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House of Representatives
COMMONWEALTH OF PENNSYLVANIA
HARRISBURG

HOUSE DEMOCRATIC POLICY COMMITTEE HEARING

Topic: Air Quality and Public Safety Issues with Oil Refineries

University of Pennsylvania – Philadelphia, PA
April 21, 2011

AGENDA

10:00 a.m. Welcome and Opening Remarks

10:10 a.m. Mike Bukowski
General Manager
Sunoco Philadelphia Refinery

10:40 a.m. Panel #1:

- Jim Savage
  President
  United Steelworkers Local Union 10-1

- Diane Heminway
  Health and Safety Specialist
  United Steelworkers International Union Health & Safety Department

11:20 a.m. Panel #2:

- Barbara Rahke
  Director
  Philadelphia Project on Occupational Safety & Health

- Cathy Brady
  Community Member and Former Oil Worker

12:00 p.m. Closing Remarks

COMMONWEALTH OF PENNSYLVANIA
Pennsylvania Emergency Management Agency

Office of the Director 717.651.2007

April 19, 2011

The Honorable P. Michael Sturla
Pennsylvania House of Representatives
414 Main Capitol Building
P.O. Box 202096
Harrisburg, Pennsylvania 17120-2096

Dear Chairman Sturla:

I received your invitation for the Pennsylvania Emergency Management Agency's Office of Homeland Security to speak at the Pennsylvania House Democratic Policy Committee public hearing on April 21, 2011, on Air Quality and Public Safety Issues with Oil Refineries and their use of hydrofluoric acid. Unfortunately, the appropriate officials from our agency are not available to attend the hearing, so I am submitting this letter to the Committee to provide the agency's perspectives on this issue.

Three federal agencies have primary control and oversight of hazardous chemical usage in the United States, which would include the use of hydrofluoric acid: the Occupational Safety and Health Administration (OSHA), the Environmental Protection Agency (EPA), and the Department of Homeland Security (DHS).

Under the applicable state law, Act 165 of 1990, as amended, *Hazardous Material Emergency Planning and Response Act*, chemical facilities are required to submit hazardous chemical inventory reports, copies of which are also submitted to the county emergency management offices and local fire departments for emergency planning and response. I must state, however, that under the Protected Critical Infrastructure Information Regulation, the locations and quantities of this chemical is protected information. In addition, under Act 165, the Pennsylvania Emergency Management Agency (PEMA) does not have the statutory authority to determine which chemicals may or may not be used at facilities.

EPA regulations and Act 165 require that any facility maintaining an extremely hazardous substance at threshold planning quantity, which would include hydrofluoric acid at 500 pounds, must develop a comprehensive emergency response plan (ERP) with their county planner. The Philadelphia Office of Emergency Management has the information on hydrofluoric acid within Philadelphia.

Under Act 165, facilities also are required to immediately notify PEMA and the county Local Emergency Planning Committee of any accidental releases of hazardous substances in excess of established reportable quantities and to provide written reports on actions taken and any medical effects. In March 2009, there was a hydrofluoric acid release at the Sunoco refinery in South Philadelphia. The Pennsylvania Department of Labor and Industry indicated that hydrofluoric acid has additional applications in varied industries including the production of organofluorine compounds (such as Teflon, fluoropolymers, fluorocarbons) and refrigerants (such as Freon). We understand that industry is aware of the potential hazards of hydrofluoric acid, and they are researching safer alternatives. We encourage and support the use of safer alternatives; however, alternatives have yet to be identified for certain chemical processes and/or applications.

If available, the safest alternatives should always be considered or used in any manufacturing or industrial processes. There is nothing more important to PEMA than the safety and well-being of our commonwealth residents. In addition, please know that PEMA's Office of Homeland Security regularly reviews critical infrastructure in the Commonwealth to help ensure their protection.

Should you have any questions, please feel free to contact me.

Sincerely,

Glenn M. Cannon

Glenn M. Cannon, Esq.
Director, PA Emergency Management Agency
Pennsylvania Homeland Security Advisor

Opening Comments - Hearing on Refinery Safety and HF

Introduction and Background:
Good Morning, my name is Mike Bukowski, and I am the General Manager of Sunoco's Philadelphia Refinery. The Philadelphia refinery occupies approximately 1400 acres in South and Southwest Philadelphia, and has the capacity to refine approximately 340,000 barrels of crude per day. We have about 850 full time employees and at any given time we have an average of 175 contractors on site. On behalf of Sunoco, I would like to thank the Committee for this opportunity to address you regarding refinery safety and the use of modified Hydrofluoric Catalyst at our refinery.

HF has been used in the US for over 70 years by many industries to manufacture a wide variety of products, including refrigerants, electronics, gasoline, detergents and medications. It has been in continuous use at our Philadelphia refinery since the 1970's. It is an important catalyst used to increase the octane in gasoline and make it burn cleaner, with fewer emissions.

We believe that our record speaks for itself when it comes to the safe use of modified HF at our refinery. In forty years of use, we have never had an incident which has caused injury to a member of the public. We treat this chemical with the care and respect it deserves, and we have the equipment, systems, people and processes in place to use it safely and appropriately.

EPA Report:
In the early 1990's, the U.S. Congress required the Environmental Protection Agency to review the safety of HF use in industry. The EPA issued a report containing its findings, which is available online, and it found that the use of HF poses hazards comparable to a variety of chemicals in common use in industry, and that given the appropriate equipment, materials, safeguards and processes, was safe and appropriate for continued use.

Philadelphia Refinery and the adoption of modified HF:
In 2006, in response to concerns expressed by our neighbors in the community and from environmental organizations, Sunoco commissioned an independent, third-party risk analysis which included all risks relating to HF and the available alternatives; risks relating to storage, operations, regeneration and transportation; and risks to workers as well as to the public.

When all risks were taken into consideration, the risk analysis showed that use of a modified form of HF, coupled with additional safeguards which I will discuss, would give the community a level of protection equivalent to or better than the available alternatives.

As a result of the recommendations contained in the risk analysis, we decided to switch to modified HF and made significant upgrades to the unit. To date, Sunoco has spent approximately $200MM to ensure the safe use of modified HF at our Philadelphia refinery. The recently completed installation of the ReVap modified HF system alone was at a cost of over $125MM. Only 6 percent of the refineries in the U.S. have installed this modified HF capability and Sunoco is proud of our leadership position when it comes to the adoption of modified HF.

Other organizations who have looked into this complex issue have reached similar conclusions. In California, refineries have been required to switch to the use of modified HF, and here in Pennsylvania, another large local refinery has announced that it will switch to modified HF in the near future.

The main safety features of our modified HF unit include:

1. A specialized inspection program for all equipment;
2. A preventive and predictive maintenance program;
3. The use of special materials for equipment, pumps and piping;
4. An inventory control procedure to keep the amount of inventory as low as possible;
5. A leak detection system, including point-source detectors, HF sensitive paint and video monitoring;
6. A system that rapidly transfers modified HF from the equipment to a dedicated storage vessel in the event of a leak;
7. A passive mitigation system that minimizes the amount of modified HF that can be involved in a leak;
8. An active water mitigation system to remove modified HF from a release and dilute any vapor;
9. A fixed barrier installed around the de-inventory vessel to minimize vapor formation in the event of a leak;
10. Remotely operated emergency isolation valves;
11. The use of a special additive called ReVap, which reduces the formation of airborne vapor in the event of a release;
12. An on-site emergency response and fire-fighting capability specifically designed for handling a release; and
13. A community warning system consisting of 11 sirens located in areas near the refinery for purposes of communicating the need to shelter in place or evacuate in the unlikely event of an emergency.

Sunoco, community and government agencies:
Sunoco works closely with our community partners and governmental agencies including our Community Advisory Panel, Homeland Security, the Philadelphia Police and Fire Departments and the Office of Emergency Management to ensure that our response to any incident would be well-coordinated and effective. We participate in Ready Notify PA, an electronic community alert system run by the Office of Emergency Management, and just last week, Sunoco attended a drill involving HF that was conducted by the Homeland Security Division of the Philadelphia Police Department.

Conclusion:
Like most industrial chemicals, HF is not without risk; however, Sunoco has a great deal of experience in the safe use of HF, we fully understand its properties, and we treat it with the care and respect it deserves. In the forty years we have used HF at our refinery, there has not been a single documented incident of off-site impact or injury to a member of the public.

Sunoco takes safety, energy efficiency and environmental responsibility seriously. We recently received the 2011 EPA Energy Star Sustained Excellence Award. We are the first Energy Star partner from petroleum and petrochemical companies to be recognized for energy conservation efforts company-wide. In addition, the environmental sustainability organization Greenopia, which ranks oil companies on their environmental progressiveness, emissions, transparency and efficiency, this year named Sunoco as the overall greenest choice among major oil companies.

Thanks again for inviting us to speak with you today, as the safety of our community and employees, and the protection of our natural environment is of the utmost importance to all of us at Sunoco. And now I will be happy to answer any questions you might have.

UNITED STEELWORKERS

USW

UNITY AND STRENGTH FOR WORKERS

Testimony of Diane Heminway

United Steel, Paper and Forestry, Rubber, Manufacturing, Energy, Allied Industrial and Service Workers International Union (USW)

Public Hearing before the House Democratic Policy Committee

Chemical Safety at Philadelphia Refineries

Philadelphia, PA

April, 21, 2011

Good morning. My name is Diane Heminway and I greatly appreciate the opportunity to speak to you today on behalf of United Steelworkers. As the largest industrial labor union in North America, we represent a total of 1.2 million active and retired members in the United States, Canada and the Caribbean. More than 125,000 of these members work in some 800 chemical industry work-places, including approximately 30,000 who work in oil refineries.

We are pleased that this hearing is being held to take a hard look at refinery safety, particularly those refineries using Hydrofluoric acid/Hydrogen fluoride (HF) in the alkylation process. In August 2009, United Steelworkers called for an industry-wide phase-out of HF because we believe that it poses an unacceptable risk to workers and the communities near the nation's 51 refineries that use it.

OSHA Recognizes HF Risks

To put the risks of HF into perspective, consider that there are over 47 million[i] chemicals commercially available with about 500,000 of those covered under OSHA's Right to Know regulation (Hazard Communication standard 29 CFR §1910.1200).

Of this vast universe of hazardous chemicals, OSHA categorizes **137 as being "highly hazardous"** and therefore subject to more stringent regulation under the Process Safety Management (PSM) standard (29 CFR §1910.119). I will not take the time to elaborate on OSHA's National Emphasis Program, which focused on process safety in refineries, but I have included an attachment to my written testimony, that describes the tens of thousands of PSM violations OSHA found at just 14 refineries during the first year of their PSM inspection program.

EPA Recognizes HF Risks

EPA also acknowledges the serious risks posed by HF. It was declared one of the 360 Extremely Hazardous Substances under the Emergency Planning and Community Right to Know Act of 1986. Industries who have as little as 100 pounds of HF stored on site must provide detailed annual inventory reports to the Local Emergency Planning Committee to enable them to plan for a community emergency and/or to alert emergency responders who may have to address a fire or other incident at the facility.

HF is also recognized for its potential to cause a catastrophic health risk to the public in the event of an accidental release. There are only 77 toxic chemicals regulated under EPA's Risk Management Program: HF is one of them. When released to the environment, HF can form a heavy, aerosol vapor cloud that can travel for miles at lethal concentrations – a risk that can result in catastrophic consequences. Acknowledging this fact, many, if not all of the refineries storing HF in quantities subject to reporting requirements under 112 (r) of the Clean Air Act (1,000 pounds), report that HF is the toxic chemical that would be involved in their "worst case scenario release." ConocoPhillips Trainer Refinery reported (June 2009) that a release of 220,000 pounds of HF from their facility could have serious offsite consequences for up to 19 miles, impacting up to 2,400,00 people, including, schools, hospitals, prisons, as well as parks, wildlife sanctuaries and recreational areas.

Sunoco's Philadelphia Refinery reported (Sept 2010) that a release of 279,501 pounds of HF could have serious offsite impacts for over 8 miles, affecting up to 1,308,395 people, including schools, hospitals, prisons and the same types of wildlife and recreational areas as would be impacted by a release from the Trainer Refinery.

Hydrofluoric acid is unique. It is so potent that even weak concentrations can cause serious damage to the body, even though pain may be not be felt until hours after the exposure. Pain associated with exposure to solutions of HF (1-30%) may be delayed for 1-24 hours. If HF is not rapidly neutralized, tissue destruction may continue for days and result in limb loss or death. HF differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers, including bone. HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. (Please note that I have provided 2 attachments, each containing rather graphic images of the damage HF can do--even when a small amount seeps through a hole in a worker's glove.)

We believe that the general public does not comprehend the extent of the risks posed by HF, but we consider it to be one of the most dangerous chemicals being used on a commercial scale as even small quantities can be lethal. For example, in January of 2007, despite medical treatment, a 37 year old USW member died within 6 and a half hours after a small amount of Hydrofluoric acid discharged onto his face during a maintenance procedure. (http://www.msha.gov/FATALS/2007/FTL07m01.asp) While skin exposure can result in death (e.g.: cardiac arrest has occurred after skin exposure affecting 2.5% of the body),[ii] exposure from inhalation of hydrogen fluoride is a well-recognized hazard, one that is not limited to occupational settings.

On July 19, 2009, a 34 year old USW member was critically injured in a fire and HF release at the CITGO refinery in Corpus Christi, TX. Company officials initially reported that approximately 4,000 pounds of HF was released, but according to news accounts, CITGO later amended their report, estimating that approximately 30 pounds of HF was released. However, according to the US Chemical Safety Board's subsequent investigation, an estimated 42,000 pounds of HF was released from equipment and at least 4,000 pounds of HF was "likely" released to the atmosphere. In the weeks following the incident, nearby residents complained not only of health effects, but also of a lack of response from CITGO and health authorities. Reports indicate that most of the HF released to the environment drifted toward a non-residential area, thereby averting what might have been an even more devastating incident. (For more information or to see a dramatic surveillance video of this release, see link on right in this Chemical and Engineering News article http://pubs.acs.org/cen/news/87/i50/8750notw6.html)

The truth is, we have been nothing short of lucky that a large release of HF has not resulted in an event of catastrophic proportion. The fact is, systems do fail, especially those that do not receive preventative maintenance, which is a common complaint of refinery workers. And people do make mistakes. These realities need to be taken into account. So one can only ask why it is that refiners would choose to risk the lives of thousands of workers and millions of community residents when safe alternatives to HF exist for this application. This is precisely the reason that USW and others concerned with safety, rely on the "Hierarchy of Controls" to address workplace hazards. (See attachment for a clear explanation of this concept.)

Presently, we are aware of at least two solid acid catalysts **licensed for commercial use**: AlkyClean (developed by ABB Lummus, Albermarle and Neste Oil) [iii] and ExSact (developed by Exelus).[iv] AlkyClean was used in a small, 2 year demonstration project in Porvoo, Finland. Exelus ran, and may still be running, a small scale continuous operation and is poised to set up their process on a commercial scale.

In fact, the Dept of Energy gave Exelus a million dollars to develop their solid acid catalyst…so why are we not seeing a push from DOE to get this safer alternative into refineries? And why are we not hearing more about the solid catalyst being used "secretly" at the Chevron refinery near Salt Lake City?

It's clear that refinery owners are not going to switch to safer alternatives because it's the right thing to do. They are all well aware of the technology, but at present do not have enough incentive to make the change. Perhaps creative approaches are needed to push the industry into making their operations safer.

Most refineries are out of compliance with not only workplace health and safety laws, but also with environmental laws. A novel approach to make refineries safer is to enforce the laws, hold violators accountable, and compel them through settlement agreements to engage in a Supplemental Environmental Project (SEP); whereby in lieu of a fine, they would be required to initiate a pilot-scale project utilizing solid acid catalyst in place of HF. To ensure that the process would be correctly and efficiently operated, monitoring and third party oversight should be required. We are told that a slip-stream pilot project could be accomplished for a reasonable cost, possibly under $5 million.

Until refinery owners are forced to make the change, they will persist in placing profits over community responsibility and continue to regard workers as disposable assets.

Nearly every week, one of our members is killed on the job, and at least one more is seriously injured. We are appalled by the tragedies endured by workers and their families whose lives are forever changed while trying to make a living. We acknowledge that many workplaces are dangerous--but the use of HF in refineries poses a senseless and unacceptable risk….a risk that does not need to exist at all.

We applaud you for holding this hearing as a first step toward awareness that must translate to change. USW knows that making refineries safer will ultimately result in lasting job security. Thank you.

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[i] Chemical Abstract Service http://www.cas.org/cgi-bin/cas/regreport.pl
[ii] IPCS INCHEM, "Hydrogen Fluoride" http://www.inchem.org/documents/pims/chemical/hydfluor.htm-
[iii] http://www.albemarle.com/Products_and_services/Catalysts/Alternative_Fuel_Technologies/Alkylation/_Technical_papers/AlkyClean_Alkylation_Process_New_Technology_Eliminates_Liquid_Acids.pdf
[iv] Exelus, "ExSact solid acid alkylation process for gasoline production" www.exulusinc.com

UNITED STEELWORKERS
USW News
UNITY AND STRENGTH FOR WORKERS

FOR IMMEDIATE RELEASE
August 31, 2009

Contact: Lynne Baker, USW Communications, (o) 615-831-6782, (c) 615-828-6169

United Steelworkers Union Calls for Industry-wide Phase-out of Hydrogen Fluoride in Oil Refinery Alkylation Units

Pittsburgh—The United Steelworkers (USW) announced today that it is calling for the nationwide phase-out of hydrogen fluoride alkylation units.

"Hydrogen fluoride is such a deadly component, and there are new and safer technologies available," said USW Vice President Gary Beevers, who is in charge of the union's oil sector.

"It's a matter of health and safety to us. It's a matter of money to the industry. We think they should change to a safer alternative," Beevers added.

Hydrogen fluoride is an acid used as a catalyst in the alkylation unit to make high-octane petroleum and is deadly in large amounts. The chemical turns into hydrofluoric acid when it is in contact with moisture and becomes an extremely corrosive liquid and contact poison that burns skin, tissue and eyes. It rapidly penetrates tissues and can cause systemic toxicity, damaging the heart and lungs and causing death. Under the right conditions, a large release could form a lethal plume of acid vapors that could extend for miles downwind, putting thousands of people at risk.

One-third of refineries use hydrogen fluoride. The other two-thirds use sulfuric acid as a catalyst, which also can burn skin, tissue and lungs but is somewhat less toxic. Most important, sulfuric acid has much less potential to form a deadly vapor plume extending outside the refinery.

Solid-state catalysts offer promise as an even safer alternative but are currently at the pilot plant stage and have not been used commercially yet for the alkylation process.

The USW will be discussing with the industry other alternatives to the use of hydrogen fluoride and if necessary will work through the regulatory agencies and Congress to get the issue resolved.

"We intend to pursue every avenue till we have safer units that don't endanger our refinery workers or the communities surrounding these facilities," Beevers said.

There have been three reported hydrogen fluoride release incidents in the past five months. At the USW-represented Sunoco refinery in Philadelphia, 10 contractors were exposed to hydrogen fluoride and sent to the hospital after the chemical's release from the alkylation unit on March 11. On July 19 hydrogen fluoride was released during a fire at Citgo's east refinery in Corpus Christi, Texas. One USW-represented employee remains in an intensive care unit as a result of thermal burns from the fire. At the non-union ExxonMobil refinery in Joliet, Ill., hydrogen fluoride was released Aug. 6 from the alkylation unit and resulted in one operator suffering from hydrogen fluoride-related chemical burns.

The USW plans to work with local community environmental groups to end the use of hydrogen fluoride. A mid-September meeting between the local and international union, the Sierra Club and Citizens for Environmental Justice in Corpus Christi is planned.

In an Aug. 13 final report to the Texas Commission on Environmental Quality (TCEQ), Citgo estimated that nearly 4,000 pounds of hydrogen fluoride had been released. According to Citizens for Environmental Justice, the TCEQ records show that this quantity was the largest hydrogen fluoride release in 20 years. The group said the company did not tell citizens the dangerous nature of the fire or that potentially deadly gas had escaped. Reportedly there were citizens who experienced adverse health effects.

According to Dr. Neil Carman, chemist and Clean Air Program director for the Sierra Club, Citgo has failed to report fugitive releases of hydrogen fluoride to the EPA for the last 21 years, except for serious fires and accidents, and may be "fudging as badly as it did" with benzene tank releases it was criminally convicted of under the federal Clean Air Act.

This points to the USW's contention that refineries must report all releases to the public. The desire for transparency is one of the main areas of disagreement the union has with the American Petroleum Institute.

The USW is the largest industrial union in North America and has 850,000 members in the U.S., Canada, and the Caribbean. It represents workers employed in metals, rubber, chemicals, paper, oil refining, atomic energy and the service sector.

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Hydrofluoric Acid

CAS Number: 7664-39-3

> ***"Danger! May be fatal if inhaled, absorbed through the skin or swallowed. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for any exposure to HF."*** ***Fisher MSDS***

Hydrofluoric Acid, also known as Hydrogen Fluoride (HF), is used as a catalyst by some oil refineries to make high-octane gasoline. HF is a potent, corrosive poison.

<u>*Inhalation*</u> of its vapors can cause severe nose and throat irritation and serious lung damage.[i] Delayed reactions up to and including fatal pulmonary edema (flooding of the lungs with body fluids) may not be apparent for hours after the initial exposure.[ii] At concentrations of 30 parts per million (ppm) Hydrofluoric Acid is immediately dangerous to life and health [iii] and airborne concentrations above 50 ppm, even after a brief exposure, may be fatal.[iv] Inhaling HF may also damage the liver and kidneys.[v]

<u>*Skin contact*</u> with HF, or solutions containing more than 30% hydrogen fluoride, produces immediate pain. Reactions to more dilute solutions may be delayed for many hours. The accompanying pain is excruciating and persistent and chemical burns from HF are typically very slow to heal. [vi]

- **HF is corrosive and readily penetrates skin, allowing it to destroy soft tissues and decalcify bone. [vii]**
- **Exposure of the eyes may result in permanent eye damage or blindness.[viii]**
- **Exposure to highly concentrated solutions of HF can cause acute hypocalcemia (low level of calcium in the blood), followed by cardiac arrest and death. It can be fatal with as little as 2% body exposure (about the size of the sole of the foot). [ix]**
- **"Absorption of substantial amounts of hydrogen fluoride by any route may be fatal."[x]**

<u>*Long Term Effects*</u> can occur some time after exposure, can last for months or years [xi] and may include:

- **Respiratory irritation, bronchitis with coughing, phlegm, shortness of breath.[xii]**
- **Fluorosis, a syndrome characterized by weight loss, brittle bones, anemia, general ill health.[xiii]**
- **Possible teratogen (can cause birth defects by damaging the fetus). Occupational studies of women exposed to fluoride identified increased rates of menstrual irregularities. Animal studies have also found that fluoride impairs reproduction and increases the rates of fetal bone and teeth malformation.[xiv]**
- **Hydrogen fluoride has also produced reproductive, teratogenic and mutagenic effects in experimental animals.[xv]**

UNITED STEELWORKERS

USW

UNITY AND STRENGTH FOR WORKERS

Hydrofluoric Acid (HF) releases can be dangerous beyond the refinery fence line

Due to the physical nature of HF (boiling point is 67° F), a release of it in an environment not substantially cooler than its boiling point is likely to form a vapor cloud. Unfortunately incidences involving HF are all too common. Recent examples include:

- **March 11, 2009 – 13 workers were sent to the hospital after a 22 pound release of hydrofluoric acid at the Sunoco refinery in South Philadelphia, Pa.[xvi]**
- **March 22, 2009 - 5000 residents were evacuated for over 12 hours after a truck carrying 33,000 lbs. of hydrofluoric acid overturned in the small town of Wind Gap, Pa., causing a small spill. [xvii]**
- **July 19, 2009 – a 34 year-old worker was critically injured during a fire and release of hydrofluoric acid at the CITGO refinery in Corpus Christi, Texas.[xviii]**
- **August 6, 2009 – 2 workers were injured, one critically, during a leak of propane and hydrofluoric acid at the Exxon Mobil's refinery in Joliet, Ill.[xix]**

While some 200,000 chemicals are now commonly used in commerce,[xx] the dangers posed by HF are well recognized:

- **HF is one of 77 toxic chemicals covered under the EPA's Risk Management Program. [xxi]**
- **HF is one of 137 "highly hazardous chemicals" covered under OSHA's Process Safety Management Program. [xxii]**
- **HF is one of approximately 360 "Extremely Hazardous Substances" covered under Emergency Planning and Community Right-To-Know Act, Section 302. [xxiii]**
- **HF is one of fewer than 200 Hazardous Air Pollutants covered under the Clean Air Act. [xxiv]**
- **The legal workplace exposure limit (OSHA PEL) is 3 ppm averaged over 8 hours.[xxv]**
- **The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) is 0.5 ppm (averaged over 10 hour work shift) and 2 ppm not to be exceeded at any time during the work shift [xxvi]**

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[i] Massachusetts Toxics Use Reduction Institute, Chemical Fact Sheet on Hydrofluoric Acid
[ii] Environment, Health and Safety Information for the Berkeley Campus Fact Sheet on Hydrofluoric Acid 6/19/08 **http://www.ehs.berkeley.edu/pubs/factsheets/40hf.pdf**
[iii] Centers for Disease Control, National Institute of Occupational Health, NIOSH Pocket Guide to Chemical Hazards http://www.cdc.gov/niosh/npg/npgd0334.html
[iv] Environment, Health and Safety Information for the Berkeley Campus Fact Sheet on Hydrofluoric Acid 6/19/08 **http://www.ehs.berkeley.edu/pubs/factsheets/40hf.pdf**
[v] Massachusetts Toxics Use Reduction Institute, Massachusetts Chemical Fact Sheet on Hydrofluoric Acid
[vi] ibid
[vii] Environment, Health and Safety Information for the Berkeley Campus Fact Sheet on Hydrofluoric Acid 6/19/08 **http://www.ehs.berkeley.edu/pubs/factsheets/40hf.pdf**
[viii] ibid
[ix] Indiana University Chemical Fact Sheet on Hydrofluoric Acid www.ehs.Indiana.edu
[x] ATSDR, "Hydrogen Fluoride."
[xi] NJ Dept of Health *Right to Know Hazardous Substance Fact Sheet on Hydrogen Fluoride,* April 2009
[xii] ibid
[xiii] Environment, Health and Safety Information for the Berkeley Campus Fact Sheet on Hydrofluoric Acid 6/19/08 **http://www.ehs.berkeley.edu/pubs/factsheets/40hf.pdf**
[xiv] Indiana University Chemical Fact Sheet on Hydrofluoric Acid www.ehs.Indiana.edu
[xv] US Dept of Labor, OSHA, Occupational Safety and Health Guideline for Hydrogen Fluoride www.osha.gov
[xvi] Andrew Maykuth, "Deadly acid poses a safety issue for Sunoco." *Philadelphia Inquirer*. Sept. 23, 2009. http://www.philly.com/philly/business/60551327.html Sept. 23, 2009.
[xvii] Timesleader.com, "Hazardous material prompts Pa. evacuation order." Mar 23, 2009. http://www.timesleader.com/news/ap?articleID=1870287 Oct. 9, 2009.
[xviii] Denise Malan, "Citgo defends its plan to restart fire-damaged unit." Caller.com, Corpus Christie, Texas. Oct 2, 2009. www.caller.com, Oct. 5, 2009.
[xix] Nick Snow, "HF release at Joliet refinery investigated." *Oil & Gas Journal.* Aug. 11, 2009. www.ogj.com Oct 9, 2009.
[xx] Chemical Abstract Service http://www.cas.org/cgi-bin/cas/regreport.pl
[xxi] USEPA List of Lists Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-To-Know Act (EPCRA) and Section 112 ® of the Clean Air Act http://www.epa.gov/osweroe1/docs/chem/title3_Oct_2006.pdf#lol
[xxii] US DOL, OSHA, List of Highly Hazardous Chemicals, Toxics and Reactives 29CFR 1910.119 Appendix A http://www.osha.gov
[xxiii] USEPA List of Lists Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-To-Know Act (EPCRA) and Section 112 ® of the Clean Air Act http://www.epa.gov/osweroe1/docs/chem/title3_Oct_2006.pdf#lol
[xxiv] USEPA The Clean Air Act Amendments of 1990 List of Hazardous Air Pollutants http://www.epa.gov/ttn/atw/orig189.html
[xxv] NJ Dept of Health *Right to Know Hazardous Substance Fact Sheet on Hydrogen Fluoride.* April 2009
[xxvi] ibid.

Occupational Safety & Health Reporter™

"The state of process management is frankly just horrible," Fairfax said.

Occupational Safety & Health Reporter: All Issues > 2009 > 08/27/2009 > News > Enforcement: Process Safety Violations at Refineries 'Depressingly' High, OSHA Official Says

Enforcement

Process Safety Violations at Refineries 'Depressingly' High, OSHA Official Says

SAN ANTONIO—The Occupational Safety and Health Administration has found an alarmingly high rate of worker safety violations at petroleum refineries, particularly those that could cause explosions and fires, an agency official said Aug. 25.

"The refinery emphasis program is probably the most, from an enforcement point of view, successful program we've ever, ever done at the agency," Richard Fairfax, director of enforcement at OSHA, said during the annual conference of the Voluntary Protection Program Participants' Association.

"And it's probably also the most depressing program we've ever done," Fairfax said.

"We were pretty shocked and dismayed by what we found," he said.

At the end of the first year of OSHA's national emphasis program for petroleum refineries, Fairfax said, inspections of 14 refineries found 1,517 violations, including 1,489 for process safety management.

"The state of process management is frankly just horrible," Fairfax said.

Process safety is a mixture of engineering and management skills focused on preventing catastrophic incidents, particularly explosions, fires, and toxic releases. Process safety management refers both to an OSHA standard and to general management systems in place to address major accident hazards.

Between 1992, when OSHA issued its process safety management standard, and 2005, there were 138 fatalities and 553 injuries in facilities covered by the standard, Fairfax said.

Explosion at BP Refinery Led to Program

After an explosion at a BP facility in Texas City, Texas, in 2005, OSHA launched a two-year emphasis program for petroleum refineries. Since the start of the program in June 2007, the agency has opened inspections at 65 refineries, Fairfax said.

OSHA has issued citations to 48 employers. The remainder of the 65 inspections are ongoing.

Because the agency could not inspect all petroleum refineries in the United States in two years, it extended the program for Region 6, which has the most refineries in the United States, until the end of fiscal year 2011.

OSHA also extended until the end of 2009 the program in Region 8, which has the most isolated refineries, Fairfax said.

OSHA compliance officers evaluate process safety management by looking at 95 inspection priority items taken from a list of 400 inspection items in the process safety management standard. In addition, the compliance officers ask an additional eight to 15 "secret" questions from the list of 400, he said.

Whereas a "typical" OSHA inspection takes about 23 hours to 24 hours to complete, an inspection at a refinery takes 2,000 or more hours, he said. Depending on the size of the refinery, an inspection can take from four weeks to six months.

Fairfax said most refineries inspected so far "have very good paper programs, but when we step out of the facility," implementation "breaks down."

An Average of 17.4 Violations at Each Refinery

On average, each petroleum refinery inspected has been cited for 17.4 violations. Fairfax said "normal" inspections at other facilities would result in a average of 2.8 to three violations.

The average proposed penalty for a refinery inspection is $98,300, he said.

The highest number of violations are for process safety management, mechanical integrity, operating procedures, and process hazard management, Fairfax said. He said most process safety violations are for equipment deficiencies.

About 20 percent of refineries under federal jurisdiction participate in OSHA's Voluntary Protection Program and have so far been exempt from programmed inspections, although not unprogrammed ones, Fairfax said.

Given the high rate of violations found at refineries, Jordan Barab, acting OSHA administrator, is looking into whether refineries in the voluntary program should be inspected as well, according to Fairfax.

"It's very frustrating—we've laid it out and told everyone what we're going to do" but "we see the same [violations] over and over," Fairfax said.

Based on its findings to date, OSHA recently sent a 25- or 30-page letter to all petroleum refineries, listing all the violations it has found, he said.

Inspections at Chemical Facilities

At the end of July, OSHA began a pilot program to investigate process safety management at chemical facilities, since they pose a potentially large risk. Fairfax said OSHA is expecting to see a high rate of noncompliance at these facilities as well.

Because OSHA is devoting so many resources to the petroleum refinery program, inspections at chemical facilities are limited to process safety issues and are scaled down for now, he said.

Instead, compliance officers are asking 10 to 15 questions at each facility, which the employers do not know in advance, he said. OSHA is concentrating its efforts at chemical plants, wastewater treatment facilities, ammonia refrigeration sites, and chemical tank storage areas, Fairfax said.

Using a large list of facilities it has compiled, OSHA will conduct random programmed inspections in Regions 1, 7, and 10 and unprogrammed inspections in the other regions, he said.

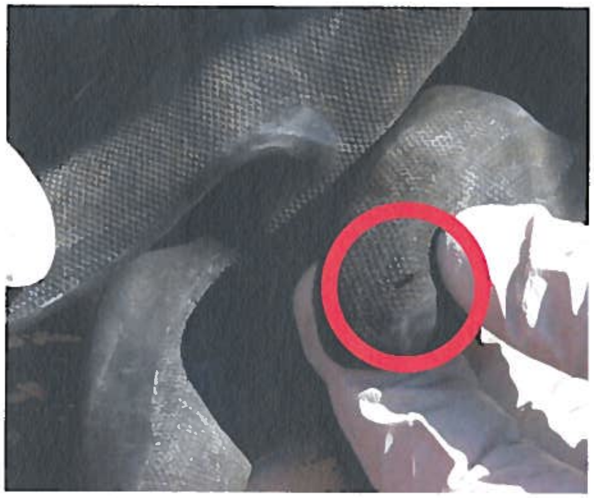
Fairfax OSHA will reassess the chemical plant program after one year of inspections.

By Patricia Ware

OSHA's directive for its Petroleum Refinery Process Safety Management National Emphasis Program is available at http://osha.gov/OshDoc/Directive_pdf/CPL_03-00-010.pdf.

OSHA's directive for its PSM Covered Chemical Facilities National Emphasis Program is available at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=DIRECTIVES&p_id=4008.

Source: ConocoPhillips Presentation on the Need to Test Gloves, 03/10/09



Small hole (highlighted in red) leads to serious injury from HF exposure

Effected area 1 day after hydrogen fluoride exposure

Effected area 3 days after exposure to hydrogen fluoride

Effected area 5 days after exposure to hydrogen fluoride

Effected area 6 days after exposure to hydrogen fluoride

Effected area 8 days after exposure to hydrogen fluoride

EMSWORLD

Excerpts from EMS World Article Originally Posted Thursday, April 29, 2010

Hydrofluoric Acid: What EMS providers need to know about this little-known acid

By Bradley Denney, RN/MICT

Incidents involving hydrogen fluoride, or hydrofluoric acid, are not common, but the consequences of exposure to this compound by any means can be devastating... I became interested in HF while working in an oil refinery... As a paramedic, I found the effects of HF on the human body fascinating. I learned what I could about it and began teaching HF safety to my coworkers.

Then, in 2001, I was involved in an HF incident in which I was seriously exposed. I had been sprayed with anhydrous HF at approximately 150 pounds of pressure when a ¾" pipe broke at an ell as I was preparing to remove a plug. The HF had eaten the threads inside the ell and the weight of my pipe wrench caused the damaged pipe to give way, spraying both my legs just below my groin, and my right forearm. That exposure began a battle for my life that continues today.

Luckily, our local EMS and emergency facility had been trained on the dangers of this acid and proper treatment. Many EMS and ER personnel have probably never heard of this dangerous compound, but all emergency services, fire or law enforcement personnel who operate near and may be called to respond to any facility that uses or manufactures a form of HF should receive yearly training on treatment for HF exposure...

Note the flame pattern on my left leg caused by the splatter from acid hitting my right leg.

THE DANGERS OF HYDROFLUORIC ACID

Although considered a weak acid, HF is one of the most dangerous inorganic acids known. Burns of as little as 1% body surface area (BSA), or approximately 25 sq in (about the size of the palm of your hand), have been known to be fatal due to the acid's unique properties.

HF penetrates tissue more quickly than typical acids. Because of this ability, systemic toxicity can occur by dermal, ocular, inhalation and oral routes. When human tissue is exposed to concentrated HF, the molecules disassociate into individual hydrogen and fluoride ions. The hydrogen ion burns like any other acid. The fluoride ion quickly penetrates dermal and muscle tissue and reacts with the calcium and magnesium found within the body, rendering these ions useless. Major organs or systems that are especially vulnerable to damage are the heart, liver, kidneys and nerves. Exposures of 6%-8% BSA burns of concentrations above 50% HF almost always prove fatal within hours.

Right leg showing burns (white is calcium gluconate).

At lower concentrations, death can still occur if definitive treatment is not sought quickly. HF interferes with nerve function, so burns from lower concentrations may not be initially painful. Accidental exposures can go unnoticed for hours or even days, delaying treatment and increasing the extent and seriousness of the injury...

After I was burned, the HF acid penetrated the Nomex coveralls I was wearing under my coat. The fluoride immediately penetrated the skin and bound to the calcium and magnesium in my blood and body tissues, which caused severe heart arrhythmias about 1 hour post-burn.

I was flown by helicopter to a burn center at Hillcrest Hospital in Tulsa, Oklahoma. There, despite the fact that I had at least 16% BSA, the burn center doctors and cardiologist refused to let me die. They called all over the world, looking for help from HF specialists and were told, "Make him comfortable, let his family say goodbye, and let him go." Thank God, they refused and kept working on me... By the grace of God, a very dedicated nurse, and those stubborn doctors, I am still here...

TREATMENT OF HF BURNS

Calcium gluconate offers another source of calcium, slowing or stopping the HF's attack on the body's own calcium and magnesium stores....

Calcium gluconate is rarely carried by EMS, but should be available with yearly continuing education to anyone who may respond to an incident involving HF. Most hospital emergency rooms that are located near facilities that use or manufacture hydrofluoric acid have in-service training on HF and recognize the importance of having calcium gluconate readily available. HF manufacturers often offer training to police, fire, EMS and local hospitals that might respond to incidents involving HF...

My legs after debridement. I had skin grafts from my back and left thigh three days later.

The long-term effects of a significant HF burn are still unknown. I am an unwitting guinea pig of sorts. So far, I have experienced end-stage kidney failure, osteoporosis, peripheral neuropathy, peripheral edema due to a compromised lymphatic system, a compromised immune system and other health problems. This doesn't even begin to account for the severe pain and disfigurement I continue to have. The best way to avoid this trouble is to be prepared and follow a well-planned and practiced response.

About the Author: Bradley Denney, RN/MICT, has been involved with the fire service for over 38 years and EMS for over 36 years. He has worked as a frontline firefighter and EMT to assistant fire chief and hazardous materials technician and paramedic. In 2007, he became a registered nurse. He has taught hazmat courses for fire, law enforcement and EMS, and taught HF-specific classes at the Kansas HazMat/WMD Symposium in 2006 and 2007. He also has over 15 years of experience working with HF acid in the oil refining industry. He was instrumental in initiating first aid protocols in the refinery emergency facility setting that ultimately would save his life.

Bibliography and full article available at www.emsworld.com.

My legs after healing. Note the reddened area on left thigh, skin used for graft.

Hierarchy of Health and Safety Controls

Most Effective → **Least Effective**

1) Elimination or Substitution	• substitute for hazardous material • reduce speed, force, amperage • reduce pressure, temperature • change process to eliminate noise • perform task at ground level • automated material handling
2) Engineering Controls	• ventilation systems • machine guarding • sound enclosures • circuit breakers • platforms and guard railing • interlocks • lift tables, conveyors, balancers
3) Warnings	• computer warnings • odor in natural gas • signs • backup alarms • beepers • horns • labels
4) Training and Procedures Administrative Controls	• safe job procedures • rotation of workers • safety equipment inspections • Hazard Communication Training • Lockout • Confined Space Entry
5) Personal Protective Equipment	• safety glasses • ear plugs • face shields • safety harnesses and lanyards • back belts

Exelus

ExSact solid acid alkylation process for gasoline production

Global demand for motor fuels continues to rise to record levels and stricter environmental standards and ethanol requirements place a premium on low RVP, clean-burning blends. A rare opportunity exists to both maximize the yield of motor fuels and enhance production of an ultra-clean blendstock: alkylation. The potential of alkylate is only limited by the costly technology that, until now, was required to produce it. Exelus has developed a new refinery alkylation process that overcomes this challenge.

Gasoline is a combination of several refinery-produced components – reformer aromatics, FCC gasoline, alkylate, ethers, ethanol, etc – that are blended to meet strict specifications. With its high octane number, low vapor pressure and absence of aromatic and olefinic compounds, alkylate is an ideal clean fuel component because it has low emissions and low toxicity. It especially aids in reducing RVP of ethanol-containing blends without sacrificing octane or other fuel properties. Industrial alkylation technologies traditionally use either hydrofluoric acid or sulfuric acid as catalyst. Both these processes share inherent safety concerns and, increasingly, high capital and operating costs.

ExSact is a new technology to combine light (C_3 -C_5) olefins with isobutane to make a high-octane gasoline blendstock (alkylate) using a unique solid-acid catalyst. The key to the ExSact technology is a revolutionary solid acid catalyst that is able to achieve a step-change in performance over conventional solid acid catalysts. The catalyst is engineered to overcome traditional solid-acid catalyst stability limitations and provide superior alkylation performance.

Engineered Catalyst

Unlike liquid acids, which are well-defined chemical compounds with fixed properties, solid acids have many properties that can be tuned to provide enhanced performance. Solid acids have for many years promised safer and cleaner alkylation. However, the short lifetimes of most solid acids have resulted in expensive processes with complex reactors and large catalyst inventories, making them uncompetitive with liquid acid technology.

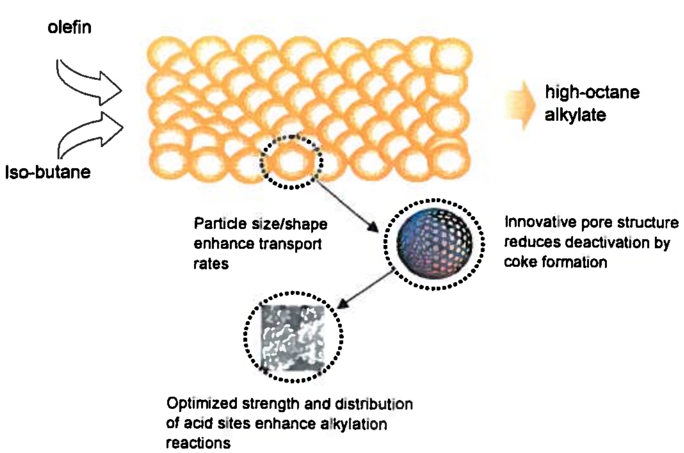


Figure 1: Innovations in the ExSact catalyst system

A new solid-acid catalyst – ExSact – has been engineered on multiple levels, as illustrated in figure 1, to outperform liquid acids. The catalyst particle shape and size are controlled to provide the proper reaction environment by manipulating the rate of mass transport into and out of the catalyst pellet. In this way, the catalyst reduces the constraints on the reactor design, simplifying the process and reducing overall cost. The catalyst pore structure has been optimized on both the macro- and micro-scale to enhance the diffusion of large coke molecules out of the catalyst pores, reducing catalyst deactivation that results from pore blockage. In addition to long cycle times, the engineered catalyst is also able to resist poisons like sulfur, water, and dienes in the feed streams.

The strength and distribution of the active catalyst sites have been tuned to promote formation of high-octane trimethylpentanes while reducing coke formation. Cracking and isomerization to low octane dimethylhexanes are minimized. By carefully tuning the catalyst properties at multiple levels, all of the desired attributes can be achieved: long life, high product octane, and simple process design.

Feedstock Flexibility

ExSact is capable of operating with a variety of olefin feedstocks, making it ideal for utilization of orphaned olefin streams. Although n-butenes produce the best alkylate, propylene, isobutylene, amylenes and mixtures of these can all be used. Process performance with these feedstocks is given in figure 2. ExSact produces higher quality alkylate than sulfuric acid systems with any feedstock.

Figure 2. ExSact performance with various olefins

Feed	Propylene	MTBE Raffinate	Mixed Butenes (30% Isobutylene)
RON	92	98.5	97.3
MON	90	94.5	94.0
Gravity (deg. API)	70	68	69
RVP (psi)	4	2.4	3.3

Process Description

ExSact uses two multi-staged fixed bed reactors. One is used for reaction while the other is being regenerated. The operation of the reactors is very similar to a conventional feed dryer system. The solid acid catalyst operates at 60-90°C and the heat is supplied by the chemical reaction. The robust catalyst is insensitive to small changes in temperature and hence the heat of reaction is removed by a heat-exchanger located on the recycle loop outside the reactor.

The catalyst is completely regenerated after each cycle. Any poisons that have accumulated on the catalyst during the cycle are removed during the regeneration process. The catalyst activity is completely restored, making the process robust against upsets.

Catalyst regeneration is performed using a circulating loop of hydrogen at an elevated temperature of 250°C. Only minimum amounts of precious metal are required. This simple flow scheme results in low capital costs and the ready ability to retrofit existing plants.

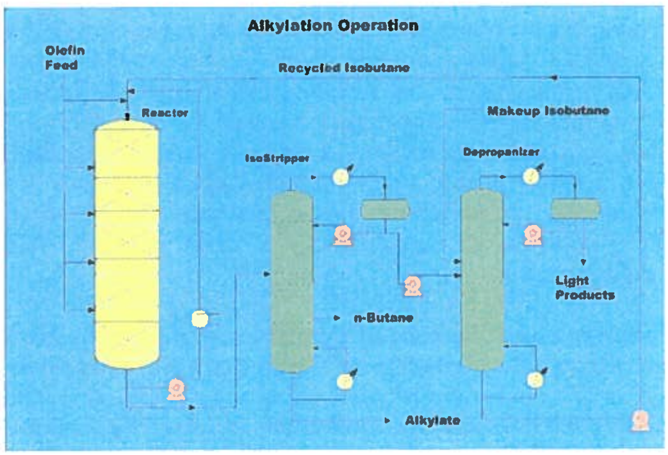


Figure 3. ExSact process diagram

Process Benefits

The advanced technology applied in the ExSact process leads to many benefits for the user. Some of these include:

- **Superior Product Quality**: Alkylate octane is higher than that obtained by other liquid and solid acid catalysts under a wide range of process conditions.
- **High Product Yield**: Reduces the production of a heavy hydrocarbon byproduct (no ASO) and hence has a higher yield of alkylate product per unit of olefin consumption.
- **Feedstock Flexibility**: The ExSact catalyst has an increased tolerance to feedstock impurities and can be operated with minimal pretreatment.
- **Lower Capital Cost**: Brick-lined process vessels, acid containment and neutralization equipment, and refrigeration loops are not necessary, reducing capital expenditures relative to liquid acid-based technologies.
- **Low Power Consumption**: ExSact operates above ambient temperature, eliminating power-intensive refrigeration.
- **Safety**: The ExSact catalyst is intrinsically safe and environmentally benign, unlike corrosive liquid acids.

Economic Benefits

The ExSact process offers significant capital cost savings by eliminating corrosive acid from the process. Removing the liquid acid eliminates the acid neutralization equipment, product washing vessels, and storage tanks for fresh and spent acid. Equipment design is also simplified, eliminating the need for brick-lined vessels and proprietary contactors.

ExSact outperforms sulfuric acid-based alkylation in many respects. Figure 4 below gives a comparison of the two technologies. ExSact has a much lower capital cost and lower overall operating costs compared to sulfuric acid systems.

Figure 4. Comparison of ExSact and sulfuric acid processes

Parameter	Sulfuric Acid	ExSact
Capital Investment	Base*	50% Base
Yields (vol/vol Olefin)		
Alkylate Yield	1.78	1.83
Isobutane Consumption	1.17	1.21
Utilities (per barrel Alkylate)		
Steam (lb)	200	237
Power (kWh)	10.5	3.5
Cooling Water (Mgal)	2.2	0.23
Sulfuric Acid (lb)	20	---
NaOH (100%, lb)	0.1	---
Hydrogen (lb)	---	0.15

**Acid regeneration facility not included.*

Revamp Opportunities

The small capital requirements of this process lead to numerous opportunities to replace older units. Revamps offer the opportunity to upgrade older technology to ExSact without sacrificing performance.

- Liquid acid alkylation units can be converted to the solid-acid catalyst process by replacing the reaction section with two fixed beds. The separation train is retained. The cost to revamp an HF alkylation unit is about 50% of the cost of a new ExSact plant.
- Cat-poly and olefin dimerization units are particularly well suited for retrofit, since the existing reactors can be used with only minor modifications. A de-isobutanizer is added to the separation train.

ExSact is a highly adaptable, low cost technology suitable for many applications. Contact us for more information about your particular situation.

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