Take care with fluoride gases

Fluorine can cause stainless steel to burn; chlorine trifluoride sets fire to human flesh, and may explode in the presence of water. Use the right techniques to handle these dangerous materials.

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A new programme of safety tests by Air Products and Chemicals, Inc. has reinforced the need for great care in handling fluorine and fluoride gases. As a result of the study, Air Products has amended its procedures for handling chlorine trifluoride and fluorine under both routine and emergency conditions. The company's material safety data sheets (MSDSs) have also changed accordingly.

As a manufacturer committed to the Responsible Care® programme, Air Products periodically tests its products to learn more about their health, safety and environmental characteristics. Fluorine, chlorine trifluoride (ClF_3) and nitrogen trifluoride (NF_3) are commonly used by semiconductor manufacturers for reactor cleaning and wafer etching, as well as in other industries (Table 1).

The latest study placed fluorine (gas), nitrogen trifluoride (gas) and chlorine trifluoride (gas and liquid) in contact with materials including nitrile rubber gloves, different types of leather glove, polycarbonate face shields, Nomex® and Tyvek® fabrics, stainless steel, asphalt, water and raw chicken—the latter simulating human flesh. Altogether there were more than 100 tests.

Burning steel and exploding chicken

The most dramatic result occurred as a result of contact between liquid chlorine trifluoride and Tyvek®. As the liquid dripped onto the fabric, it soaked in and slowly evaporated. When a single drop of water was added, however, there was an explosion that blew the fabric into pieces. It is easy to imagine what might happen if an operator wearing a Tyvek® suit were to be contaminated with a spill of liquid chlorine trifluoride and then to step under a safety shower.

Another gruesome effect was shown by liquid chlorine trifluoride dripped onto raw chicken. As each drop hit the chicken skin it exploded, sending out a shower of smaller droplets which reacted again as soon as they touched the skin. Volatile material such as fat appeared to vaporise and burn above the skin surface, and one drop of chlorine trifluoride blew out a piece of flesh. Liquid chlorine trifluoride also caught fire on contact with nitrile and leather gloves, Nomex® fabric and asphalt.

Both gaseous chlorine trifluoride and gaseous fluorine showed dangerous reactions with many materials. Neither gas ignited a new nitrile glove, but a glove contaminated with a thin film of oil ignited immediately in both cases. Such a film of oil could well be present on a glove that had been used for other jobs, or simply from skin contact. Leather gloves also burned, with the worst effects when the leather was dirty.

Both gases burned through Tyvek® and Nomex® suits in as little as two seconds. In the case of chlorine trifluoride and Tyvek®, the gas did not even have to be flowing; the small amount of chlorine trifluoride remaining in a un-purged delivery tube was enough to start a fire.

Chlorine trifluoride gas burned immediately on contact with raw chicken. Fluorine did not react until some hair was placed on the skin surface, at which point it ignited both the chicken and the stainless steel tube through which the gas was being delivered.

Chlorine trifluoride liquid and gas reacted violently with liquid water, though with few, if any, sparks or flames. The main danger, as shown with the Tyvek® test, is that if chlorine trifluoride touches a flammable material and does not immediately cause a fire, contact with water is likely to cause a fire or explosion. The pure fluorine gas used in these tests did not react with water, but there are reports that crude fluorine can react violently with water.

Nitrogen trifluoride did not react in any of these tests. NF_3 has similar oxidising potential to oxygen; for instance, it causes a smouldering cigarette to flare up.

Keep it clean, dry and safe

The first lesson from these tests is the need for cleanliness. None of the three gases discussed here is flammable in itself; instead, they are strong oxidants which can cause other materials to burn. Extended surface areas and the presence of contaminants such as oil are likely to cause serious fires; smooth, clean surfaces are safer.

Equipment and systems should be oxygen cleaned and passivated, and personal protective equipment (PPE) should be new or very clean. Do not place a leaking cylinder of chlorine trifluoride or fluorine in a containment vessel, since reactive materials will be present on both the outer surface of the cylinder and the inner surface of the containment vessel.

Second, it is important to eliminate contact with water. The heat of reaction released when chlorine trifluoride is in contact with water makes fires more likely when flammable substances are present. Video records of the tests show that in several cases, liquid chlorine trifluoride did not react until it had spread far enough to make contact with moisture.

In contrast to the absorbent materials tested here, impermeable materials used for PPE (such as PVC, Responder, Tychem and CPF4) do not react with liquid chlorine trifluoride as long as no water or other contaminants are present. If they are present, even these materials will burn. Impermeable clothing should be wiped dry before decontaminating with water.

Absorbent materials are dangerous because they can hold liquid chlorine trifluoride and provide a large surface area for reaction. As these experiments show, the combination of absorbent material and water can trigger an explosion. A spill of liquid chlorine trifluoride can take a long time to evaporate, but resist the temptation to use absorbent or to wash it away. If liquid chlorine trifluoride is splashed onto absorbent clothing, remove the clothing before going under the safety shower.

Since no glove material held up under all conditions, Air Products recommends new disposable nitrile gloves (for chemical protection) worn over new smooth leather gloves (for thermal protection if the nitrile ignites). Gloves should be loose-fitting and not taped to the suit, so that they can be removed easily. Polycarbonate face shields are highly resistant to reaction as long as they are clean.

Both chlorine trifluoride and fluorine are colourless and do not fume on contact with air, which makes any emergency release hard to locate. Both materials are also toxic.

Air Products is continuing to test fluoride gases. In July 2004 the company plans to present details of this work, including videos, at Semicon West, San Francisco, as part of the SEMI Technology Symposium on Environmental Technologies and Management Systems.

Gas name	Chlorine trifluoride	Fluorine	Nitrogen trifluoride
Supplied as	Liquefied gas	Compressed gas at 400 psig @ 70°F (27.6 bar g @ 21°C)	Compressed gas at 1450 psig @ 70°F (100 bar g @ 21°C)
Colour	Colourless	Pale yellow	Colourless
Odour	Low concentrations described as "bleach-like". Higher concentrations described as "acidic" or "suffocating"	Repulsive and irritating. Distinctive, and detectable at very low concentrations	Odourless
Formula	ClF_3	F_2	NF_3
CAS number	7790-91-2	7782-41-4	7783-54-2
UN number	1749	1045	2451
Molecular weight	92.45	38.0	71.0
Vapour pressure	6.8 psig @ 70°F (21°C)	Not a liquefied gas	Not a liquefied gas
Gas density	0.2443 lb/ft^3 @ 70°F (3.19 g/l @ 21°C)	0.098 lb/ft^3 @ 70°F (1.570 g/l @ 21°C)	0.184 lb/ft^3 @ 70°F (2.95 g/l @ 21°C)
Liquid density	136.7 lb/ft^3 @ 77°F (1.785 kg/l @ 25°C)	NA	NA
Toxicity	TLV = 0.1 ppm LC_{50} = 299 ppm IDLH = 20 ppm	TLV = 0.1 ppm LC_{50} = 185 ppm IDLH = 25 ppm	PEL = 10 ppm LC_{50} = 6700 ppm IDLH = 1000 ppm
Transport hazard labels	Toxic gas Oxidising Corrosive	Toxic gas Oxidising Corrosive	Non-flammable gas Oxidising In Japan and Korea also: Toxic gas because of PEL
Atmospheric boiling point	53.2°F (11.75°C)	–307°F (–188°C)	–200.2°F (–129°C)
Atmospheric freezing point	–105.4°F (–76.3°C)	–363°F (–220°C)	–340.2°F (–206.8°C)
Critical temperature	367°F (186°C)	–200°F (–129°C)	–38.50°F (–39.2°C)
Other emergency response information	Gas is 3.3 times denser than air. Gas specific volume is	Gas is 1.3 times denser than air. Gas specific volume is	Gas is 2.5 times denser than air. Gas specific volume

	4.094 ft^3/lb @ 70°F (256 cm^3/g @ 21°C). Not flammable. Strong oxidiser. Thermal dissociation begins at 250°C and reaches 50% at 450°C. Reacts violently with water.	10.17 ft^3/lb @ 70°F (615 cm^3/g @ 21°C). Not flammable. Strong oxidiser. Thermally stable. Slightly soluble in water, forming hydrofluoric acid. May contain impurities that react with water.	is 5.43 ft^3/lb @ 70°F (338 cm^3/g @ 21°C). Not flammable. Strong oxidiser. At 482°F (250°C) dissociates into nitrogen difluoride (NF_2) and fluorine. Slightly soluble in water.

Table 1: Properties of chlorine trifluoride, fluorine and nitrogen trifluoride