

**GAS HANDLING**

# Gassy cleaning

Eugene Y. Ngai, of Air Products & Chemicals, discusses exposure testing of fluoride gases

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**S**emiconductor device manufacturers use a variety of fluoride gases for reactor cleaning and wafer etching. Air Products and Chemicals has been a basic manufacturer of fluorine and the fluoride gases for more than 50 years. As a worldwide supplier of gases and chemicals, Air Products has an extensive EHS program in place to provide to its employees, customers, first responders, transporters and others with the information necessary to carefully handle these products. As part of its overall Responsible Care program, testing is periodically conducted on unique packages or gases to better understand the consequences and behaviour of an accidental release or impact. The information is then used to develop unique emergency response equipment, procedures and/or safeguards for the product.

The following paper summarises select results of the exposure testing that was conducted on three fluoride gases: chlorine trifluoride, fluorine and nitrogen trifluoride. More than 100 tests were conducted on variety of materials, PPE (Personal Protective Equipment), metals, building materials, elastomers and other common materials. It will assess the results and what the data will mean in routine and emergency response activities for these products.

## Test conditions

All testing was conducted at the residual gas treatment area of the Air Products' Hometown, Pennsylvania, speciality gas facility. The exposure testing experiments were conducted in a ventilated walk-in booth, which exhausted into a large liquid scrubbing system. The concentration of gas for these experiments was:

- 100% ClF<sub>3</sub> gas released at its vapour pressure
- 100% ClF<sub>3</sub> liquid dripped by gravity from a tube
- 100% F<sub>2</sub> released after regulation down to 10 psig



- 100% NF<sub>3</sub> released after regulation down to 50 psig.

## Test results

The testing reinforced the need to maintain surface and system cleanliness when handling oxidising gases. This was readily apparent with the chlorine trifluoride and fluorine test results and is demonstrated by the exposures to new nitrile gloves. When they were new and unused, there was no reaction with fluorine or chlorine trifluoride gas.

- A film of oil was placed on the surface of a new glove simulating contamination from body oils or from touching other surfaces. The chlorine trifluoride gas and fluorine immediately ignited the glove
- The liquid chlorine trifluoride reacted without the presence of the oil
- Chlorine trifluoride gas and fluorine reacted with all leather gloves tested
- Chlorine trifluoride and fluorine reacted immediately with Nomex, burning through the material quickly

- Chlorine trifluoride gas and fluorine reacted immediately with Tyvek

● Of all the gas exposures the most interesting was with a raw piece of chicken. The purpose of this experiment was to simulate what would happen upon exposure to human flesh

- Pure fluorine did not react immediately with the raw chicken. To better simulate human skin, some human hair was placed on the chicken skin. This immediately ignited and started the skin on fire. The reaction was so hot that it ignited the stainless steel tubing, which sprayed the chicken with molten stainless steel. This continued to react until the fluorine flow was stopped.

Of all the materials and conditions tested, the most dramatic results were from the liquid chlorine trifluoride dripping onto a piece of raw chicken and onto Tyvek.

When 2cm<sup>3</sup> of liquid chlorine trifluoride were dripped onto a piece of Tyvek, it did not react nor vaporise very quickly and

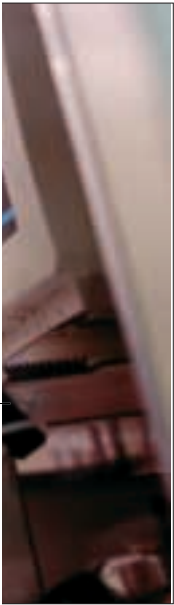
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instead started to soak into the material. A drop of water was dripped onto this triggering the detonation

The liquid chlorine trifluoride onto raw chicken was also very dramatic. The single drop explodes when it hits the surface of the chicken breaking into many smaller droplets, which react again.

## Key findings

- All three gases are colourless and under the test conditions used for these experiments they did not fume
- Fluorine reactions were much hotter than the chlorine trifluoride
- The highest reactivity fluoride tested was liquid chlorine trifluoride, which is followed by chlorine trifluoride gas and fluorine. There was no reactivity under any condition with the nitrogen trifluoride. Nitrogen trifluoride is similar to oxygen in reactivity
  - Surface cleanliness is absolutely critical
  - The high purity fluorine used in the test was not water reactive. Crude grade fluorine coming from the manufacturing process has been reported to be violently reactive with water.



All Emergency Responders to chlorine trifluoride or fluorine incidents must be well trained on the unique hazards of these gases so that they can take quick and the safest actions. Some learnings from our experiments include:

- Chlorine trifluoride and fluorine are highly reactive with oil or any hydrocarbon, while chlorine trifluoride is also highly reactive with water. All PPE, systems and equipment should be new or as clean as possible
- Since chlorine trifluoride and fluorine are colourless and do not fume when released into the environment, a critical visual indicator of a problem is missing
- During routine cylinder handling and ER, the most vulnerable part of the body is the hands. The AP ER Team practice is to use new disposable Nitrile gloves over new smooth leather gloves to provide a modest level of protection while retaining physical dexterity
- The face is the second most vulnerable area, the eyes and respiratory system. Chlorine trifluoride and fluorine will frost borosilicate glass very quickly, blinding the responder if it is used for the facepiece while polycarbonate will not
- Fluorine also can create a significant hazard due to the molten metal that is sprayed if the metal is ignited



- Liquid spill of chlorine trifluoride can take a long time to vaporise. It is not safe to try any remediation such as absorption, dilution or neutralisation
- Most of the chemical protective PPE that were coated and impermeable were not reactive with the chlorine trifluoride liquid. The greatest danger appears to be non-reactive materials, which allow the liquid to wick into the surface. Absorbents can also act like this
- As a precaution, if liquid chlorine trifluoride is splashed onto clothing, remove the clothing before going under the Safety Shower. If it is onto ER PPE, dry wipe the surface before wet decon
- A leaking cylinder of chlorine trifluoride or fluorine cannot be placed into a cylinder containment vessel since the interior or the cylinder exterior cannot be easily cleaned.

As a result of the testing described in this paper changes were made to the Air Products MSDS sheets for chlorine trifluoride and fluorine, including a new PPE

policy for routine handling as well as emergency response for chlorine trifluoride and fluorine.

A new emergency response kit for chlorine trifluoride was designed and distributed to all Air Products locations that handle and distribute the material. And more than 400 customers and employees were retrained on the hazards.

## Future work

Testing of the fluoride gases will continue this spring.

The author will be presenting more details of the study including videos at Semicon West, which is being held in San Francisco in July 2004.

Air Products  
 Tel: +1 610 481 4911  
[NGAIEY@airproducts.com](mailto:NGAIEY@airproducts.com)  
[www.airproducts.com](http://www.airproducts.com)

Or enter 119 on enquiry card