



#### Properties, Classification and First Aid Hydrogen Fluoride – Hydrofluoric Acid Solutions



Eurofluor (European Technical Committee for Fluorine)

www.eurofluor.org





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#### INTRODUCTION

- This Recommendation is based on the various measures taken by member companies of Eurofluor.
- It in no way is intended as a substitute for the various national or international regulations, which should be respected in an integral manner.
- It results from the understanding and many years experience of the AHF/HF producers in their respective countries at the date of issue of this particular document.
- Established in good faith, this recommendation should not be used as a standard or a comprehensive specification, but rather as a guide which should, in each particular case, be adapted and utilised in consultation with an AHF/HF manufacturer, supplier or user, or other experts in the field.







#### INTRODUCTION

- It has been assumed in the preparation of this publication that the user will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance it has been prepared.
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#### USAGE OF AHF / HF

Industry	Usage of AHF/HF
ELECTRONICS	Production of microchips, cleaning agents for electronic circuits
METALLURGY	Metal cleaning/aluminium production
PETROCHEMICALS	As catalytic agent when alkalising petrol
GLASS INDUSTRY	Glass etching
COOLANTS	Air conditioning, refrigerators
EXTINGUISHING AGENTS	Fire extinguishers
FLUOROCHEMISTRY	Production of fluoride salts, production of Fluoroplastics
MEDICINES	Propellant for medication, anaesthetic gases, production of antibiotics, production and coating of surgical prostheses, production of medicines
NUCLEAR INDUSTRY	Processing of uranium ore
AGROCHEMISTRY	Pesticides
CLEANING AGENTS	Rust removers, outer wall cleaners







#### CLASSIFICATION OF AHF / HF











#### GENERAL INFORMATION ABOUT ANHYDROUS HF

Concentration %	CLP CLASSIFICATION  CLP - Classification, Labelling and Packaging	ADR / RID CLASSIFICATION  ADR - European Agreement on International Carriage of Dangerous Goods  RID - Regulations Concerning the International Carriage of Dangerous Goods
AHF HF > 85%	ACUTE TOXICITY (oral, dermal and inhalation) Cat. 1 and 2 SKIN CORROSION Cat 1A	HYDROGEN FLUORIDE, ANHYDROUS CLASS 8 PG I CT1 : CORROSIVE SUBSTANCE, TOXIC, LIQUID  886 1052
	Hazard statements (H Statement)  H300: Fatal if swallowed H310: Fatal in contact with skin H330: Fatal if inhaled H314: Causes severe skin burns and eye damage	HYDROFLUORIC ACID with more than 85% of hydrogen fluoride CLASS 8 PG I CT1 : CORROSIVE SUBSTANCE, TOXIC, LIQUID  886 1790







#### GENERAL INFORMATION ON AQUEOUS HYDROFLUORIC ACID (HF)

Concen- tration	CLP CLASSIFICATION  CLP - Classification, Labelling and Packaging	ADR / RID CLASSIFICATION  ADR - European Agreement on International Carriage
%		of Dangerous Goods RID - Regulations Concerning the International Carriage of Dangerous Goods
HF > 60% HF < 85%	ACUTE TOXICITY (oral, dermal and inhalation) Cat 1 and 2 SKIN CORROSION Cat 1A	HYDROFLUORIC ACID  with more than 60% but not more than 85% hydrogen fluoride  CLASS 8 PG I  CT1: CORROSIVE SUBSTANCE, TOXIC, LIQUID  886  1790
HF ≤ 60%	Hazard statements (H Statement)  H300: Fatal if swallowed H310: Fatal in contact with skin H330: Fatal if inhaled H314: Causes severe skin burns and eye damage	HYDROFLUORIC ACID with not more than 60% of hydrogen fluoride CLASS 8 PG II CT1 : CORROSIVE SUBSTANCE, TOXIC, LIQUID  86 1790







SUBSTANCE NAME	HYDROGEN FLUORIDE (AHF) HYDROFLUORIC ACID (HF)	
CHEMICAL FORMULA	HF	
IDENTIFICATION	CAS NUMBER: 7654-39-3 EINECS NUMBER: 231-634-8 UN NUMBER: 1052 / 1790 RTCES/NIOSH NUMBER: MW 7875000	
STATE OF MATTER	Liquid. When its vapours get in touch with humidity create abundant and dense white fumes.	
COLOUR	Colourless	
ODOUR	Sharp Pungent Odour. Odour Threshold: 0.04 - 0.13 p.p.m.	
PH	<1	
STABILITY	Stable under normal conditions. There is a great tendency to polymerization, not considered dangerous	
SOLUBILITY IN WATER	100% by weight	







SUBSTANCE NAME:	HYDROGEN FLUORIDE (AHF) HYDROFLUORIC ACID (HF)
MOLECULAR WEIGHT	20.01 (ANHYDROUS)
BOILING POINT	19.55°C a 1013 mbar (ANHYDROUS)
MELTING POINT	-84°C
SPECIFIC GRAVITY (LIQUID)	0,97 gr/cm <sup>3</sup> at 21°C y 1013 mbar
SPECIFIC GRAVITY (GAS)	Varies according to degree of polymerization subject to variation with temperature
VAPOUR PRESSURE	1,03 bat at 21°C
FLASH POINT	Non flammable
BURNING SPEED	Non flammable
COMBUSTION HEAT	Non flammable
EXPLOSIVE RANGE	Non applicable
OXIDIZING PROPERTIES	Non oxidizing







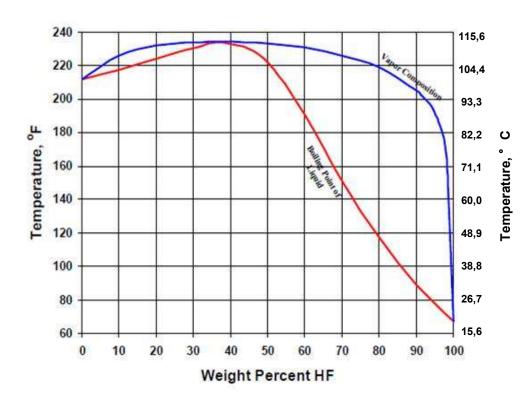
SUBSTANCE NAME:	HYDROGEN FLUORIDE (AHF) HYDROFLUORIC ACID (HF)
REACTIVITY WITH WATER	It is dissolved in water releasing heat
HEAT OF DILUTION	See figure
VISCOSITY OF LIQUID	0.25 mP a 0°C.
HEAT OF VAPORIZATION	347,5 kJ/kg at 19,54°C (boiling point)
SOLUBILITY IN OTHER CHEMICALS	Very soluble in ethanol and soluble in various organic solvents such as alcohols, ether, benzene, toluene and xylene
CORROSIVITY	Attacks natural rubber, leather, many organic materials, ceramics, silica, silicates, glass, concrete and certain metals, especially those such as cast iron containing silica.
STABILITY	Stable under normal conditions. There is a great tendency to polymerization, not considered dangerous
SOLUBILITY IN WATER	100% by weight







#### Boiling Point of HF-H<sub>2</sub>O System



#### Reference Honeywell

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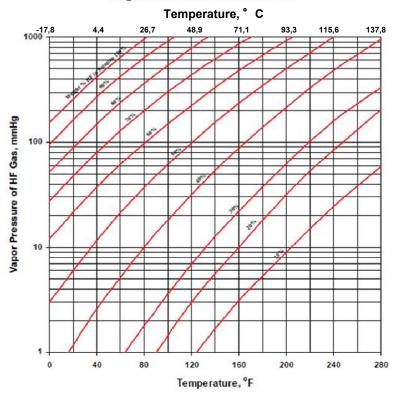
Celsius scale added by EUROFLUOR







#### Partial Vapor Pressure of HF over Aqueous Solutions of HF

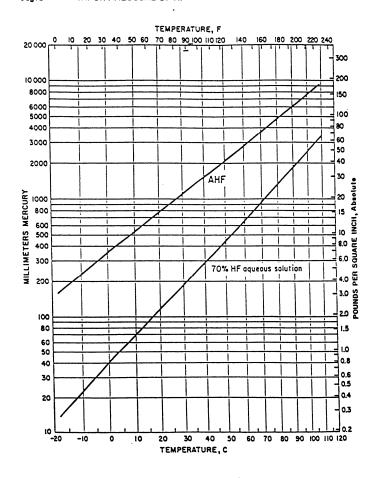


Celsius scale added by EUROFLUOR

Reference Honeywell

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Fig. 2 VAPOR PRESSURE OF HF











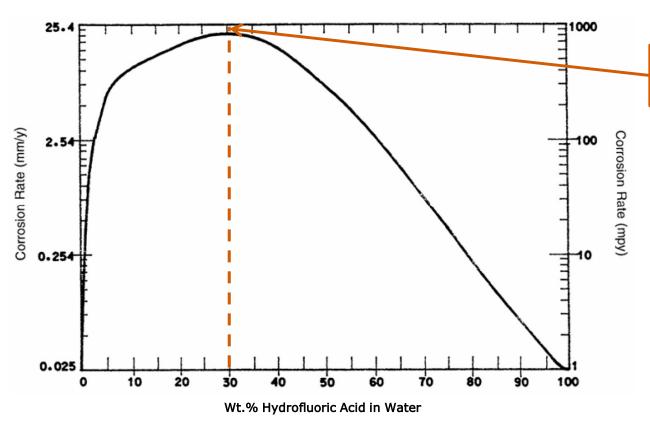


FIGURE 2. HF Corrosion Data for Carbon Steel at 21 to 38° C (70 to 100° F)

#### reference:

"Materials for Receiving, Handling and Storing Hydrofluoric Acid"

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This information is for guidance only. It represents corrosion rates on carbon steel at the indicated temperature range in hydrofluoric acid that is free of contamination and at low- or noflow conditions.

Rates shown for 70 to 100% represent laboratory data and service experiences







#### GENERAL HAZARDS OF AHF/HF



#### HAZARDS FOR HUMAN HEALTH

- Fatal if inhaled, if swallowed and in contact with skin
- Causes severe skin burns and eye damage
- It needs specific medical treatment
- In case of prolonged exposure may cause occupational disease
- Sharp, pungent and suffocating odour



#### **HAZARDS FOR ENVIRONMENT**

- It can pollute surface and groundwater and the soil
- Air pollutant
- Hazardous for aquatic life







#### EXPOSURE TO AHF / HF

# ANY EXPOSURE OF AHF / HF MUST BE CONSIDERED AS BEING SEVERE!







#### RISKS OF AHF/HF



Properties of AHF/HF:		
Corrosive (acid)	$\rightarrow$	serious tissue destruction/burns
Toxic	$\rightarrow$	systemic effects
Dangerous in the event of inhalation (gas)	$\rightarrow$	inhalation trauma

## Types of exposure by AHF/HF: Liquid (Note: also a risk in low concentrations!) Gas Combination of liquid and gas

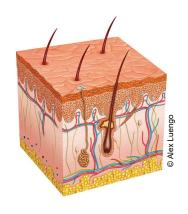




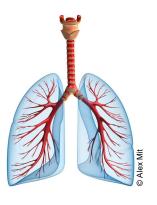


#### **CONTACT THROUGH:**

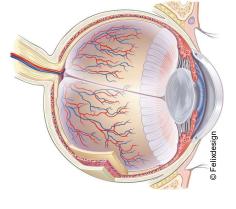
**SKIN** 



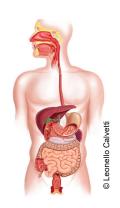
**AIRWAYS** 



**EYES** 



MOUTH (gastrointestinal system)

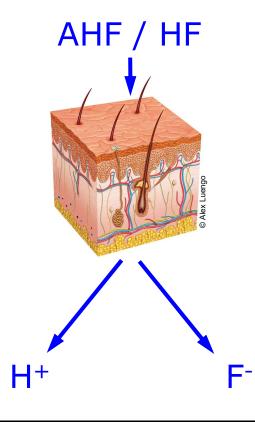








#### **SKIN CONTACT:**



- Rapid dissociation at pH 7.4 (body)
- Fluoride forms salts

$$2 F^{-} + Ca^{2+} = CaF_{2}$$
  
 $2 F^{-} + Mg^{2+} = MgF_{2}$ 







After ionisation the fluorine forms insoluble and soluble salts

#### Insoluble salts:

$$2 F^{-} + Ca_{2}^{+} = CaF_{2}$$
 (Calcium fluoride)  
 $2 F^{-} + Mg_{2}^{+} = MgF_{2}$  (Magnesium fluoride)

#### Soluble salts:

$$F^- + Na^+ = NaF$$
 (Sodium fluoride)  
 $F^- + K^+ = KF$  (Potassium fluoride)







#### Acute/primary



- Corrosive effects
  - Concentration >50% results in immediate serious tissue destruction/blisters,
  - exceptionally painful



- Systemic effects
  - Low calcium level in the blood (cardiac rhythm disorders/arrest) and
  - fluoride intoxication (hepatic and renal disorders)









#### Sub-acute/secondary

- Symptoms depending on concentrations of AHF/HF
  - HF > ~14%:symptoms immediately evident
  - HF ~12%:symptoms not evident until an hour later
  - HF < ~ 7%:symptoms possible >24 hours after exposure!

- Systemic effects
  - Low calcium level in the blood (cardiac rhythm disorders/arrest) and
  - fluoride intoxication
     (hepatic and renal disorders)









#### Sub-acute/secondary

- Tightness of the chest (sometimes not occurring until hours after exposure),
- Lung oedema

Danger: delayed pain and skin destruction









#### Long term

- Effects of tissue damage through the corrosive and toxic effect (scar formation and hepatic and renal disorders)
- Note: no effects documented or reported in the case of chronic exposure to very low concentrations of HF







#### AHF/HF IS CORROSIVE AND TOXIC AND MAY CAUSE:



- 1. Severe and painful burns of the skin
- Irritation of air ways that can lead to bronchitis or even pulmonary oedema
- 3. Asphyxia (severely deficient supply of oxygen)
- 4. Severe and painful burns of the eyes
- 5. Blindness
- 6. Severe and painful burns of the digestive track and,
- 7. Serious Toxic Systemic Effects, that will require specialized (intensive) care
  - metabolic,
  - surgical,
  - thoracic,
  - ophthalmic intervention

Note: All or any of the above effects may be delayed in onset and/or be accompanied by toxic systemic effects.







#### APPROACH TO MEDICAL TREATMENT



- Industrial experience indicates that prompt treatment, as described, will prevent the development of serious injury
- Therefore, speed is essential.
- Delays in decontamination, first aid care or medical treatment or improper medical treatment will likely result in greater damage or may, in some cases, result in a fatal outcome.
- Relief of pain is an important guide to the success of the treatment; therefore local anaesthesia should be avoided







#### APPROACH TO MEDICAL TREATMENT



AHF/HF exposures are different from other acid exposures:

- AHF/HF penetrates all tissue it comes in contact with and does not remain on their surface.
- Once absorbed AHF/HF rapidly dissociates into ionic Hydrogen and Fluoride. Hydrogen is in this context of little importance.
- Fluoride migrates and continues to destroy deep tissue layers as it migrates and will create soluble and insoluble compounds that are the basis for the systemic toxic effects.
- And unlike other acids that are rapidly removed or neutralized, the corrosive and toxic effects may continue for days if left untreated.







#### ADVICE FOR FIRST AIDERS



### Pay attention not to get yourself contaminated

Wear appropriate PPE and AHF / HF resistant gloves







#### FIRST AID



- DO NOT DELAY
- Demands immediate contact with First Aid Team
- Remove victim from exposure area, and
- START WITHOUT DELAY FIRST AID TREATMENT
- As a rescuer: PROTECT YOURSELF
- Ensure that the victim is accompanied by a rescuer
- Obtain medical attention immediately







#### DECONTAMINATION



 Use huge amounts of water of a safety shower / eyewash to decontaminate the affected areas



- AHF/HF is very water soluble, so water decontamination is highly effective
- Begin decontamination as soon as possible
- Clothing, personal protective equipment and jewellery/ watches/ shoes should be assumed to be contaminated and removed during showering
- Check with pH paper (on skin and in eye) if decontamination was efficient







#### FIRST AID - SKIN



- Principle: flush off and dilute
- Remove <u>all</u> contaminated clothing (jewellery/watches/shoes etc.!) under the safety shower
- Finally, remove protective goggles, looking towards the shower spray with closed eyes.
- 1 minute of flush after undressing is sufficient!
- Continue with showering until Calcium Gluconate is available!
- Rub in Calcium Gluconate 2.5% gel as soon as possible
- Continue massaging for at least 15 additional minutes after the pain disappears
- Transport to hospital:

"WET & NAKED....."

(completely decontaminated)









#### **DECONTAMINATION - EYES**



- Initial decontamination with huge amounts of water from an eyewash or similar high flow device
- Flow and open and close your eye lids. It must be assured that there is adequate irrigation under the lids and in the corners of the eyes
- There is considerable discomfort associated with irrigating under the eyelids and in the corners of the eyes
- Therefore, if available for application by trained personnel, use of a topical anesthetic is recommended after an initial brief decontamination







#### FIRST AID - EYES



- Once decontamination has been completed, continue irrigation with a low flow solution
- Irrigate each eye with 1% calcium gluconate solution (if allowed by local legislation, otherwise, irrigate with 0,9% saline solution (Ringer solution))
- This should be continued while the individual is transported for medical evaluation by an eye specialist.
- Obtain medical attention immediately, especially specialised ophthalmic attention.







#### FIRST AID - INHALATION



- Administer 100% oxygen by mask.
- Nebulize 2.5% calcium gluconate in normal saline solution continuously until medical evaluation.
- If respiratory assistance is needed use indirect methods such as "microshields®" or "ambu" bag







#### FIRST AID - INGESTION



- Do not induce vomiting
- Maintain life support
- Bring to medical attention immediately







#### SYSTEMIC EFFECTS



- Monitor for signs of systemic fluoride toxicity, especially low serum calcium
- strongly consider the infusion of calcium gluconate intravenously as presumptive treatment for impending systemic effects of AHF/HF (hypocalcemia being the most immediate).







#### FIRST AID KIT FOR AHF / HF

- ✓ Calcium Gluconate Gel 2,5%.
- Eyewash bottle
- Gauzes, bandages...
- ✓ Scissors (to rip the clothes).
- ✓ HF resistant gloves
- ✓ Instructions:
  - + details
  - + (filled) form for medical doctor







#### CALCIUM GLUCONATE AS RECOMMENDED TREATMENT

#### <u>Use calcium gluconate because:</u>



- ✓ It is an excellent Calcium source
- ✓ It is easy to prepare and use at workplace, during transportation and at hospital.
- It can be used such as gel, solution, infusion and nebulized.
- ✓ It can be used for first aids as well as medical treatment.
- ✓ There is a huge clinical experience which supports its use.





#### Be careful!

#### DO's and DON'Ts when working with HF



#### CTEF - Comité Technique Européen du Fluor

CTEF (Comité Technique Européen du Fluor) represents the major producers and users of hydrogen fluoride (HF) and fluoride chemicals in Europe. CTEF aims to assure safe production, storage, transportation and use of hydrofluoric acid.

For more information, visit our website: www.eurofluor.org







#### MORE INFORMATION FIRST AID

#### More information/brochures:

It is strongly recommended to download

- First Aid Brochure (seven languages)
- Guidelines in Case of HF Exposure
- AHF / HF Safety Data Sheets

on website <u>www.eurofluor.org</u> under <u>safety recommendations</u>

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