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EUROFLUOR HF

A snapshot of the fluorine industry

Fourth edition





**“Welcome to
the world of the
fluorine industry”**

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“Safety is the major concern for both producers and users.”



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Introduction

Hydrogen fluoride (HF), better known as hydrofluoric acid, is one of the basic raw materials for a wide variety of both commercial and industrial products. It is produced by reacting a naturally occurring mineral, fluor-spar, with sulphuric acid. HF is a strong corrosive acid which must be handled with extreme caution. Safety is therefore the primary concern of both producers and users.

The major activity of Eurofluor (the European Technical Committee for Fluorine) has been the issuance of recommendations on the safe handling of hydrofluoric acid during production, storage, transportation and use.

The socio-economic importance of the fluorine industry

In 2015, European hydrofluoric acid production reached 232,000 tons with a value of around 270 million EUR.

Around three hundred people are directly employed at nine HF production sites in four European countries. It is estimated that the total number of jobs related to the fluorine industry, including downstream products, amounts to more than 50,000.





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What is fluoride?

Fluorspar

The chemical element fluorine forms fluorides when it is combined with other chemical elements. Fluorine is found mainly in a mineral called fluorspar which is also sometimes known as fluorite. It is a naturally occurring mineral which may contain up to 45% calcium fluoride (CaF₂). In its natural shape it is formed with other minerals such as barytes, galena, pyrites and other sulphides. In its pure form it is colourless and transparent or translucent, with a glossy lustre. Impurities in the mineral can cause it a wide variety of colours, and some types may exhibit fluorescence. It is in fact one of the most colourful minerals in the world, appearing in a variety of shades from yellow and green through rose, red, pink and reddish orange to blue and black.

The main deposits of fluorspar are now to be found in China, Mexico, Mongolia, South Africa and Namibia. Europe still has a small number of viable fluorspar mines, although the total has declined gradually over the years. It is a truly international business with worldwide consumption estimated at around 4.5 million tonnes per year.

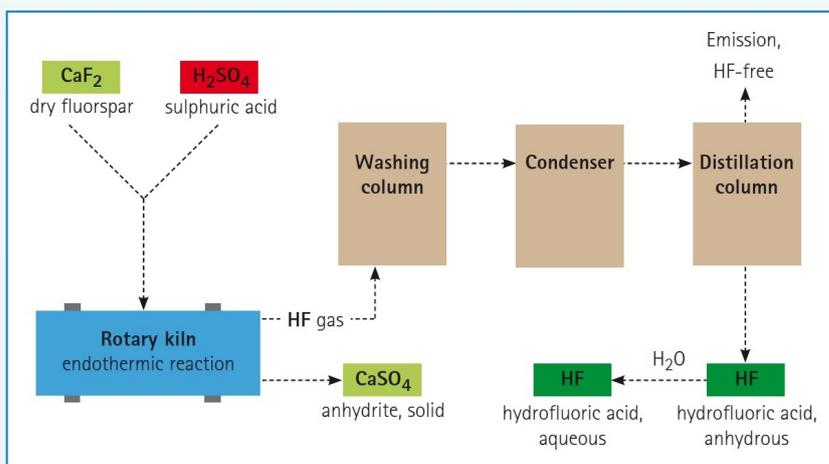
The most demanded is the acid grade, used as raw material to produce hydrofluoric acid, its worldwide production capacity being more than three million metric tonnes.

After the ore is dug from mines or from open quarries, impurities are removed to leave a fluorspar which contains a minimum of 97% calcium fluoride. Most of the co-products are also separated and collected, to serve a variety of industrial purposes. The acid grade fluorspar is then transported to the hydrofluoric acid plants by ship, road, rail or barge. Here it reacts with sulphuric acid to form hydrogen fluoride gas. This is either collected and stored for use as a liquefied gas, or it can be diluted with water to produce aqueous solutions of hydrofluoric acid.

The main grades of fluorspar available are

- crude ore 25–30 %
- metallurgical grade 75–82%
- ceramic grade 94–96%
- acid grade 97%
- crystalline grade 99%

Production of hydrofluoric acid (HF)



Safety recommendations

Safety in the transport of hydrofluoric acid

For hydrogen fluoride producers and users, safety is a key component of their Responsible Care® commitment. From production right through to the consumer, safety recommendations cover every aspects of processing, handling, storage, transportation and use, as well as important aspects of health and the environment.

Due to its unique properties, hydrofluoric acid and products derived from it are essential for our daily lives. They all need to be transported from manufacturing plants to customers' sites. HF has been transported by road, rail and by ship for more than fifty years, and has never during this time been the subject of a major incident in Europe.

This enviable safety record is due in large measure to the high quality of the tanks used to transport the material. Designed in accordance with a number of international regulations and built in steel, they meet the highest safety criteria. In addition, the units are regularly inspected and certificated by independent bodies.

“ The safe
transport units
are regularly
inspected.”



Should any kind of incident occur, specially trained technicians are on call in every European country in which this product is transported, to give professional advice and minimise the consequences.

For more information, visit our web sites: www.eurofluor.org and www.cefic.org.

APPLICATIONS

- ⇒ Fluorocarbons
- ⇒ Fluoropolymers
- ⇒ Electronics
- ⇒ Metallurgical industry
- ⇒ Petroleum production
- ⇒ Pharmaceuticals
- ⇒ Crop protection
- ⇒ Consumer products
- ⇒ Detergents
- ⇒ Crystal glass
- ⇒ ceramics



Applications

Fluorocarbons

The main application for hydrogen fluoride is in the manufacture of fluorocarbons. Around 60 % of HF manufactured worldwide is used in this area. Since the signing of the Montreal Protocol in September 1987, in which Parties agreed to phase out chlorofluorocarbons (CFCs), there have been two major developments. Firstly, hydro chlorofluorocarbons (HCFCs) replaced CFCs. HCFCs however still had some ability to deplete the ozone layer and were an intermediate solution to the problem. Manufacturers reacted very quickly to develop hydrofluorocarbons (HFCs) which are chlorine-free, and have no potential to deplete the ozone layer but have some global warming potential (GWP). The latest generation of hydrogenated fluorinated olefins (HFO) is under development and show already meaningless GWP. There are two main application areas:

1. Refrigeration

The main product for refrigeration applications is HFC 134a, which has proved to be an excellent replacement for CFC 12. Although partly restricted, it is used wherever cooling, freezing, or other heat transfer processes are required. HFOs are currently discussed to be used for similar applications. These include:

- process cooling, food processing, industrial refrigeration
- transport, commercial and domestic refrigeration
- air conditioning

2. Foam blowing

A range of plastics, including polyurethane and polystyrene, possesses high insulation properties. The process to produce them is known as „foam blowing“. When „foam blowing“ is achieved using fluorocarbons, it provides very high performance and low density insulation foams. HFCs with no ozone de





pletion potential have replaced CFCs and partly replaced HCFCs. HFOs are also under development for this segment.

The main foam application areas are:

- domestic appliances
- building insulation
- insulation in transport

Fluoropolymers

Most fluoropolymers are based on a combination of fluorocarbons. Among other fluoropolymers, polytetrafluoroethylene (PTFE) is used for wire and cable insulation, pipes, valves and vessels, coatings in general e.g. for cookware, waterproof laminates on textiles etc.

Their peculiar properties include fire resistance, mechanical strength, insulation, low surface tension and resistance against chemicals.

Electronics

In the electronic industry hydrofluoric acid is the key chemical in the manufacture of silicon based semi-conductor devices. Its ability to attack silicon oxide and to transform it into soluble compounds is the basis of multiple applications in cleaning and etching processes.

Hydrofluoric acid is used in conjunction with nitric acid for silicon etching, as buffered oxide etch in combination with ammonium fluoride solutions, and as dilute HF for final cleaning steps and the removal of native oxides.

Semi-conductor devices are crucial for the functioning of many consumer articles designed to make life easier, such as washing machines, PCs, refrigerators, mobile and smart phones, camcorders and many others, but they are also key elements in the electronic systems in cars, planes and trains.

Metallurgical industry

Hydrofluoric acid and its salts are used at several stages in the processing of many metals, in industries such as primary aluminium manufacture, stainless steel, and foundries.

1. Metal extraction

HF is used to separate essential metals from mineral ores. Tantalum and niobium for example are used in electronics and other important applications. Tantalum is essential in the production of mobile phones.

“Hydrofluoric acid
is used as a catalyst
for higher process
efficiency.”



2. Metal manufacture

Aluminium is obtained from bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) by electrolysis. The electrolyte used is sodium aluminium fluoride, known as sodium cryolite. The other principal raw material in this process is aluminium fluoride (AlF_3). AlF_3 serves as a melting point reducer which leads to significant energy savings.

3. Metal processing

Another example of the importance of fluorine is in metal surface treatment. Hydrofluoric acid is used, together with nitric acid, in the manufacture of stainless steel to remove unwanted oxides and other impurities from the surface of the finished metal sheet.

4. Miscellaneous

New products and technologies are continually being developed. Hydrofluoric acid and its derivatives are increasingly being used:

- as fluxing agents, reducing the melting point and therefore saving energy
- as refining agents for metals
- as protective materials for metal surfaces prior to decorative finishing

Petroleum production

In addition to the many uses of HF as a process chemical, it is also used in important industrial applications as a catalyst. A catalyst is a material which promotes a chemical reaction without itself being consumed in the reaction. The use of a catalyst yields benefits in terms of process efficiency and economy.

In the petrochemical industry the naturally occurring components of crude oil are traditionally separated by the process of distillation. However, this process does not change the relative proportions of the individual components, some of which have a higher commercial value than others.

The process of alkylation, where HF is employed as a catalyst, offers an opportunity to increase the yield of petroleum grade fractions. Typically, low boiling fractions such as propylene and butylene are reacted with isobutane to generate high-octane products.

They contribute to produce a fuel which burns efficiently, providing longer engine life and lower emissions. By boosting the octane rating of fuels, alkylates avoid the need for such environmentally harmful substances as lead, without compromising engine performance.



“Fluorine plays
an important role
for asthma sufferers.”



Pharmaceuticals

Fluorine has played an important role in the pharmaceutical and agrochemical industries already for several decades. It is well known that the effectiveness of many complex molecules is significantly enhanced by the presence of even a single fluorine atom.

In the early days, hydrofluoric acid was extensively used to provide the required fluorine addition. Subsequently potassium fluoride was used, particularly in halogen exchange reactions where it is necessary to remove a chlorine atom and replace it with a fluorine atom. Potassium fluoride is much easier for the user to handle and has a much greater degree of selectivity than hydrofluoric acid. It is still popular nowadays and is used as the preferred fluorine source in a number of insecticides and herbicides, as well as in some proprietary analgesic preparations, antibiotics and anti-depressives.

Even more recently, significant progress has been achieved in the development of a range of organic fluorine compounds based on CF₂ and CF₃ groups. These included an anaesthetic preparation and a well-known anti-malaria drug.

In the last couple of years, giant steps in this area of research have led to the development of a range of increasingly complex organic intermediates. They are still based on the old building blocks, but manufactured now in modern industrial processes. This development has opened up a wide range of opportunities for manufacturers of both pharmaceutical and agrochemical products.

Most of the leading agrochemical companies are currently carrying out research into the use of these chemicals for both insecticides and herbicides. Modern medicines which now benefit from these developments include a leading anti-arthritis drug as well as a very promising treatment for HIV.

There is another extremely important area of medicine where fluorine chemistry plays a vital part. For many years, chlorofluorocarbons were used as the propellant in metered dose inhalers. Since the Montreal protocol and the subsequent agreement to ban CFCs, a new generation of propellants has been developed. These gases, whose effect on the ozone layer is zero, are known as hydrofluorocarbons, usually abbreviated to HFCs. Asthma patients around the world who rely on inhalers for their treatment now benefit from this development. Work continues also to use these gases to deliver other medicines to the lungs to treat a broad range of medical conditions.

Crop protection

Hydrofluoric acid is also used in the production of modern crop protection agents. Here, the fluorine component offers a considerable increase in the reactivity and selectivity of both insecticides and herbicides. The active substances work much more efficiently, and are much less harmful to the environment than many traditional formulations.

Detergents

Hydrogen fluoride is used as a catalyst in the production of detergents. The process has a number of parallels with the petroleum alkylation process, except that in this case, linear alkylbenzene (LAB) is produced. This is used mainly in the manufacture of linear alkylbenzene sulphonate (LAS) detergents for laundry and dishwashing applications.

Compared with a traditional detergent such as soap, these products are more soluble in water. This solubility allows them to penetrate soiled articles much more efficiently. The action of a detergent depends largely upon the presence of a polar and a non-polar component in the molecule. The polar component attracts water, while the non-polar component attracts oils and greases. In this manner an emulsion is formed in which dirt can be effectively washed away.

In both petroleum and detergent applications there is some loss of catalyst due to conditions of operation. This means there is a continuing demand for HF.



Consumer products

As long ago as 1925 it was observed in the United States that fluorine ingested from fluoride-rich water sources could lead to a significant decrease in the incidence of tooth decay. Following years of research, fluoridation of drinking water began in Grand Rapids, Michigan, in 1947. The water distribution system in Switzerland did not lend itself to this type of fluoridation, but in the 1950's, Swiss scientists determined that fluorine in the form of potassium fluoride could be added to edible salt.

Extensive tests showed that results were similar to those achieved by water fluoridation. A World Health Organisation programme recommended fluoridation of edible salt as the best way of preventing dental caries wherever water fluoridation was not possible, and potassium fluoride is now routinely added to edible salt in many parts of Central and South America. Fluoridated salt is also available to a limited extent within the European Union.

Two other compounds, sodium fluoride and sodium monofluorophosphate, are also essential components of toothpaste formulations, and are similarly important in helping to prevent dental caries. Nevertheless, there is no doubt that controlled levels of ingested fluoride are many times more effective than any topical application.





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“HF gives
crystal glass the
sparkling finish.”

Crystal glass

The main raw materials used in the manufacture of nearly all types of glass are silica sand and sodium carbonate. Additionally, lead oxide is used for crystal glass. In its molten state, the glass is formed, either mechanically or by blowing, into the required shape. In many cases, using a diamond wheel, a quite complex pattern may be cut into the surface of the glass after cooling.

The final stage of the manufacturing process is to pass the glass slowly through a bath containing a mixture of hydrofluoric acid and sulphuric acid. Aqueous hydrofluoric acid solutions are the only acids capable of dissolving the raw material, silica, in an acceptable time. It is this final acid treatment which gives crystal glass the sparkling finish for which it is revered throughout the world.

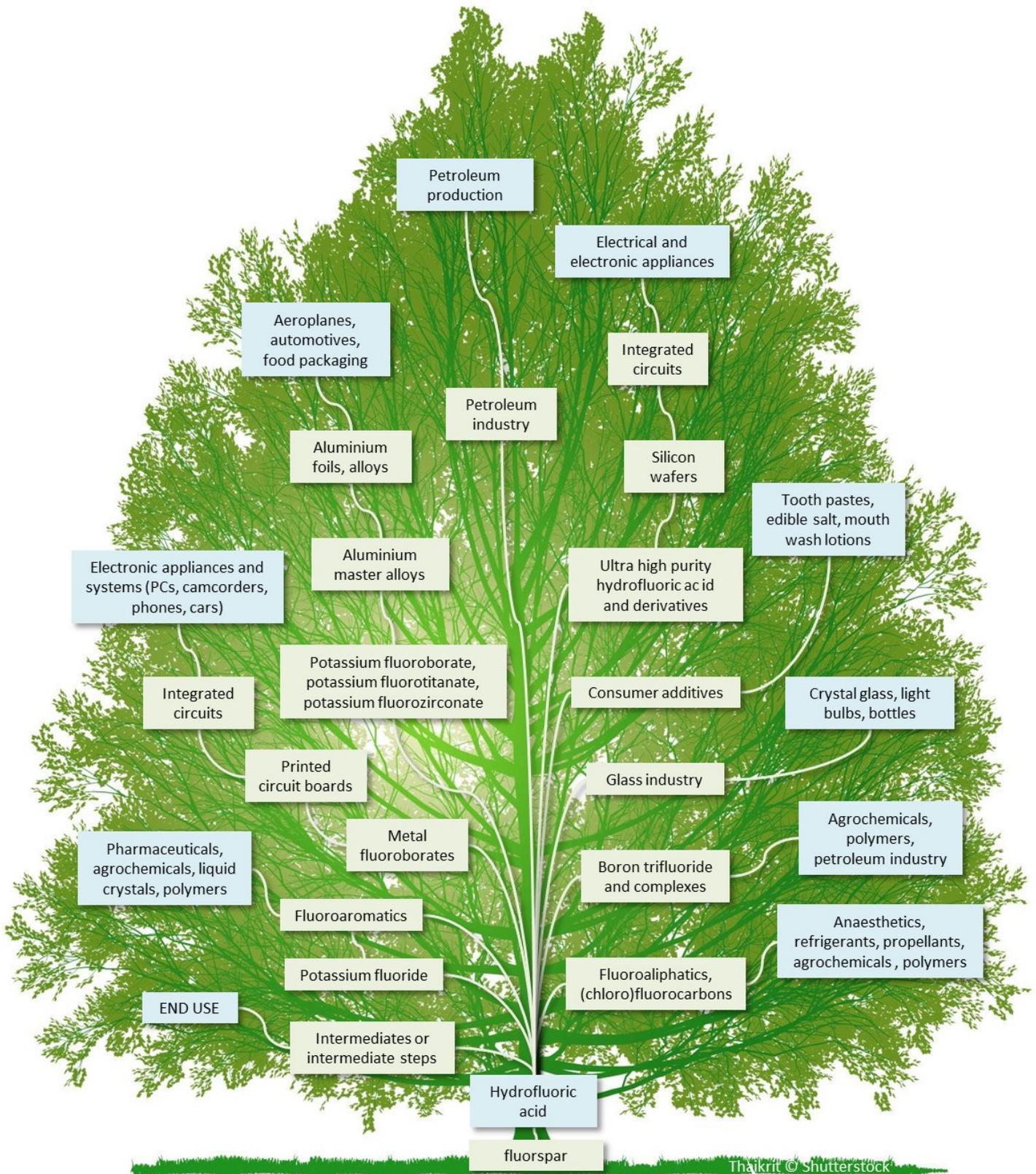
Ceramics

Inorganic fluoride compounds are important components of frits and ceramic glazes. In ceramic applications, unlike glass, the fluoride compound is actually incorporated into the final product. The most frequently used product in this area is probably barium fluoride, which serves as both a fluxing material and as an opacifier.



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APPLICATION TREE





Who produces HF in Europe?

- ◆ Derivados del Fluor SAU (ES-Ontón)
- ◆ Fluorchemie Dohna GmbH (DE-Dohna)
- ◆ Fluorchemie Stulln GmbH (DE-Stulln)
- ◆ Fluorsid SpA (IT-Assemini - Porto Marghera)
- ◆ Honeywell Specialty Chemicals Seelze GmbH (DE-Seelze)
- ◆ LANXESS Deutschland GmbH (DE-Leverkusen)
- ◆ Solvay Fluor GmbH (DE-Bad Wimpfen)





“Eurofluor represents
the major producers
and users of HF
in Europe”

About Eurofluor

The CTEF (Comité Technique Européen du Fluor), who became Eurofluor in 2012, was formed in 1975 to ensure safe production, storage, transportation and use of hydrofluoric acids.

Eurofluor represents the major producers and users of hydrogen fluoride and fluoride chemicals in Europe.

The sector group aims to

- ⇒ ensure the proper production, handling, transportation and use of hydrofluoric acid
- ⇒ ensure effective protection of workers, the environment and the people living around hydrofluoric acid plants
- ⇒ ensure proper medical treatment in case of accidental hydrofluoric acid burns
- ⇒ study the trends in hydrofluoric acid consumption in view of the rapidly changing legislation for downstream products
- ⇒ ensure adequate communication on its products and recommendations





“to ensure safe
production,
storage,
transportation
and use of
hydrofluoric acid
since 1975.”

Eurofluor Members

- ◆ Alufluor AB (SE) www.alufluor.com
- ◆ Arkema (FR) www.arkema.com
- ◆ Chemours (NL) www.chemours.com
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ABOUT CEFIC

Cefic, the European Chemical Industry Council, founded in 1972, is the voice of large, medium and small chemical companies in Europe, which provide 1.1 million jobs and account for 15% of world chemicals production.

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