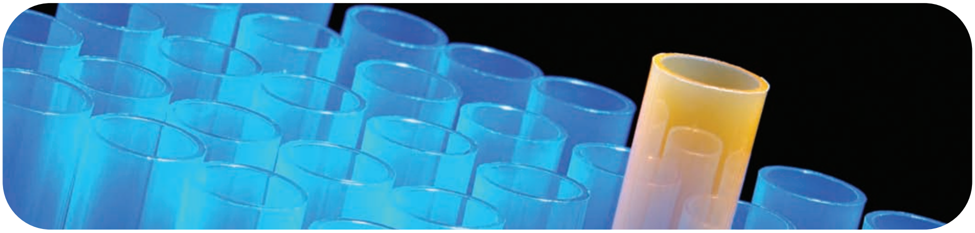
Figure 7 : Advantages and limits of washing with water followed by application of calcium gluconate.

6.1.2. Washing with Hexafluorine®

Performing active washing keeps the mechanical effect of tap water washing, while optimizing the process of decontamination.

Washing with Hexafluorine® counteracts the dual corrosive and toxic potential of HF.

- Its action on the acid proton enables the pH to return extremely rapidly to a physiologically acceptable zone.
- Moreover Hexafluorine® can chelate the fluoride ions, therefore preventing or limiting their cellular toxicity.
- Its hypertonicity limits the deep penetration of acid because it generates a flux from the inside to the outside of the tissue (*Schrage, 2004*).



Thus, with its combined action on the H+ protons and on the fluoride ions F-, Hexafluorine® can achieve complete washing by controlling both the corrosive and the toxic dangers of HF for eye and/or skin tissue.

6.2. Experimental evidence

There are numerous *in vitro*, *ex vivo* and *in vivo* studies on the management of hydrofluoric acid splashes and on the use of Hexafluorine® in comparison with other washing methods. They are all reported in detail in Prevor's Hexafluorine® File. In the present document, the most noticeable elements have been reported for a better understanding of the role and benefits of washing with Hexafluorine®.

6.2.1 *In vitro* studies

The evaluation of the efficacy of Hexafluorine®, in comparison with other washing methods such as washing with tap water alone or 10% calcium gluconate, was made on both the corrosive potential (measurement of pH – fig. 8) and the toxic potential (measurement of pF – fig. 9) of hydrofluoric acid.).

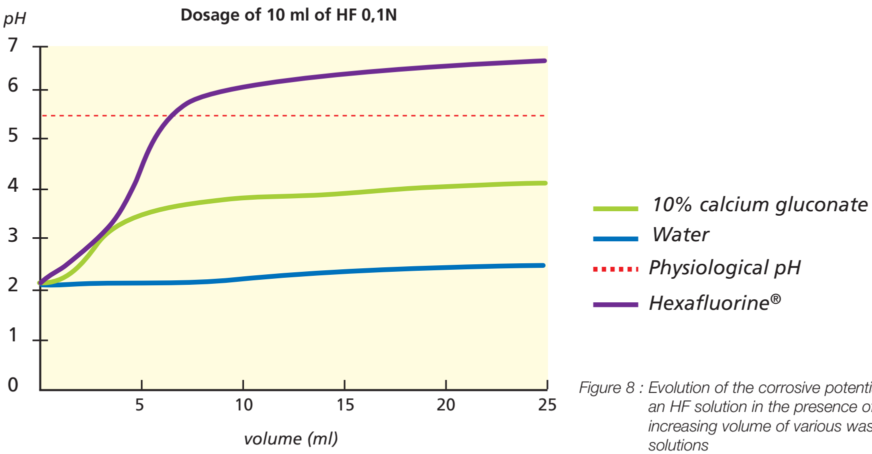
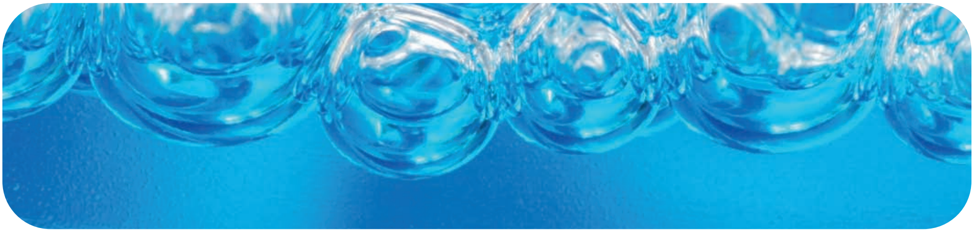


Figure 8 : Evolution of the corrosive potential (pH) of an HF solution in the presence of an increasing volume of various washing solutions



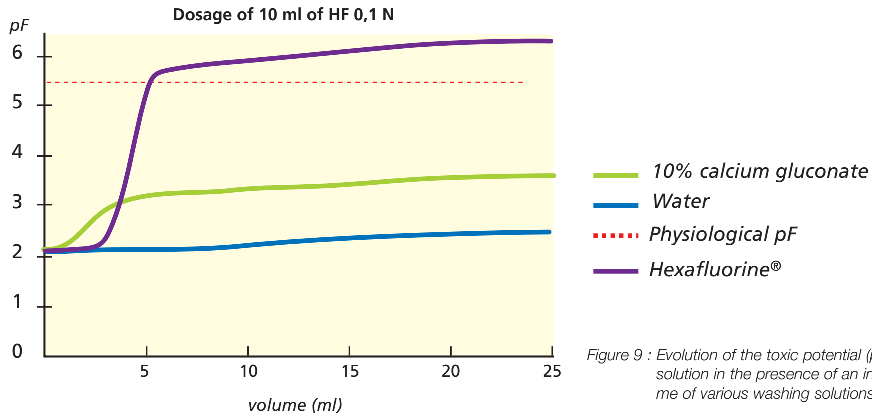


Figure 9 : Evolution of the toxic potential (pF) of an HF solution in the presence of an increasing volume of various washing solutions

These experiments show the simultaneous action of Hexafluorine® on the acid protons (the pH is rapidly restored to a physiologically acceptable zone, between 5.5 and 9) and on the fluoride ions (pF > 5 meaning a concentration of fluoride ions $[F^-] < 10^{-5}$ mol/l).

By contrast, the pH or pF were not restored to a physiologically acceptable zone neither by the addition of tap water nor by the addition of a 10% calcium gluconate solution.

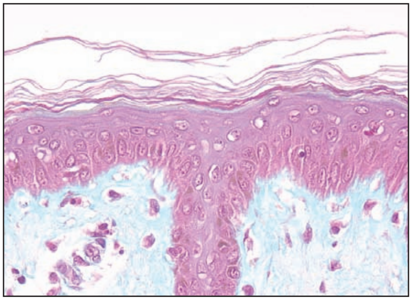
6.2.2 *Ex vivo* studies

For cutaneous chemical injuries, the model of human skin explants, preserved in a BEM medium (Bio Ec Medium) to keep the skin tissue alive, was chosen in order to avoid the difficulties of extrapolation faced with animal models. With this model, concentrated chemicals can also be tested in conditions very similar to the actual conditions of an accident *(Mathieu, 2008)*.

The explants are exposed for 20 seconds to 70% HF then:

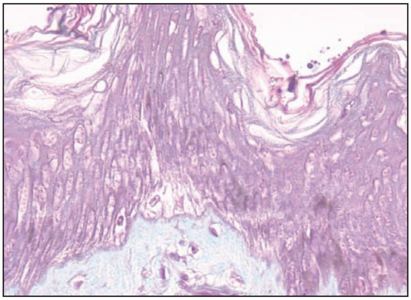
- An exposed group is given no treatment in order to follow the spontaneous evolution of burns over time.
- A group is washed with tap water for 15 minutes then 2.5% calcium gluconate gel is superficially applied.
- A group is washed with Hexafluorine® for 10 minutes.
- A 4th group, neither exposed to HF nor washed, is kept as a control, in order to insure the right preservation of the model over time.

No exposure to HF, no washing



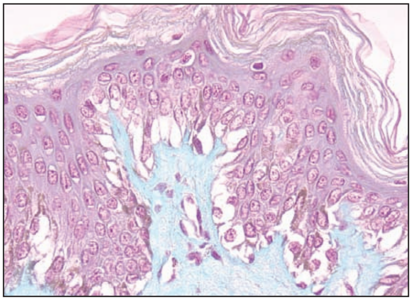
Normal morphology after 24 hours

20 s exposure to 70% HF



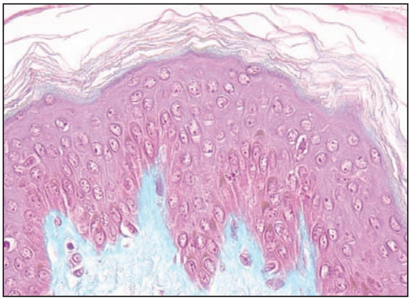
Necrosis on the epidermis (grey cytoplasm). Dermis has been clearly altered in its entirety.

20 s exposure to 70% HF, washed with tap water followed by calcium gluconate application



Large number of edematous cells in the epidermis. The upper part of the dermis is also altered, the lower part of the dermis less so.

20 s exposure to 70% HF, washed with Hexafluorine®



Normal morphology in all skin layers.

Figure 10: Histological sections of human skin explants after 24 hours

Results (fig. 10): In these experimental conditions, the comparative study of two washing protocols (15 minutes washing with tap water followed by application of 2.5% calcium gluconate *versus* 10 minutes washing with Hexafluorine®) shows that, even if the first protocol delays the damage of the tissues, one application of calcium gluconate is not enough and the lesions develop anyway. This confirms the usefulness of the widely spread protocols recommending multiple and deep applications of calcium gluconate.

Only Hexafluorine® allows damage of the structures of the epidermis and of the dermis to be avoided.

For ocular chemical injuries, the « Acute-EVEIT » model *(Spöler, 2007)*, on enucleated rabbit eyes (eyeballs preserved at 4 °C in humid atmosphere), combined with visualization by HR-OCT (High Resolution - Optical Coherent Tomography), gives accurate and reproducible results by visualizing the development over time of the tissular lesions of the cornea. The efficacy of comparative decontamination of ocular splashes can also be studied with this model *(Spöler, 2008)*. It was used after a 20 seconds exposure of the corneas to 2.5% HF in order to compare washing for 15 minutes using the following methods:

- Washing with tap water
- Washing with a 1% calcium gluconate solution
- Washing with Hexafluorine®
- No washing

Exposure to 2.5% HF without decontamination

Exposure to 2.5% HF followed by decontamination with tap water for 15 minutes

Exposure to 2.5% HF followed by decontamination with 1% calcium gluconate for 15 minutes

Exposure to 2.5% HF followed by decontamination with Hexafluorine® for 15 minutes

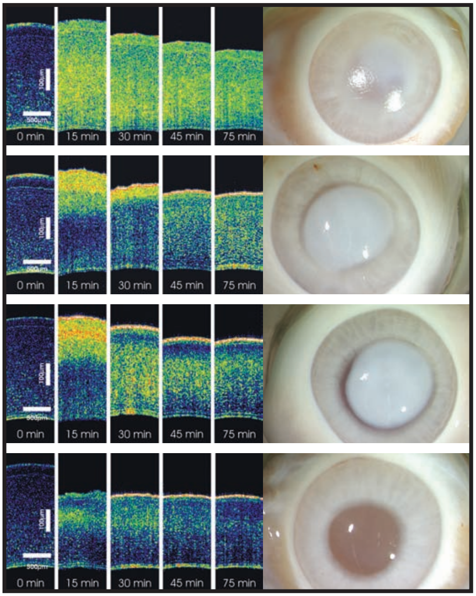


Figure 11: Comparative study of washing solutions after a 2.5% HF splash on ex vivo rabbit corneas

The comparison of washing methods (fig. 11) shows that even if water and calcium gluconate washing delays acid penetration, they do not prevent it. One hour after washing has ended; the entire cornea has been penetrated, which leads to a loss of transparency of the center with a milky appearance, which is specifically characteristic of HF burns.

Only Hexafluorine® in a single application allows a transparent cornea to be preserved, with no lesions, even one hour after washing has ended.

6.2.3 *In vivo* studies

The efficacy of washing solutions for HF splashes have also been tested on animal models, before setting up the *ex vivo* methods presented above. Rabbits and rats were chosen for the following experiments.

1st experiment, on the evolution of cutaneous burns in rabbits (Hall, 2000):
After exposure to 70% HF for 20 seconds, various washing methods are compared:

- Washing with tap water only for 5 minutes (10L/min)
- Washing with tap water for 3 minutes, followed by a 5 minute massage with 2.5% calcium gluconate gel
- Washing with Hexafluorine® for 3 minutes (0.2L/min).

Then the histological effects are observed for 6 days (fig. 12). The intensity of the observed effects was evaluated according to the modified Draize scale, from 0 to 4 (0-1 for no mark, 4 for extended lesions).

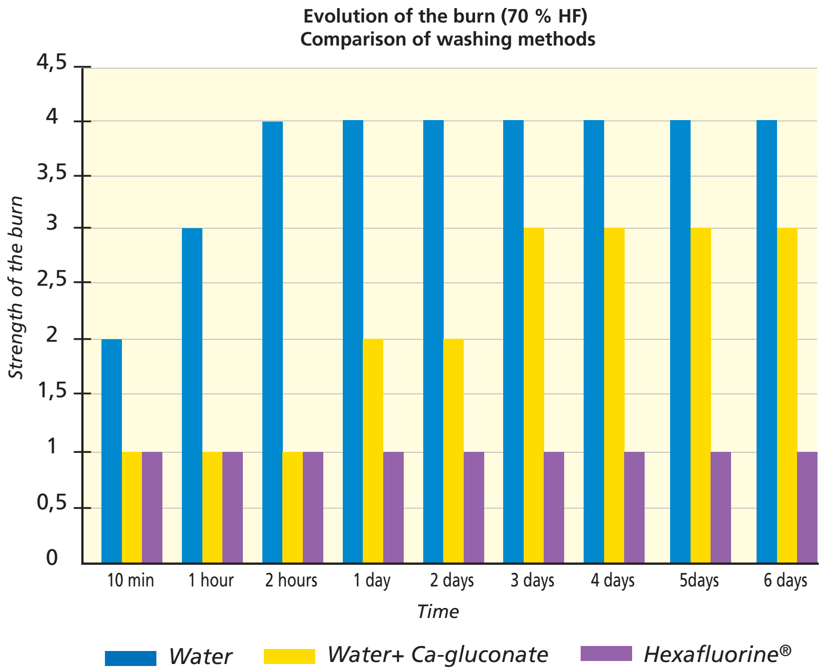


Figure 12: Comparison of various washing methods on the development of HF burns on rabbits

Results:

- Washing with tap water alone is not enough to stop the development of injuries which become severe as of the first day.
- Adding calcium gluconate use to tap water washing delays the appearance of lesions, at least within the first 24 hours. However a single application is not sufficient to prevent the presence of visible lesions, due to the persistence of free fluorides.
- **The appearance of lesions can be avoided by the immediate use of Hexafluorine®, for the whole 6 days experiment.** Acting directly on HF, Hexafluorine® prevents acid lesion development and simultaneously prevents the fluoride ions from linking with the calcium from the body tissues.

2nd experiment, on the development of calcemia on rats *(Hall - 2000)*:

This experiment follows the same protocol as the previous study, with an additional group:

- Washing with tap water for 3 minutes (10L/min) followed by washing with 10% $CaCl_2$ for 3 minutes (0,2L/min)

The development of calcemia in blood is monitored for 5 days. Then an anatomopathological analysis of the liver and kidneys of each animal is performed.

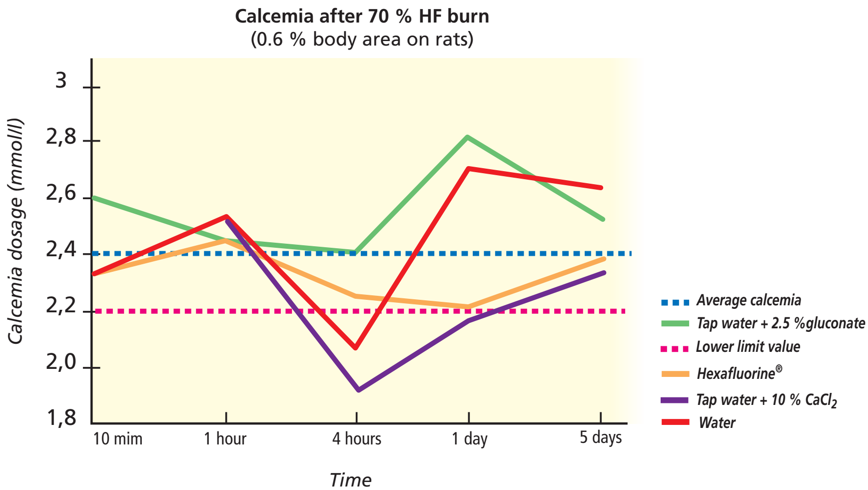


Figure 13: Development of calcemia in a 70% HF cutaneous burn on rats

Results:

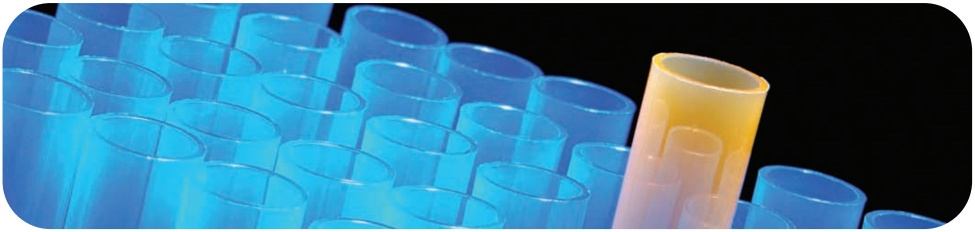
- The analysis of data shows that all the washing methods have similar results after one hour. After 4 hours, for the water or water + $CaCl_2$ methods, there is a clear hypocalcemia and an improvement after 24 hours.
- **Calcemia remains constant after washing with Hexafluorine®, at a physiologically acceptable rate.**
- In optical microscopy, the histological analysis of the liver and kidneys showed no significant lesions.

6.3. Feedback on the use of Hexafluorine®

6.3.1 Isolated cases with early management
(Sinochem, Woeste, Krupp, Alcan, Arques International)

> A case in Sinochem Modern Environmental Protection Chemical Co. Ltd, Xi'an, China, 2008

A worker was splashed on the back of the hand by a drop of anhydrous HF in liquid phase. A lesion appeared immediately. The splash was washed for 2 minutes using a Hexafluorine® DAP (autonomous portable shower) within the first minute after the splash. This was followed by a single application of calcium gluconate gel. The victim was back to work the next day, without hospitalization.



The following cases have been published in a review. They are also mentioned on PREVOR's website, www.prevor.com, in the "Testimonies" section.

Described below, the cases in Woeste, Krupp, Alcan and Cristalleries d'Arques have been published.

> A case at WOESTE, Verbert, Germany, 1997

Figure 14: Automated surface treatment assembly line – Source: web

A worker fell into a bath comprised of 1505 liters of water, 30 liters of 31/33% hydrofluoric acid and 233 liters of 59% hydrofluoric acid, in which he was completely immersed. Thanks to the immediate action of his colleagues, his body was quickly washed with Hexafluorine® and his eyes were rinsed with an ocular water shower.

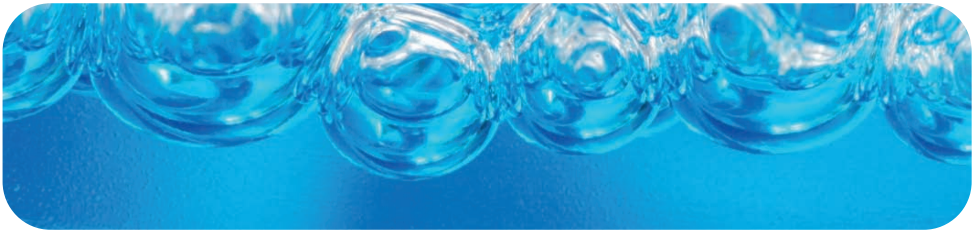
In the end the victim only suffered from a severe burn of the left eye, probably due to insufficient decontamination, although, given the extreme aggressiveness of the mixture involved and of 100% affected body surface, this case could have been lethal.

> A case in Krupp, Werdohl, Germany, 1996

While filling a bath with hydrofluoric and nitric acids, a worker was the victim of an ocular 38% hydrofluoric acid splash. He immediately washed his eye with Hexafluorine®. He suffered no damage. He returned to work the next day.

> A case in Alcan, Göttingen, Germany, 1993

Two workers were splashed by 5% hydrofluoric acid. Both were rapidly decontaminated with Hexafluorine®. The workers went back to hospital for routine exam the next day. No sick leave was necessary.



> A case of a facial splash of 70% hydrofluoric acid vapors, Cristalleries d'Arques, Arques, France, 1996

Since 1993, in order to improve the management of victims of hydrofluoric acid splash, instead of using water, the medical and the safety services of the company have chosen to use Hexafluorine® instead of tap water. The use of calcium gluconate is maintained as a secondary treatment.

A 35 year old technician, with 12 years of seniority, was exposed on the right cheek to 70% HF vapors when opening a gate in the hydrofluoric acid circuit. He immediately felt pain in the splashed area. Although he was wearing permeable protective glasses, his eyes were not exposed. He immediately used the Hexafluorine® DAP (autonomous portable shower), available at his workstation. He felt a cooling sensation and mentioned the immediate and complete disappearance of pain. In accordance with the protocol for Hexafluorine® use for which he had been trained on site, he used the whole 5 litre contents, which accounts for the 6 minutes of washing.

After medical examination, no injury was observed, except a slight and painless erythema. The technician was not given any sick leave.

The next day, the erythema had almost disappeared, the patient did not feel any pain, but, as a precaution, calcium gluconate gel was applied. The following week, the patient underwent a medical consultation, where the clinical examination proved normal. One month after the accident, another medical examination led to the same conclusion.

6.3.2 Series of splashes in industry

> 11 cases in Mannesmann, Remscheid, Germany (Söderberg - 2002)

OCULAR SPLASHES	40% HF	6% HF + 15% HNO_3
Number	1	1
Splashed area	1 eye	1 eye
Primary washing	Hexafluorine®	Hexafluorine®
Secondary washing	Hexafluorine®	Hexafluorine®
Secondary treatment	0	0
Sequelae	0	0
Sick leave	0	0

Figure 15: Emergency washing of ocular HF burns using Hexafluorine®

CUTANEOUS SPLASHES	40% HF	6% HF + 15% HNO_3
Number	5	5
% body surface	0,2 %	0,2 %
	1 %	4,5 %
	4,5 %	4 %
	4,5 %	4,5 %
	16,5 %	10,5 %
	0,2 %	
Primary washing	Hexafluorine®	Hexafluorine®
Secondary washing	Hexafluorine®	Hexafluorine®
Secondary treatment	0	0
Sequelae	0	0
Sick leave	0	0

Figure 16: Emergency washing of cutaneous HF burns using Hexafluorine®

> 16 cases in Outokumpu (formerly Avesta), Sweden

NOMBER OF CASES	CORROSIVE PRODUCT	SPLASHED AREA	TIME OF CONTACT	SICK LEAVE (DAYS)
2	70 % HF	Left forearm + oral cavity	< 1 min	0-1
1	HF (unknown concentration)	One eye	< 1 min	0
2	HF + HNO_3 pH=1	One eye	< 1 min	0-0
1	HF + HNO_3 pH=1*	One eye	3-5 min	3
1	HF + HNO_3 pH=1	Two eyes	< 1 min	0
1	HF + HNO_3 pH=1	One thigh	< 1 min	0
2	HF + HNO_3 pH=1	Two thighs	1h - 1h30	2 –2
1	HF + HNO_3 pH=1*	Face	3-5 min	3
2	HF + HNO_3 pH=1	Face + oral cavity + forehead	< 1 min	1-1
3	HF + HNO_3 pH=1	Forearms + arms + hand + elbows	< 1 min	0-0-1
1	HF + HNO_3 pH=1	Wrist	2 h	0

** HF + HNO_3 + H_2SO_4 (pH = 1) is involved in one ocular and one cutaneous splashes*

Figure 17: Series of cases of HF burns in Outokumpu (Avesta) Sweden

In total, 32 cases of ocular or cutaneous splashes caused by hydrofluoric acid (both pure or mixed, and concentrated (70%) or diluted) and washed with Hexafluorine®, have been published *(Hall, 2000 – Mathieu, 2001 – Söderberg, 2004)*.

No confirmed burn developed after washing with Hexafluorine®. No secondary care was necessary in more than 75% of the treated cases, including the two cases of splash by very concentrated 70% HF. There were no deaths, although in 5 out of 32 cases, the combination of the HF concentration and the percentage of total body surface could have jeopardized the vital prognosis, according to the criteria developed in figure 1.

On average, only one day of work was lost.

> Isolated case with delayed management

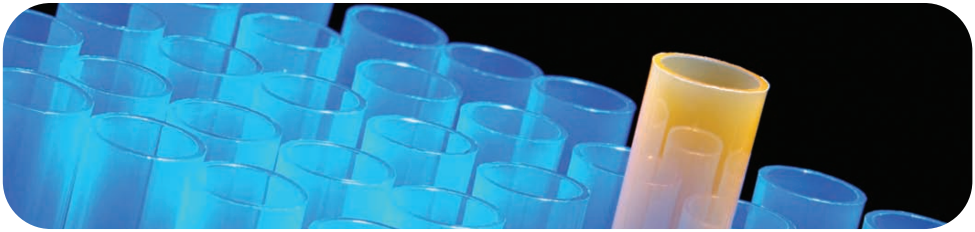
In a firm in Sao Paulo, Brazil *(Yoshimura, 2009)*, a worker is the victim of a 70% HF splash on about 10% of his body surface (left cheek, external side of the left arm and left thigh, external and anterior sides of the same leg).

The victim is immediately showered with tap water for « some minutes », his clothes are then removed in the changing room and he is showered for the second time. Some blisters on the face and leg, as well as persistent pain, then appear, revealing the first systemic effects.

To counter these systemic effects, compresses soaked in a magnesium oxide solution are applied (Fig.18) and the patient is given an analgesics intravenously injected.

Figure 18: After washing with water and application of magnesium oxide

Figure 19: Late secondary washing with Hexafluorine®



At this stage, the decontamination with water is not clinically sufficient, pain has already developed and pain is persistent.

Transferred to hospital, the victim is decontaminated with Hexafluorine® exactly 3 hours after accident. The spraying of a 5 liters Hexafluorine® DAP (autonomous portable shower – fig. 19) for 5 or 6 minutes soothes the pain and brings a feeling of coolness on the burn injuries clinically estimated between the first and third grades, depending on the damaged area. The red patch rapidly disappears from the areas that were initially only erythematous.

In addition to the cutaneous decontamination, the secondary treatment includes the administration of calcium gluconate in intraveinous and subcutaneous injections (fig. 20), in local application (fig. 21) and by inhalation.

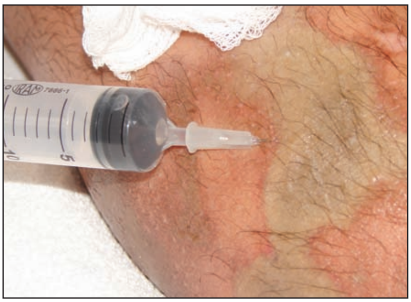
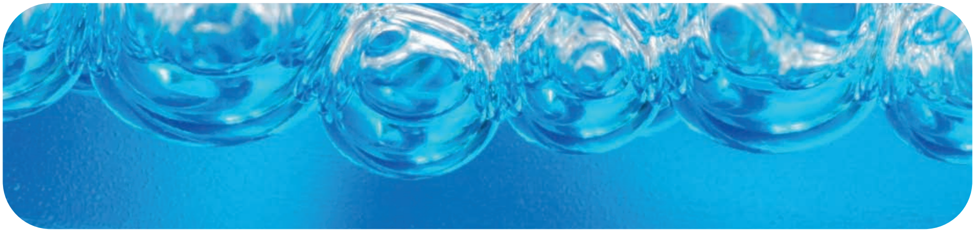


Figure 20: Subcutaneous injections of calcium gluconate

Figure 21: Application of calcium gluconate gel

The patient left the intensive care unit after 2 days. On the 4th day, the patient didn't feel pain anymore. Skin grafts were necessary and complete cicatrization was achieved within 90 days (Fig. 22).



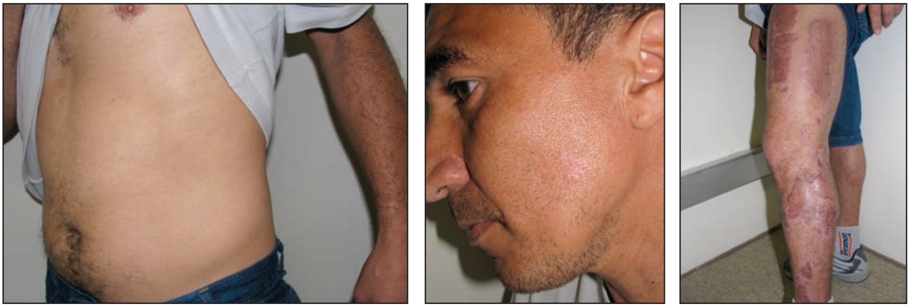


Figure 22: Final condition of the victim after skin transplants, 90 days after splash

70% HF was involved in this accident. Even if immediate and followed by the application of magnesium oxide, washing with water could prevent neither the development of lesions nor the persistent pain. By using Hexafluorine® as delayed washing, the development of the HF burn can be stopped, and thus the secondary care management of the patient facilitated. Systemic risk was avoided by the combined use of calcium gluconate. Complete healing was achieved within 90 days, after graft.

7. IN CONCLUSION, HOW SHOULD HEXAFLUORINE® BE USED?

HF is an acid with the capacity to cause very severe and early lesions when concentrated. The development of symptoms may be delayed for less concentrated solutions and even then, delayed care management can become critical. The earliness and efficacy of the washing then become key factors. This is the reason why it is crucial to set up washing devices next to the hazardous handling or storage areas, and ideally devices containing an active solution such as Hexafluorine®.

The superficial HF splash will be washed by the immediate use of Hexafluorine®. Thus, the penetration and the HF effect on skin/eye tissue will be avoided or diminished, limiting thus lesions development.

GENERAL WASHING INSTRUCTIONS:

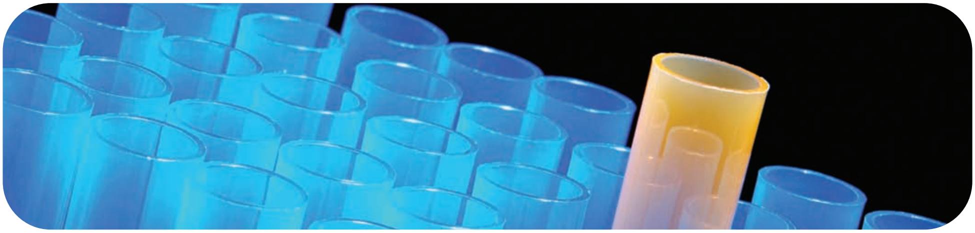
- Never delay washing.
- Wash with Hexafluorine® as the primary action, within the first minute and ideally within the 20 first seconds after splash.
- If no Hexafluorine® is available on the spot, never delay washing. Use water and then continue washing with Hexafluorine®.
- The use of calcium gluconate may be considered if necessary.

In the case of an ocular or cutaneous splash , of hydrofluoric acid (HF) we strongly recommend performing a rapid and prolonged washing with Hexafluorine®.

Hexafluorine® stops the aggressiveness of this product.

In case of an ocular splash of HF with a time of contact shorter than 1 minute, use a 500 ml eyewash then complete washing with a 200 ml bottle of Afterwash II® in order to facilitate a faster return of the eye to physiological conditions.

In case of a cutaneous splash and with a time of contact shorter than 1 minute, use a 5 liter Autonomous Portable Shower (DAP).



For cutaneous contact longer than 1 minute with HF, and depending on the concentration of the acid, the burn may have already developed.
We recommend continuing the initial washing with a second washing using Hexafluorine®, 3 to 5 times longer than the time of contact with the chemical, in order to stop the corrosive effect. Moreover in cases of delayed washing, the systemic risk requires medical care with the administration of an appropriate antidote, such as calcium gluconate.

In cases of ocular lesions and after more than 1 minute of contact, we recommend continuing the initial washing performed with 500 ml Hexafluorine®, with a second washing ideally lasting 5 minutes. It is not necessary to wash the eye for more than 15 minutes.

Then, in all cases, the patient must be taken to a specialist who will decide on the appropriate actions to take according to the initial lesions observed.

Please note that INRS highlights the importance of extended washing. The disappearance of the feeling of pain does not indicate the end of washing. It is therefore necessary to systematically use the entire contents of the container.

After study by the French national technical committee of metalwork industries, the CNAMTS *(CNAMTS, 2008)* also recommends setting up devices of ocular and cutaneous washing containing Hexafluorine® in order to deal with splashes from hydrofluoric acid-based stripping/pickling baths and the INRS uses it in their research laboratories *(Peltier, 2000)*.

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Risk statements (European classification):

R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed
R34	Causes burns
R35	Causes serious burns
R36/37/38	Irritating to eyes, respiratory system and skin

Hazard statements (CLP regulation):

H300	Fatal if swallowed
H310	Fatal in contact with skin
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H319	Causes serious eye irritation
H330	Fatal if inhaled