

# Handling, storage and distribution of packaged Hydrofluoric acid



# **Disclaimer**

The information in this Guidance is given in good faith and belief in its accuracy at the time of publication, but it does not imply any legal liability or responsibility by the CBA.

Users of this Guidance should pay regard to any relevant legislation or authoritative recommendations, which may have evolved prior to or subsequently to the date of publication.

This guidance sets out what is considered to be best practice in the industry regarding the control of hydrofluoric acid during handling, storage and distribution. The Guidance is not mandatory and employers may adopt a different approach in a particular situation, where to do so would maintain an equivalent level of safety, as would have been achieved by following this Guidance.

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# Foreword

The Health and Safety Executive (HSE) was involved with the Chemical Business Association in producing this guidance. HSE endorses the guidance as it follows a sensible and proportionate approach to managing health and safety.

Health and Safety inspectors seeking to secure compliance with the law may refer to this Guidance as illustrating good practice.

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# Introduction

- 1. Hydrogen Fluoride (HF) and its aqueous form, Hydrofluoric acid (HA) are essential in the chemical industry and there is a need for HF & HA to be produced, transported, stored and used. These uses include:
  - Oil refining
  - Manufacture of semi conductors
  - Glass and metal etching
  - Chemical manufacture
- 2. There are numerous pieces of guidance available from Eurofluor (CTEF), the Hydrogen Fluoride sector group of CEFIC. However, many of these documents cover very specific topics and do not readily address aspects specific to the dilution and distribution of hydrofluoric acid in packages.
- 3. The HF & HA industry have a very good safety record; nevertheless, this document is designed to promote continuous improvement in the standards of safety associated with HA distribution.

# First aid measures / plan

- **4.** Hydrofluoric Acid exposures are different from other acid exposures because:
  - HF penetrates all tissue it comes in contact with and does not remain on their surface.
  - Once absorbed 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.
  - Unlike other acids that are rapidly removed or neutralized, the corrosive and toxic effects may continue for days if left untreated.
  - In the case of contact with HF, control or treatment by medical personal is essential.
- 5. Hydrogen Fluoride is corrosive to the skin, eyes, and the mucous membranes of the respiratory and digestive tracts. Hydrofluoric acid is readily absorbed into the body causing acute and severe toxic systemic effects, mainly attributable to a rapidly developing serum hypocalcaemia caused by the formation of calcium fluoride or fluoroapatite, serum hypomagnesaemia and serum hyperkaliemia.
- 6. Hydrofluoric acid skin burns are usually accompanied by severe pain, which is thought to be due to irritation of nerve endings by increased level of potassium ions entering the extra-cellular space to compensate for the reduced levels of calcium ions, which have been bound to the fluoride. Relief of pain is an important guide to the success of the treatment; therefore local anaesthesia should be avoided.
- 7. The extent and the intensity of these systemic complications are directly related to the amount of hydrofluoric acid absorbed, and the concentration of the hydrofluoric acid when in solution. There are also indications that subcutaneous deposits of hydrofluoric

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- acid under the burnt area may be responsible for a slow supply of fluoride ions to the circulation.
- 8. Symptoms of serious intoxications include hypotension, hypocalcemia tetany, and/or laryngospasm, often-respiratory failure (possibly due to pulmonary hypertension), ventricular tachycardia, ventricular fibrillation and cardiac arrest. Renal and hepatic functions may be impaired and muscular damage may be secondary to tetany.
- 9. Companies are strongly recommended to download the document 'First Aid Brochure' from the CTEF website: <a href="http://www.eurofluor.org/download/english-management-of-hydrofluoric-acid-injury-notes-for-health-professionals/">http://www.eurofluor.org/download/english-management-of-hydrofluoric-acid-injury-notes-for-health-professionals/</a>

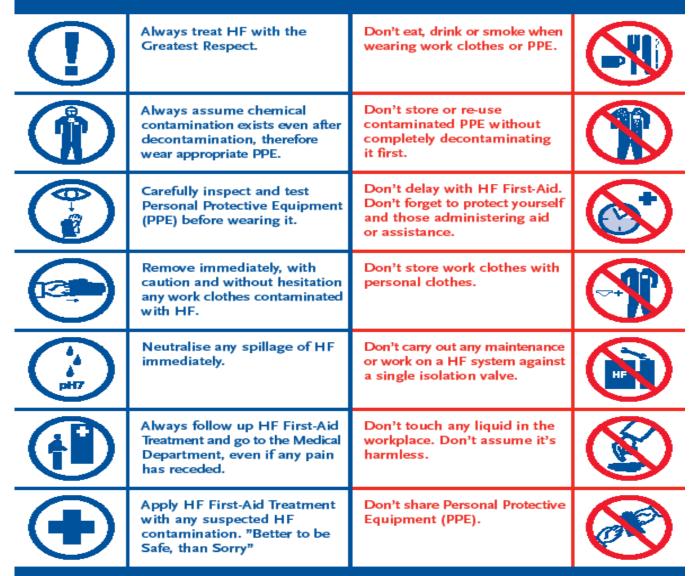
# Information and training

- **10.** All CBA members must implement rigorous control regimes for the training of personnel who deal with hydrofluoric acid within their organisations. All staff involved in the supply chain must be given training in hazard awareness so they are informed as to the dangers involved with hydrofluoric acid.
- 11. There is specific guidance available from CTEF, which provides training recommendations for hydrofluoric acid handling. Companies are strongly recommended to download the document 'STS 98/113 Training Recommendations for HF handling' from the CTEF website: http://www.eurofluor.org.
- **12.** All personnel involved in the physical handling of hydrofluoric acid (Drivers, Fillers and warehouse staff) must be trained in Emergency First Aid and then given extra training regarding the application of Calcium Gluconate gel.
- **13.** Speed and thoroughness in washing off the acid is of primary importance. Vehicles should be provided with sufficient water. There should be an installed water supply e.g. an emergency shower on a site handling and storing hydrofluoric acid.
- **14.** Distributors should offer hazard awareness training to customers who purchase hydrofluoric acid and advise all customers to inform the local hospital that they handle the substance so they can plan for an incident.
- 15. All organisations involved in the handling of hydrofluoric acid either in filling or storage must have a written emergency plan to ensure that effective treatment of hydrofluoric acid contact is given immediately and that the local hospital is aware of the likelihood of a hydrofluoric acid incident. All involved personnel should be aware of this plan. Industrial experience indicates that prompt treatment, as described, will prevent the development of serious injury. In the majority of cases caused by industrial accidents, little more than skin effects occur after prompt treatment.
- 16. Therefore, speed is essential. Delays in 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.

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- **17.** CTEF have published a guidance document (STS 94/96) that contains a number of concise flowcharts detailing the correct treatment for each possible exposure route:
  - Skin;
  - Eyes,
  - Inhalation; and
  - Ingestion
- 18. Companies are strongly recommended to download the document 'STS 94/96 Guidelines in case of HF Exposure' from the CTEF website:
  <a href="http://www.eurofluor.org/download/sts-9496-guidelines-in-case-of-hf-exposure/">http://www.eurofluor.org/download/sts-9496-guidelines-in-case-of-hf-exposure/</a>

# 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.or

# **Legal duties**

- **19.** The use of Hydrofluoric acid is directly legislated by the Control of Substances Hazardous to Health (COSHH) Regulations 2002 <sup>a</sup>.
- Other legal duties arise from many other sources, and the references contain a number of those most relevant. For the purpose of this guidance those duties may be summarised as requiring safety to be actively managed through a process that starts with risk assessment. Risk assessment in turn starts with a recognition of the hazards presented by any substance and process, identifying who or what (e.g. the environment) may be affected, and to what extent, and putting in controls that are adequate to eliminate or minimise those risks.
- 21. The guidance and reference sections list the most relevant legislation

# Risk assessment

- **22.** The transport, handling and storage of Hydrofluoric Acid within packages, at concentrations below 70% are an area of concern for the distributors sector.
- 23. Package goods, within the scope of these discussions, are containers with a capacity of 1,000 Litres (Intermediate Bulk Containers (IBCs)) or lower.
- **24.** Guidance in the following areas will be given:
  - Transport requirements
  - Handling and Storage infrastructure
  - Training and awareness
  - First aid measures
  - Filling Operation
- **25.** Risk assessment is the systematic evaluation of work activities using the following five steps:
- Step 1: Identify the hazards.
- Step 2: Identify the exposures. Who and what could be harmed and how?
- Step 3: Evaluate the risks arising. Decide whether existing precautions are adequate or if more should be done.
- Step 4: Record the findings.
- Step 5: Review the assessment regularly and revise if necessary.
- **26.** Advice on carrying out risk assessments is contained in an UK HSE Guidance leaflet INDG163 <sup>b</sup>.
- **27.** The remaining sections of this guidance help to identify many of the hazards associated with the distribution of Hydrofluoric acid solutions and give guidance on how to reduce the risks.

- **28.** The assessor must ensure that all relevant local factors are taken into account. The main principles of the COSHH regulation are the "hierarchy of control". These elements should be an integral part of the overall risk assessment process, they are:
  - Eliminate
    - Does the product need to be handled or used in that way?
    - Can the work be done in a different way, taking care not to introduce new hazards?
  - Substitute
    - Could dangerous product or process be substituted with a less dangerous one?
  - Isolate
    - fitting local exhaust ventilation to dusty processes; mechanising the process so the person is separated from the hazard; changing the system of work to one which involves less handling
  - Information, Instruction, Training and Supervision
    - Ensure that workers and others understand the risk and know what they must do.
  - PPE
    - This should only be used as a last resort as it is the least reliable form of protection.
- 29. It is important to set out the limitations of the risk assessment. A complete risk assessment will also have to consider other hazards, which are not within the scope of this guidance. The responsibility for ensuring a suitable and sufficient risk assessment is performed remains with the employer.
- **30.** The risk assessment should consider adjacent storage, including storage in other forms of packaging and/or bulk, as well as other classes of dangerous goods and low hazard goods.
- **31.** Where an employer has five or more employees the significant findings of the risk assessment should be recorded. Further guidance can be found in HSE guidance L21 Management of Health and Safety at Work Regulations 1999 (MHSW) <sup>c</sup>.

# **Transport**

- **32.** The recommendations within this section cover detailed safety aspects of carriage, which are not covered by the ADR  $\frac{d}{d}$  provisions and so should be taken into consideration in addition to the ADR requirements.
- **33.** Within ADR Hydrofluoric acid solutions are subject to specific carriage requirements depending on the concentrations transported. The details of the classifications are reproduced below:

in excess of 60% concentrations	Below or equal to 60% concentration
<ul> <li>UN1790;</li> <li>Class 8 (corrosive);</li> <li>Class 6.1 (Toxic);</li> <li>Packing group, I; and</li> <li>No "limited" or "excepted" quantities exemptions</li> </ul>	<ul> <li>UN1790;</li> <li>Class 8 (corrosive);</li> <li>Class 6.1 (Toxic);</li> <li>Packing group, II; and</li> <li>Limited Quantities = 1L</li> <li>Excepted Quantities = E2</li> </ul>

- **34.** For solutions in excess of 60% the absence of any "limited quantity" exemption results in a more onerous regime, as follows:
  - All packaging used must be UN certified, regardless of the volume;
  - Any load in excess of 20 litres is subject to ADR in full
    - Due to load thresholds in chapter 1.1.3.6.3 ADR for packing group I
  - Transport security issues
    - As per ADR chapter 1.10 (see site security section for details)
  - A reduction on the quantity of other dangerous goods that can be carried before ADR in full needs to be applied
    - See ADR chapter 1.1.3.6.4 "summation" calculation

# **Carriers**

- **35.** Due to the nature of the distribution industry within UK a "hierarchy of controls" for transport of Hydrofluoric Acid solutions in packages has been agreed as follows:
  - Own fleet
  - Approved carriers
  - General carriers
- **36.** Each of the options within the hierarchy involves an increasing degree of risk to be accounted for and it would be the responsibility of each organisation to apply the appropriate risk control measures for the movement to be undertaken safely.

# **Hierarchy of measures**

- **37.** The use of 'own drivers and own vehicles' for Hydrofluoric Acid deliveries is the preferred choice of many CBA members. This is to ensure that the level of training and competence necessary to safely transport Hydrofluoric Acid is maintained throughout the journey.
- **38.** The use of 'contract hire' vehicles and drivers, to supplement these arrangements during holidays etc, is acceptable so long as the vehicle and driver are suitably equipped and trained to handle hydrofluoric acid deliveries.
- **39.** There will also be times when the logistics required to service some remote locations could make this preference uneconomical, so company fleets will often be supplemented by a number of "authorised carriers".
- **40.** These carriers must be strictly controlled, audited and monitored to ensure that they are:
  - 1. Trained regarding the hazards
  - 2. Trained regarding the extra First Aid measures necessary
  - 3. Arrive at depots for collection with the correct equipment
- **41.** "Authorised Carriers" should ideally, wherever possible, be restricted to single trip deliveries.
- **42.** However, in exceptional cases the need for trans-shipment<sup>1</sup> of packages and/or use of other carriers may be unavoidable. In these cases CBA members should make every effort to ensure that the supply of information, training and the First Aid equipment, including an antidote kit, is maintained throughout the whole journey.

Storage overnight and then onward distributor the next day.

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<sup>&</sup>lt;sup>1</sup> Trans-shipment, within the scope of these discussions, is defined as the removal of packages from a vehicle for either:

<sup>□</sup> Immediate reloading onto another vehicle; or

# Description and standardisation of Personal Protection Equipment (PPE) for drivers, including Calcium Gluconate kit

**43.** CTEF have given recommendations for 'Standard Equipment' personal equipment applicable to drivers (*Level Delta* ( $\delta$ )), which can be found within the CTEF document STS 98/111:



# **Figure: Level Delta Personal Protective Equipment**

Delta Level is the minimum level of personal protective equipment required to enter a hydrofluoric acid handling facility and is not designed for use when there is a risk of potential exposure to hydrofluoric acid.

δ Level of PPE is specified when the risk assessment has indicated that no physical contact with acid containing equipment is likely and, therefore, only minimal protection is needed. It is intended to give protection against potentially small, unforeseen exposures e.g. drips, surface contamination, etc.

δ Level personal protective equipment is defined as:

- Standard hardhat (EN 397).
- Safety spectacles with side shields or chemical goggles (EN 166-345-B).
- HF resistant Wellington-type boots, over boots or safety shoes with steel toe (EN 345).
- HF resistant gloves (EN 374-3) may also be required.
- Escape air packs or suitable filtration systems should also be readily available to enable an escape in the unlikely event of a leak.
- **44.** All drivers involved in the carriage of hydrofluoric acid in packages must be trained in Emergency First Aid measures including extra training regarding the need for rapid extensive decontamination and application of Calcium Gluconate gel.
- **45.** Speed and thoroughness in washing off the acid is of primary importance. Vehicles should be provided with sufficient water, e.g. a water extinguisher or multiple eye wash bottles.
- 46. Vehicles carrying HF or sites containing hydrofluoric acid must have immediate access to emergency First Aid kit<sup>2</sup>, which contains a minimum of six tubes of Calcium Gluconate gel and if available a copy of CIA Label 14 or CTEF (Eurofluor) treatment card. These kits must be regularly audited to ensure they are still suitable for use. The Eurofluor treatment card document can be found in appendix 2 of <a href="STS94/96">STS94/96</a>.

<sup>&</sup>lt;sup>2</sup> HF First Aid kit is detailed in the CTEF publication "Management of hydrofluoric acid injury (notes for Health Professional)" available on the website <a href="http://www.eurofluor.org/download/group-7/">http://www.eurofluor.org/download/group-7/</a>

# **Procedure for empty packaging**

**47.** All transport and handling of 'returnable or reusable' packaging for hydrofluoric acid must be treated as if the containers were full. All staff must be trained and have immediate access to hydrofluoric acid first aid kits.

# **Delivery only to "authorised" customers**

**48.** No material should be sold to a customer who does not have an account set up with the distributor. CBA members should also make sure that customers buying hydrofluoric acid are trained regarding the risks associated with handling and storage hydrofluoric acid.

# Handling, Storage and Filling Operations

- **49.** Due to the specific hazardous properties of hydrofluoric acid there will be a wide difference of philosophies within the CBA membership regarding the dilution, handling and filling of hydrofluoric acid into packages.
- **50.** All filling and bulk storage areas must be bunded. The bunds must be designed to contain 110% of the largest container or storage/blending tank and constructed to resist chemical attack.
- **51.** Tertiary containment should also be considered, but the emphasis should be placed on primary and secondary containment aspects.
- **52.** Access to all areas where filling operations take place must be restricted to 'authorised and trained' personnel only during any filling operation.
- 53. During the filling of hydrofluoric acid into packages there must be procedures to ensure that any accidental contact with hydrofluoric acid can be treated immediately to increase the effectiveness of emergency treatment regimes. The exact nature of the supervisory/manning requirements will depend on the likelihood of potential contact.
  - Areas within a bunded area round a tank/ valve inspections or repairs should be "double manned"
  - Filling operations, where the operator is dressed in full PPE and in direct proximity to the filling heads and packages should be constantly monitored.
  - Remote filling operations, where the operator is dressed in full PPE and located behind a protective screen during filling will require frequent monitoring.
- **54.** CTEF have given recommendations for 'Routine operation' personal equipment applicable to operators (*Level Gamma* (γ)), which can be found within the CTEF document STS 98/111:

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Level Gamma (γ) Personal Protective EquipmentRoutine Operation

Level Gamma ( $\gamma$ ) personal protective equipment is used for routine operational tasks involving non-invasive interactions with process equipment. It is designed to give a greater degree of protection against incidental contact with process fluids for individuals working in the HF handling area.

Level Gamma ( $\gamma$ ) personal protective equipment is defined as:

- Standard hard-hat (EN 397) with HF resistant nape (EN 467: 1995) and face visor (EN 166-B). Visor MUST be in the down position when within the HF handling area.
- Chemical goggles (EN 166-345-B). Goggles MUST be worn under visor when within the plant boundaries.
- HF resistant gloves (EN 374-3).
- HF resistant jacket with sleeves sealed at gloves (EN 467: 1995).
- HF resistant high waisted trousers sealed at Wellingtontype boots (EN 467: 1995).
- HF resistant Wellington-type boots or overboots with steel toe and shank (EN 345 with additional testing to EN 369 [specifically for HF]).

Level Gamma ( $\gamma$ ) personal protective equipment should be used for operations which involve interaction with the process but which are NOT expected to cause a release of process fluids. Training is required to ensure that  $\gamma$   $\Box$ Level personal protective equipment is fitted correctly.

- 55. Where Personal Protective Equipment is provided to operators involved in the filling of hydrofluoric acid it is absolutely essential that the PPE must be suitable for the operation. The choice of PPE must not be taken lightly and operator interaction is vital to agree a suitable specification.
- There must be a rigorous regime in place to ensure that the maintenance and quality of the equipment is guaranteed and that the operators understand the necessity for wearing the equipment. The CTEF guidance document STS 98/111 contains recommendations for standardised levels of PPE pertaining to the operation to be performed. This document can be referenced in company procedures and used when assessing equipment to reduce risk. Companies are strongly recommended to download the document 'STS 98/111 Personal protective equipment for use with HF' from the CTEF website: <a href="http://www.eurofluor.org/download/personal-protective-equipment-classification-uses/">http://www.eurofluor.org/download/personal-protective-equipment-classification-uses/</a>.
- **57.** Packaged hydrofluoric acid must be stored within controlled sites to ensure the correct level of training and safety when handling the material. The following aspects should also be considered.

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### **Pallets**

- **58.** The transport and storage of containers other than IBCs, usually requires the use of a "pallet" to allow the grouping of containers to aid handling and minimise manual handling of numerous small containers.
- **59.** CBA members can use wooden pallets for hydrofluoric acid in packages but must ensure that they have strict rigorous regimes in place to:
  - 1. Use only high quality pallets
  - 2. Check the integrity of the pallet before use to minimise the potential of nail damage

# No storage at height, only on ground or first level

**60.** The storage areas can be secure external compounds or secure ground level or first level racked storage in warehouses.

# Site security

- **61.** Certain concentrations of hydrofluoric acid are subject to very specific security provisions within parallel legislation. As previously stated, Hydrofluoric acid solutions in excess of 60% are classified as:
  - UN1790;
  - Class 8 (corrosive);
  - Class 6.1 (Toxic);
  - Packing group I; and
  - Have no "limited" or "excepted" quantities exemptions

Carriage of these concentrations of HA are within the scope of the transport of dangerous goods legislation and as such are subject to the High Consequence Dangerous Goods (HCDG) security provisions within chapter 1.10.3 of ADR d

- **62.** ADR 1.10.3 require carriers, consignors and any other participants engaged in the carriage of HCDG shall adopt, implement and comply with a "security plan".
- 63. The UK Department for Transport Transport Security ABD Contingencies Division (DfT Transec) in conjunction with industry trade associations has published a suite of guidance documents to enable companies to comply with the HCDG provisions. These can be obtained through the following weblink:

https://www.gov.uk/government/uploads/system/uploads/attachment\_data/file/5 06624/quidance-secure-carriage-dangerous-goods-road-rail.pdf

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- 64. Maritime and land Transport Security division of DfT is responsible for auditing companies who are subject to the ADR 1.10.3 provisions. As part of their role they will visit sites to ensure that the site has:
  - Written a security plan;
  - Implemented the plans recommendations; and
  - Appointed a responsible officer

These audits will be repeated at regular intervals to ensure continued compliance and that identified improvement actions have been completed satisfactorily.

- 65. Hydrofluoric acid solutions below the 60% in concentration are classified as packing group II and therefore not subject to the legal requirements of ADR 1.10.3 although they are subject to the general provisions as written into chapters 1.10.1 & 1.10.2.
- 66. Due to the hazardous nature of hydrofluoric acid CBA members are recommended that sites involved in the handling, filling and storage of hydrofluoric acid solution in concentrations below 60% should download and implement aspects of the security plan. These requirements are not legally binding but represent the implementation of "best practice".
- 67. As a minimum requirement hydrofluoric acid (<60%) should be stored in a secure area with limited access to personnel with the requisite training and equipment to ensure safe handling and specifically limit the possible access by the general public.

# **GLOSSARY**

Hazard: That property of a material that has the potential to cause harm to people, property or the environment.

Risk: The chance that somebody or something could be harmed by the hazards, together with an indication of how serious the harm could be.

IBC (for the purposes of this guide)

"Intermediate Bulk Container" (IBC) means a rigid, or flexible portable packaging.... that:

- has a capacity of not more than 3m<sup>3</sup> for solids and liquids of packing groups II and III;
- is designed for mechanical handling;
- is resistant to the stresses produced in handling and transport as determined by the tests specified in Chapter 6.5 of ADR

**Composite IBC with plastic inner receptacle:** These are IBCs comprising a rigid outer structure encasing a plastic inner receptacle. It is constructed so that the outer and inner assemblies are used as an integrated single unit to be filled, stored, transported or emptied.

# REFERENCES

- a) The Control of Substances Hazardous to Health Regulations (COSHH) 2002
  - 1. INDG136 COSHH: A brief guide to the Regulations ISBN 0-7176-2982-1
  - 2. L5 The Control of Substances Hazardous to Health Regulations 2002 (as amended). Approved Code of Practice and guidance (Fifth edition) ISBN-0-7176-2981-3
  - HSG193 COSHH essentials: Easy steps to control chemicals. Control of Substances Hazardous to Health Regulations HSG193 (Second edition) -ISBN 0-7176-2737-3
- b) INDG163 Guidance 5 Steps to Risk Assessment ISBN-0-7176-6189-X
- c) L21 Management of Health and Safety at Work Regulations 1999 Approved Code of Practice and Guidance ISBN 0-7176-2488-9
- d) ADR European Agreement concerning the International Carriage of Dangerous Goods by Road ISBN 92-1-139112-1 <a href="https://www.unece.org/trans/danger/danger.html">https://www.unece.org/trans/danger/danger.html</a>

# **GUIDANCE**

# o HSE

	Publication Title	ISBN Number
INDG347	Basic advice on first aid at work leaflet <a href="http://www.hse.gov.uk/pubns/indg347.pdf">http://www.hse.gov.uk/pubns/indg347.pdf</a>	0-7176-2423-4
L74	First aid at work. The Health and Safety (First Aid) Regulations 1981. Approved Code of Practice and Guidance (3 <sup>rd</sup> edition 2013) <a href="http://www.hse.gov.uk/pubns/priced/l74.pdf">http://www.hse.gov.uk/pubns/priced/l74.pdf</a>	0-7176-1050-0
HSG71	Chemical Warehousing - the storage of packaged dangerous substances <a href="http://www.hse.gov.uk/pubns/priced/hsg71.pdf">http://www.hse.gov.uk/pubns/priced/hsg71.pdf</a>	0-7176-1484-0

# NATIONAL POISONS INFORMATION SERVICE (NPIS)

Publication Title
Hydrofluoric acid poisoning leaflet
http://www.npis.org/HFguidance.pdf

# o CTEF

	Publication Title	
STS 98/111	Personal protective equipment for use with HF	
STS 99/113	Training Recommendations for HF handling	
STS 94/96	Guidelines in case of HF Exposure	
STS 81/37	Chemical Safety Data Sheet - Hydrogen Fluoride (70% solution)	
STS 07/138	HF Neutralization Table	
First Aid Brochure	Management of hydrofluoric acid injury (notes for Health Professional) Second Edition	

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