Let's Take a PEEK at the PEAC software

An example using the PEAC tool

This month our example is Fluorosulfonic Acid which has a UN# of 1777 and a US DOT Guide Number of 137 which is titled <u>Substances - Water-Reactive - Corrosive</u>. As the reader will soon see, Fluorosulfonic Acid differs considerably from some of the hazardous material examples we shown in previous issues of this newsletter.

When compared with other examples, we find the amount of information available on fluorosulfonic acid in the PEAC-WMD database is rather sparse. This is because there really isn't a great deal of information available in the public domain. Fluorosulfonic acid is primarily used for the following industrial purposes:

- Fluorinating agent
- Catalyst in alkylation, acylation, polymerization & condensation reactions
- Hydrofluorination of olefins
- Production of substituted pyridines
- Preparation of magic acid
- Glass industry

Its chemical formula is FSO3H. Because of its molecular structure it is referred to as a "super acid". This is primarily due to the presence of the fluorine atom and its strong negative effect on the molecular structure. Although no toxicity values are currently displayed in the PEAC-WMD database, during the basic research for this article the OSHA PEL for the general industry workplace for an 8 hour work day TWA of 2.5 mg(as F)/m³ was found as stated in the CFRGBR.[1] With a melting point of -125° F and a boiling point of 325°F the material is a liquid under normal conditions. One very important point is that when exposed to moisture, even from the humidity in the air, it will react to form Hydrogen Fluoride. As was pointed out a couple of months ago in our example of PEAC for the newsletter, Hydrogen Fluoride is very toxic and can create a very dangerous toxic vapor cloud. As long as the material is in a container it should provide few problems; once open to the surrounding environment it must be treated carefully as if it is Hydrogen Fluoride particularly if it has an opportunity to come in contact with large amounts of water.

Hazards and protection

Protection Wear appropriate protective gloves, clothing and goggles.

Respirators Wear positive pressure self-contained breathing apparatus (SCBA).

- **Small spills or leaks** Keep material out of water sources and sewers. Build dikes to contain flow as necessary. Use water spray to knock-down vapors. Do not use water on material itself. Neutralize spilled material with crushed limestone, soda ash, or lime.
- **Stability** Fumes in moist air; stable to 900°C.
- **Incompatibilities** Reacts exothermically with chemical bases (examples: amines, amides, and inorganic hydroxides). Reacts violently with water to generate hydrofluoric acid and sulfuric acid. Reacts with active metals, including such

structural metals as aluminum and iron, to release hydrogen, a flammable gas. Reacts with cyanide compounds to release gaseous hydrogen cyanide.

Hazardous Decomposition When heated to decomposition, they emit highly toxic fumes of fluorides and oxides of sulfur.

Fire related information

- **Fire fighting** Extinguish fire using agent suitable for type of surrounding fire. (Material itself does not burn or burns with difficulty.) Use water in flooding quantities as fog. Cool all affected containers with flooding quantities of water. Apply water from as far a distance as possible.
- **Fire potential** May burn but not ignite readily. May ignite combustibles (wood, paper, oil, clothing, etc.).
- **Hazards** Substance will react with water (some violently), releasing corrosive and/or toxic gases.
- **Combustion products**Toxic and irritating fumes of hydrogen fluoride and sulfuric acid may form in fires.

Health related information

Exposure effects

- **Ingestion** Epigastric pain, nausea, dysphagia, salivation, hematemesis, and diarrhea may be noted. These effects may be delayed for several hours following exposure. Gastrointestinal symptoms are noted when 3 to 5 mg/kg of fluoride are ingested.
- **Inhalation** Respirations are first stimulated then depressed. Death is usually from respiratory paralysis. Following inhalation, coughing and choking may be noted.
- **Skin** Urticaria and pruritus have been reported following exposure to fluoride.
- **Eyes** See Inhalation.

<u>First aid</u>

- **Ingestion** Seek medical assistance.
- **Inhalation** Remove victim to fresh air; if he is unconscious, give artificial respiration.
- **Skin** Flush with water until medical help arrives; soak burned area in strong Epsom salt solution; pay particular attention to area around fingernails.

Eyes Flush with water until medical help arrives.

One interesting thing we ran across when researching this article was a different symbol used for very corrosive acids. While it might be familiar to many of our reads, it was new to us and we thought we would share it with you, see Figure 1.



Figure 1 – Corrosive Symbol sometimes used with Fluorosulfonic Acid

A recent incident reported by the U.S. Chemical Safety and Hazard Investigation Board (CSB), occurred in Claymont, DE, at the General Chemical facility. Acid leaked from a rail car Tuesday July 2, 2002, at the facility, causing a white mist to linger in the area late into the evening. About 5:25 PM, workers were loading the rail car with fluorosulfonic acid when the car began leaking, said Jacob Morente, spokesman for the Claymont Fire Company. About 9,700 gallons of the chemical, used in making silicones, were in the tank when it began leaking, said Sam Waltz, a General Chemical spokesman. Some of the 170 firefighters at the scene sprayed the cloud with water in an attempt to disperse it, Morente said. He said they were spraying about 3,000 gallons per minute. The runoff was being contained and would be treated at the General Chemical facility. The cloud never left the General Chemical site, officials said.

From the report, its tough to say how much material was leaking but a good guess is that on a July day in Delaware, the white mist was probably Hydrogen Fluoride that was formed as the Fluorosulfonic Acid leaked from the railcar and reacted with the moisture in the air. If it didn't react with the moisture in the air then it surely reacted with the water spray provided by the firefighters. As long as the runoff was contained and treated on the premises there was probably no problem with this procedure. How well the water spray knocked down any Hydrogen Fluoride vapor cloud again would be based on the amount of Hydrogen Fluoride vapor created and it sounds like there was plenty of water spray to deal with even a substantial amount of vapor being produced.

In using the PEAC application we access information for the chemical by first locating Fluorosulfonic Acid in the database. We can either lookup the chemical by name or by UN# which was 1777. The following figures show the screens displayed for chemical properties, Figure 2 for the *PEAC-WMD for Windows* application and Figure 3-5 for the *PEAC-WMD for the Pocket PC* application.



Figure 2 – Selecting Fluorosulfonic Acid using UN#1777 Using the PEAC-WMD for Windows application



In addition to the **Chemical Properties** listed in the PEAC database, a user could check on the **Chemical Properties** for Hydrogen Fluoride. Additional information is available regarding how to prevent skin contact by checking the CPC listing, i.e., **Chemical Protective Clothing**. This is shown in Figure 6, and as with the Chemical Properties checking the CPC entries for Hydrogen Fluoride might also be useful. As shown, for Fluorosulfonic Acid only miscellaneous and suits are listed. The miscellaneous category is how the PEAC database dealt with the DuPont CPC fabrics that were used in many suits, e.g., DuPont Tychem products, but weren't manufactured as final products by DuPont. This has changed to some degree since DuPont has recent purchased Kappler, a manufacturer of CPC garments.

For those unfamiliar with the PEAC database and how CPC garments are displayed, there are two possible display screens for CPC garments. The **All Chemical Protective Clothing** displays <u>all</u> entries in the PEAC database for the specific chemical selected. The Available Chemical Protective Clothing selection is based on filtering the **All Chemical Protective Clothing** listing for only those manufacturers that the user has already indicated they have in their inventory. Without a great deal of explanation, there is a simple to use feature where the user indicates what manufacturers' products they have in their inventory so a "short list" can be provided rapidly to the user when on the scene.

Lookup By: UN Number										
.ookup: 1777 Fluorosulfonic Acid	All Chemical Protective Clothing									
777 Fluorosulfonic Acid 778 Hydrofluorosilicic Acid	Fluorosulfonic Acid									
778 Fluorosilicic Acid 779 Formic Acid 780 Fumaryl Chloride	GUIDE 137 Substances - Water-Reactive - Corrosive UN 1777									
781 Hexadecyltrichlorosilane 782 Hexafluorophosphoric Acid 783 Hexamethylenediamine solution	MISC Mfr: DU PONT TYCHEM 10.000									
784 Hexyltrichlorosilane 786 Hydrofluoric Acid and Sulfuric Acid Mixtures 787 Hydriodic Acid	Material: UNKNOWN Breakthrough: > 480 min									
788 Hydrobromic Acid 789 Hydrochloric Acid 790 Hydrofluoric Acid	MISC Mfr: DU PONT TYCHEM 9400 Material: UNKNOWN									
791 Hypochlorite Solution 792 Iodine Monochloride	Breakthrough: > 480 min									
793 Isopropyl Acid Phosphate 794 Lead Sulfate with more than 3% free acid 796 Nitrating Acid Mixture	MISC Mfr: DU PONT TYCHEM TK Material: UNKNOWN									
798 Nitrohydrochloric Acid 799 Nonyltrichlorosilane	Breakthrough: > 480 min									
800 Octadecyltrichlorosilane 801 Octyltrichlorosilane 802 Perchloric Acid with not more than 50% acid	SUIT Mfr: DU PONT TYVEK SARAN Materiat: SARANEX-23									
803 Phenolsulfonic Acid liquid 803 Hydroxybenzenesulfonic Acid 804 Phenyltrichlorosilane	-(Polyethylene/Polyvinylidene chloride) Breakthrough: > 360 min									

Figure 6 – Displaying the CPC entries in the PEAC database for Fluorosulfonic Acid

Another benefit of using the PEAC tool is access to development of an evacuation zone for those chemicals that produce a toxic vapor cloud. Fluorosulfonic Acid has a relatively low vapor pressure (2.5 mm Hg), so if spilled and no significant contact with water occurs, then an evacuation may not be required. If water does come in contact wit the chemical, then Hydrogen Fluoride will be formed and an evacuation may be in order. Even moisture in the air can react with Fluorosulfonic Acid to form Hydrogen Fluoride.

As seen at the top of the data display screens, there is a yellow icon displayed, this is the PEAC icon for notifying the user that a Protective Action Distance can be calculated. Clicking or tapping on the PAD icon will display a screen as shown in Figure 7. For those readers of recent newsletters and users of the PEAC tool this will appear different than what you typically see with the PEAC system. This is called the **Simplified**

Source screen or default when the PEAC database doesn't have sufficient data to use the PEAC dispersion model.



Figure 7 – The PEAC Simplified Source Screen

When the PEAC system doesn't have enough data to run the model, it reverts back to the US DOT Emergency Response Guidebook's "green pages" and the Protective Action Distances provided for Small vs. Large spills for either Daytime or Nighttime conditions. Since the PEAC tool always knows the current time and where you are located geographically, it only needs to know the relative size of the spill. If we select the Large Spill, to simulate the incident that occurred in Delaware, we see first a warning or notification screen as shown in Figure 8.

PEAC-WMD	×
The PAD assumes that the chemical has reacted with water to form Hy	drogen Fluoride.
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Figure 8 – Notification screen before the PAD screen is displayed

The notification screen is simply to let the user know that the following PAD displayed was created assuming that the chemical has reacted with water to form Hydrogen Fluoride. If only a portion of the chemical has reacted or in the case of the Delaware incident a water spray was used to mitigate or knock down any vapors, then this distance maybe overly conservative and a shorter distance may be more appropriate (see Figure 9).



Figure 9 – PAD using the distances from the US DOT ERG2000 "green pages"

The incident started at 5:30 PM on July 2nd. This would have been in the daytime and this is what is shown for the above PAD. As the incident progresses and daytime fades into nighttime the atmospheric conditions will change another PAD may be in order. If the user changes their internal clock to later in the evening so it was nighttime conditions, then for a Large Spill of Fluorosulfonic Acid a larger PAD area is recommended, see Figure 10. If you look in the "green pages" of the US DOT ERG2000 (excerpt from the ERG2000 shown in Figure 11) you can also see the distances that are displayed in these figures. The one difference is that the PEAC system displays distance less than a mile in yards and the ERG2000 provides distances in miles or kilometers.



Figure 10 - PAD using Nighttime Conditions

177	77 Fluorosulfonic acid (when spilled in water)	30 m	(100 ft)	0.2 km	(0.1 mi)	0.2 km	(0.1 mi)	60 m	(200 ft)	0.5 km	(0.3 mi)	1.4 km	(im e.0)
177	1777 Fluorosulphonicacid (when spilled in water)												



Portions of this discussion were adapted from the **University of Akron Chemical Database**located on the Internet at http://ull.chemistry.uakron.edu.

^[1] Code of Federal Regulations (U.S. Government Printing Office, Supt. of Documents, Washington, DC 20402) Volume(issue)/page/year: 29,1910.1000,1994