Chlorine Trifluoride Exposure and Reactivity Study

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Abstract: Chlorine Trifluoride (ClF_3) was first synthesized in the 1930's and is recognized as one of the most reactive halogen fluorides. In fact, with the possible exception of elemental fluorine, ClF_3 may represent one of the most reactive products known. Active research and commercial use of ClF_3 began in the late 1940's. ClF_3 has been utilized in such diverse applications as military weapons, rocket fuel oxidant, nuclear fuels processing, oil well rod cutting, mineral analysis, and electronics manufacturing tool cleaning. Such fluoride compounds present toxic, oxidizing, highly reactive, and/or environmental challenges in their onsite delivery, use, handling, and treatment. Air Products has been the primary manufacturer of ClF_3 in North America for about 35 years and the compound is one of the highest reactivity products that Air Products handles worldwide. However, not much information has been available in the industry regarding its reactivity with specific materials. Therefore, Air Products conducted testing to expose various materials of construction (metals, plastics, and elastomers), building materials, PPE, and other common materials to both vapor-phase and liquid-phase releases of ClF_3. This paper will discuss the history of ClF_3 development and usage, its properties and hazards, exposure testing methods employed, test results, and lessons learned regarding improved handling and usage recommendations for ClF_3 suppliers and consumers.

1. INTRODUCTION

1.1 "Chlorine Tri-What?"

Chlorine Trifluoride (ClF_3) is one of those molecules that your high school chemistry teacher would claim can't exist. Whenever I mention the name of this compound to someone for the first time, their response usually is, "Chlorine Tri-What?". The valences for the constituent atoms to bond together and produce this molecule don't seem to make sense. How can you oxidize elemental chlorine, which is already a strong oxidizer? It is possible because fluorine is a more powerful oxidizer than chlorine and it can oxidize almost any element or material, even including most of the Noble gas family. The result of this unlikely union of chlorine and fluorine is Chlorine Trifluoride. ClF_3 is a toxic, corrosive, very reactive liquefied compressed gas packaged in cylinders as a liquid under its own vapor pressure of 1.55 kg/cm^2 at 21°C (22 psia at 70°F). ClF_3 is a very useful chemical in operations requiring a high-energy fluorinating agent or incendiary material, especially since it can be handled at room temperatures. However, those same factors that make it quite useful also contribute to several high hazard potentials for the product.

Air Products has been the primary manufacturer and distributor of ClF_3 in North America for the past 35 years and the compound represents one of the highest reactivity products that Air Products currently manufactures or handles worldwide.

1.2 Initial Discovery

Fluorine is recognized as the most powerful oxidizing agent of all known elements. However, fluorine (F_2) has the inherent disadvantage that the liquid must be stored and handled in a cryogenic state, with a normal boiling point of -188°C (-306°F). Therefore, it is impractical or exceedingly difficult to use liquid-phase F_2 to provide maximum density product, thus enhancing its fluorinating reactivity performance. Gaseous usage of F_2 utilizes a much more dilute density (vapor-phase) contacting the reactants and thus yields lower reactivity performance than liquid F_2 contact. Therefore, various fluorinating substitutes were evaluated in the late 1920's that possessed the highly reactive properties of F_2 but posed fewer handling difficulties. ClF_3 was first successfully isolated by Ruff and Krug in 1930 after experimental tests with chlorine monofluoride suggested the presence of a higher fluoride species.[1] Liquid ClF_3 is considered more reactive than vapor-phase F_2 reactions since more moles of fluorinating agent are present per unit area of reactant surfaces. Also, liquid ClF_3 may demonstrate even higher reactivity in certain circumstances than liquid fluorine since the F_2 liquid temperature is cryogenic, thus reducing its activity potential.

1.3 First Bulk Application – Military Weapons

German interest in ClF_3 during World War II prompted the first industrial bulk production capability for the material. The Germans produced ClF_3 in tonnage quantities for military use during World War II to use in flame-throwers due to the liquid's extreme hypergolic nature with fuels (self-igniting) and as a general incendiary material. ClF_3 was

originally produced in large quantities using a two-step synthesis method developed by the Germans. This process caused fluorine and chlorine to react under heat to form chlorine monofluoride. The second step in the reaction brought chlorine monofluoride together with excess fluorine to produce ClF_3 on a scale of approximately 135 kg/hour (300 lb/hour) with 96% to 98% yield results. Following the war, interest in the use of ClF_3 for organic synthesis work increased although the material was eventually considered to be too reactive for practical use and mostly abandoned for these applications.[2] Synthesis reactions proved difficult to control and usually lead to a wide variety of reaction by-products that were hazardous.

1.4 Early History - Rocket Science and the Atomic Age

Many fluorinating compounds were evaluated as potent oxidizers for liquid-fueled rockets in the late 1940's and through the early 1950's to overcome the storage and handling disadvantages of liquid F_2. Some of the combinations of compounds considered were chlorine-fluorine, nitrogen-fluorine, and fluorine-oxygen. During this time, various U.S. agencies and companies did considerable testing using ClF_3 as the oxidizer for liquid-fueled rocket research. ClF_3 was first tested in the U.S. in 1948 on a liquid propellant 45-kg (100-pound) thrust rocket motor using hydrazine as the fuel. Later the performance of hydrazine-nitrogen tetroxide and hydrazine- ClF_3 were compared in a larger 135-kg (300-pound) thrust rocket motor. In 1951, ClF_3 was tested with both ammonia and hydrazine as liquid rocket fuels. Further related work with ClF_3 included its use as an ignition source in various non-hypergolic rocket fueled systems.[2] It was determined to be so rapidly hypergolic when exposed to various fuels that no ignition delay was ever successfully measured during experiments. Rocket performance results with the compound were very positive, yielding smooth engine operation, immediate reaction (which allowed a small reaction chamber size), and near theoretical energy output. ClF_3 was concluded to approach solid-propellant rocket convenience since it could be stored stably in liquid-phase at room temperature and relatively low pressure. Also, it was deemed as one of the most promising storable oxidizers available at the time since it contains 62% by weight elemental fluorine. However, all rocket materials of construction (including metals and seals) that could contact ClF_3 had to be scrupulously selected, cleaned, and passivated to prevent the components from burning during reaction.[3] ClF_3 was also recognized as an extremely hazardous propellant due to its reactivity, toxicity, and toxic by-products of fluorination.

Beyond ClF_3's use as an oxidizer for liquid-fueled rockets, other interest in chlorine trifluoride increased in the late 1940's due to various potential applications in the developing nuclear industry. For example, ClF_3 was investigated for use in uranium enriching applications during the early atomic Manhattan Project and later Oak Ridge nuclear effort.

1.4.1 Famous Industrial Incident – "The concrete was on fire!"

There is one major incident involving ClF_3 that occurred during the liquid rocket propellant era that is relatively famous in the industry. A domestic chemical company

was a major supplier of ClF_3 for US governmental applications. They had an incident at one of their chemical facilities when personnel for the first time loaded a one-ton steel container with liquid ClF_3 for bulk shipment. The container had been cooled with dry ice to perform the liquid transfer and help make the product safer to handle since the ClF_3 vapor pressure would only be about 0.007 kg/cm^2 (0.1 psia) in the sub-cooled state. However, the dry ice bath embrittled the steel container wall and, while maneuvering the full container onto a dolly, it split open and instantaneously released 907 kg (2,000 lb) of cold ClF_3 liquid onto the building floor. The material "consumed through" (reacted) the 30 cm (12 inch) thick concrete floor and through about another 90 cm (36 inches) of gravel underneath the spill. The fumes that were generated (chlorine trifluoride, hydrogen fluoride, chlorine, hydrogen chloride, etc.) severely corroded everything that was exposed.[3] One eyewitness described the incident by stating, "The concrete was on fire!"

1.5 Recent Past Uses – The Oil Crises

During the decades of the 1960's and 1970's, ClF_3 was used in several diverse industries, including use for performing mineral analysis by actually dissolving the rock or mineral sample thus facilitating analytical testing.

One interesting application during the increased oil exploration activity of the 1970's and 1980's involved use of ClF_3 as a chemical cutting agent primarily for oil drilling rigs. The device that was used to perform the cutting had three chambers stacked in a vertical column configuration. The top chamber contained a small explosive charge, the middle chamber contained liquid ClF_3, and the bottom chamber housed a catalyst. The device would be lowered into an oil well to any desired depth and the explosive charge was detonated. The explosion pushed the liquid ClF_3 through the catalyst chamber where its temperature was rapidly increased and the explosive energy then forced the heated ClF_3 out of small nozzles located at the bottom of the device, which were aimed radially outward. The high pressure, heated stream of ClF_3 contacted the well tubing wall and/or drill rod where an extremely rapid and vigorous reaction cleanly cut the metal in less than one second. The tube or rod could then be withdrawn from the well and recovered.[4]

1.6 Modern Usage – IC Chip Manufacturing

The only surviving major industrial application for ClF_3 in the present is its use in the nuclear industry for the reclamation of uranium from irradiated fuels. This is accomplished by reacting the nuclear fuel with ClF_3 and forming the corresponding fluoride compounds. The gaseous uranium hexafluoride is then recovered from the other compounds present via distillation.[4]

However, in the 1990's the semiconductor industry developed a high-purity application that uses ClF_3 in the cleaning process for certain chemical vapor deposition (CVD) tool chambers. CVD involves decomposing source gases (such as silane, dichlorosilane, silicon tetrafluoride, and tungsten hexafluoride) using heat or a plasma as the energy source. These film forming reactions in CVD tools are driven to the wafer surface and are precisely deposited to impart specific electrical characteristics to the

integrated circuit device. However, during CVD, material is deposited not only on the silicon substrate, but also on the walls of the process chamber. Periodically, the tool chamber requires cleaning to preempt particle shedding and maintain an ultra-high purity environment for the wafers being processed. In situ cleaning of the tool is desirable because the solid residues on the chamber interior are removed from the walls without dismantling the tool or risking personnel exposure to the hazardous residues or cleaning agents. In situ cleaning also yields quicker turn-around time for the tool to resume wafer processing. Fluorine atoms readily react with these solid residues to form volatile reaction products that can be purged and evacuated from the system.[5] The primary advantage ClF_3 has over other gaseous fluorine cleaning sources (such as nitrogen trifluoride, hexafluoroethane, or carbon tetrafluoride) is that the high reactivity of ClF_3 allows the operation to be accomplished at relatively low temperatures, without requiring plasma or high temperature heating to disassociate it for use during the cleaning process. The use of vapor-phase ClF_3 for CVD chamber cleaning has demonstrated the ability to prolong chamber component life through the lack of high temperature or plasma use, and tool dismantling requirements.

Because the use of ClF_3 in semiconductor applications has started to expand due to its effective tool cleaning performance, Air Products personnel and customers involved in serving these applications are required to handle increasing amounts of ClF_3. The various safety reviews that were used to design and operate Air Products' ClF_3 manufacturing facility and develop the safety requirements for our operators do not translate well to a consumer's site. Also, most of the publicly available information regarding ClF_3 was dated and of questionable value since the tested product had impurities that are no longer present in Air Products' electronics grade material (99.9% minimum purity). Finally, because past applications using ClF_3 were mostly government-controlled, many of the handling procedures that were utilized for governmental services were classified. Therefore, Air Products decided to empirically test the reactivity of ClF_3 with currently used materials of construction, personal protective equipment, contaminants commonly found in systems and equipment, and other materials with may come into contact with the product. The following paper discusses the test results of the exposure of various materials to both vapor-phase and liquid-phase contact with ClF_3. The results of this analysis were then used to reevaluate the materials of construction utilized in ClF_3 service, improve Air Products' knowledge of personal protective equipment performance, and to establish improved recommendations to those manufacturing, handling, and performing emergency response with the product.

2. GENERAL PROPERTIES OF CHLORINE TRIFLUORIDE

2.1 Physical and Chemical Properties

Molecular Weight	92.447
Boiling Point (1 atm)	11.75^{o}C (53.15^{o}F)
Melting Point	-76.32^{o}C (-105.38^{o}F)
Gas Density (21.1°C)	3.913 kg/m^3 (0.2443 lb/ft^3)
Specific Volume (21.1°C)	0.2556 m^3/kg (4.094 ft^3/lb)
Specific Gravity (air=1)	3.260
Vapor Pressure (21.1°C)	1.55 kg/cm^2 (21.5 psia)
Appearance	Gas colorless
	Liquid pale green
	Solid white
	Odor varies with hydrolysis by-products; low concentrations are described as bleach-like while higher concentrations are described as acidic or suffocating

2.2 Toxicological Properties

LC$_{(50)}$	299 ppm for 1 hour rat (death due to respiratory failure)
OSHA PEL	0.1 ppm Ceiling
ACGIH TLV	0.1 ppm Ceiling
NIOSH IDLH	20 ppm
AIHA ERPGs	ERPG-1 = 0.1 ppm
	ERPG-2 = 1 ppm
	ERPG-3 = 10 ppm

3. SAFE HANDLING AND USE

Chlorine trifluoride is a strongly oxidizing, toxic, corrosive liquefied gas at typical storage temperatures. It is normally packaged in specially cleaned and prepared carbon steel or stainless steel cylinders and ClF_3 is most safely used as a vapor to limit its potential reactivity with system components and other materials. Unless special precautions are taken, ClF_3 should only be removed from the cylinder as a vapor and care must be taken to prevent its condensation in piping or other equipment. Employees working with ClF_3 should be specially trained to assure they understand the system requirements and the physical and exposure hazards of ClF_3 and its reaction products.

3.1 Main Hazards of Chlorine Trifluoride

The main hazards of ClF_3 are:

- It is an extremely vigorous fluorinating agent and unstable when exposed to easily fluorinated materials.
- It reacts with water and many oxide compounds to produce chlorine oxides which are also unstable and toxic.
- It is a toxic product and its byproducts of fluorination or reaction are often also toxic.

3.2 System Preparation

Systems used for chlorine trifluoride must be very carefully cleaned to remove readily-oxidized impurities and must be meticulously maintained to prevent contamination. Cleaning agents must be thoroughly removed prior to admitting ClF_3 into systems (normally by extensive purging with high purity nitrogen or other inert gases) as they can also become fuels in the presence of ClF_3. Heating of system components during purging should be considered to assure removal of low-volatility cleaning agents and moisture adhered onto the walls metallic or elastomer components.

To minimize potential problems, users should avoid excessive use of mechanical connections (to limit potential leakage sites) and elastomers (to limit potential reactivity and contamination) in ClF_3 systems. Similarly, system valves incorporating metal seats should be used if possible to reduce the chance of ignition of elastomeric seats. Chlorine trifluoride systems should be passivated before use with increasing vapor concentrations of either ClF_3, fluorine, or a fluorine/inert gas mixture. Passivation allows the formation of a thin metal fluoride surface that is resistant to further reaction with ClF_3 and, most importantly, allows a controlled reaction with any remaining contaminants left behind by imperfect cleaning. The system should be observed during passivation for unexpected overheating of any components that would indicate an excessive reaction with the components.

3.3 System Operations

Chlorine trifluoride systems must be kept dry to minimize corrosion and contamination from acids that will form on contact of ClF_3 with moisture. Equipment should be de-pressurized when not in use and should be purged with dry inert gas and kept sealed under positive pressure with dry inert gas for extended out-of-service periods.

As with any hazardous gas cylinder, operators should confirm the cylinder valve is firmly closed before loosening the valve outlet seal to connect a cylinder to the system. The outlet seal should be loosened slowly to limit the release rate of any ClF_3 that may have leaked into the valve outlet space. The same procedure should be used to disconnect the cylinder from the system and the pigtail must be vented and purged thoroughly before loosening the connection.

When connecting new ClF_3 cylinders, care is needed to prevent contamination of the valve outlet connection, especially if a gasketed connection is used (e.g., CGA 670 or CGA 728). New gaskets must be thoroughly degreased and dried prior to installation unless specially cleaned and packaged gaskets are used directly from the manufacturer. New cleanroom gloves or equally clean alternatives should be used to install replacement gaskets. Similar precautions must be taken when changing other system components to avoid introduction of easily ignited contaminants.

When ClF_3 supply cylinders are initially opened, the operator should always be prepared to quickly re-close the valve in case any evidence of reaction, overheating, or leaks develop. If any uncertainty exists about the cleanliness of system components, the cylinder valve should only be opened to admit a minimal amount of ClF_3 vapor and then immediately closed. This will limit the amount of ClF_3 available to sustain ignition if a problem develops.

It is very important that chlorine trifluoride systems be kept well below the ClF_3 condensation pressure of the coolest component in the process to prevent liquefying the ClF_3 vapors. This is primarily to avoid the heightened reactivity of liquid-phase ClF_3 in the system and to allow proper flow control. Use of an absolute pressure regulator is recommended whenever possible to control system pressure below the ClF_3 condensation pressure. With its relatively high boiling point, ClF_3's vapor pressure is low at typical use temperatures which can result in unacceptably low system pressure and flowrates, especially from cylinders with little remaining inventory. If the supply cylinder is heated to permit higher flows it is even more critical to protect against condensation in cooler downstream components. System heating can also be considered to avoid condensation, but it can be difficult to maintain uniform heating throughout the entire system.

Prior to any maintenance, including supply cylinder changes, special care must be taken to assure no hazardous quantity of ClF_3 remains in the equipment. Thorough purging with inert gas should always be done after the ClF_3 cylinder valve is firmly closed. If there is any suspicion of condensed ClF_3 in the system, the process should be heated and ideally evacuated to confirm no ClF_3 remains before the system is opened.

3.4 National and Regional Code Requirements

ClF_3 is a challenging material to properly manage from a code compliance and usage standpoint. This is because ClF_3 possesses both physical hazards (very strong oxidizer and very reactive) and health hazards (toxic and corrosive). The physical hazards of ClF_3 often cause local authorities to require the source containers be positioned remote from the consumer's main facility or occupancies. However, the low vapor pressure of the product at room temperature provides challenges to distribute the vapor any significant distance.

ClF_3 is classified as a "Hazardous Production Material" (HPM) per regional Code definition based on its NFPA 704 ratings (Figure 1).

Figure 1: NFPA Hazard Diamond for Chlorine Trifluoride
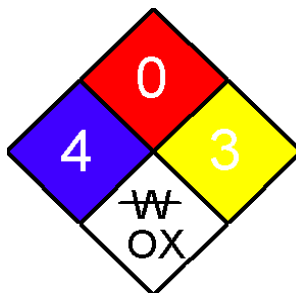
An HPM is a solid, liquid, or gas associated with semiconductor manufacturing that has a degree of hazard rating in health, flammability, or reactivity of Class 3 or 4 as ranked by NFPA criteria. Also, an HPM requires that the material is used directly in research, laboratory, or production processes that have as their end product materials which are not hazardous (e.g., integrated circuits).

The physical hazards or ClF_3 often drive low threshold or exempt quantities for the material based on local code requirements. However, proper facilitation and usage of ClF_3 does provide a safe supply and distribution system if the hazards and code requirements are adequately addressed. One method to effectively manage ClF_3 hazards is through the use of properly designed and facilitated gas cabinets that are specially engineered to house ClF_3 cylinders and distribution control piping and components. One example of the unique design thinking for ClF_3 equipment is that Air Products, in the early semiconductor experimentation phase with the product, did not recommend installing a water sprinkler inside of the gas cabinet for fire mitigation. Chlorine trifluoride is so water reactive that alternate means were deemed preferred for prevention and mitigation of fires, both internal and external to a ClF_3 gas cabinet. This position was supported in 1997 by a major industrial insurance company's specific recommendation to prohibit sprinklers in ClF_3 gas cabinets used for the semiconductor industry.[6]

3.5 Gas Cabinet Supply Safety Considerations

When chlorine trifluoride is used in semiconductor or research facilities, consideration should be given to the following gas cabinet system design elements:

- Automatic sprinkler protection is not recommended for ClF_3 gas cabinets due to the potential for violent reaction with leaking ClF_3.
- Pneumatically operated cylinder valves should be considered to allow automatic and immediate supply shutdown should there be a downstream incident.
- A gas detector should be located in the cabinet to monitor and cause an automatic shutdown alarm on either hydrogen fluoride (HF) or chlorine dioxide (ClO_2) indication.
- A heat or smoke detector should be located in the gas cabinet to monitor and cause an automatic shutdown alarm on an internal or external fire condition.
- The delivery pipe or tubing should be co-axial (double contained) with a monitoring alarm for loss of primary containment.

4. TEST CONDITIONS FOR EXPOSURE AND REACTIVITY STUDY

4.1 Vapor-Phase Exposure Testing

The testing was conducted at Air Products' manufacturing facility in a large walk-in vent booth that is continuously exhausted to a caustic wet scrubber. The ambient temperature averaged 26.7°C (80°F) during the testing with relative humidity approximately 40% for the duration. A 2.8 liter (0.1 ft^3) DOT cylinder containing 1.6 kg (3.5 lb) of chlorine trifluoride was used as the source. The initial vapor pressure of the chlorine trifluoride was 1.87 kg/cm^2 (26.6 psia) at the test temperature.

The vapor-phase exposure testing was conducted using a 51 cm (20 inch) long piece of 0.312 cm (0.125 inch) diameter stainless steel tubing connected directly to the cylinder with the use of a CGA-670 nut and nipple. The cylinder was mounted upright in the vertical position inside the vent booth on a metal stand. The outlet of the vapor discharge tubing was directed at the target piece, which was held by a laboratory clamp and stand (Figure 2). For added safety, a local vent snorkel was positioned behind the target piece to assist in fume removal. The flow of the vapor was controlled by manual operation of the cylinder valve.

Figure 2: Chlorine Trifluoride Vapor-Phase Exposure Testing Apparatus

4.2 Liquid-Phase Exposure Testing

The liquid exposure testing was conducted by inverting the cylinder to access the liquid phase and mounting it above the metal stand. Two metal-to-metal seat pneumatic nickel valves were connected to the cylinder. The first valve was connected directly to the valve outlet. The second valve was coupled as close as possible to the first valve with

about 2.5 cm (1 inch) of 0.635 cm (0.25 inch) stainless steel tubing. The second valve discharged to a 20 cm (8 inch) length of 0.635 cm (0.25 inch) diameter copper tubing which directed the chlorine trifluoride to the target piece by gravity. The target pieces were positioned on the metal stand immediately below the tubing outlet. The testing was done by remote operation of the two pneumatic valves. The cylinder valve was opened admitting liquid chlorine trifluoride up to the first valve seat. The first valve was cycled opened and closed. This trapped approximately 2 ml of liquid between the pneumatic valves. When the second valve was opened the trapped liquid was dropped onto the target piece through the copper tube (Figure 3). The tests were conducted in this manner to limit the amount of liquid chlorine trifluoride available to the sample being exposed.

Figure 3: Chlorine Trifluoride Liquid-Phase Exposure Testing Apparatus

It is important to note that all equipment used in this testing was specially selected, assembled, and cleaned to meet Air Products' standards for fluorine and its oxidizing compounds. Also, the testing was performed and attended by personnel very experienced in the hazards and behavior of ClF_3 reactions.

5. EXPOSURE TEST RESULTS

Chlorine trifluoride exposure testing was conducted over a two-day period and the results were recorded using digital video and still cameras. The results are summarized in five major categories of target materials:

- Personal Protective Equipment (Table 1)
- Metals (Table 2)
- Plastics / Elastomers (Table3)
- Building Materials (Table 4)
- Miscellaneous (Table 5)

In some cases where no reaction occurred with the target sample, a drop of water was added to the liquid to observe if a reaction could be initiated.

Table 1: Personal Protective Equipment Exposure Test Results

Personal Protective Equipment		
Material	**Vapor Exposure**	**Liquid Exposure**
Faceshield – Polycarbonate	No reaction.	No reaction. Liquid left white deposit on plastic.
Glove, Latex – New	No reaction.	No reaction until liquid contacted a contaminant and then material ignited.
Glove, Nitrile – New	No reaction	Ignited immediately after liquid exposure and burned vigorously after first drop charred it.
Glove, Nitrile – Oil Film Contamination	Ignition as soon as exposed to vapor.	Not tested.
Glove, Smooth Leather – New	Burning at point of impingement and shriveling of leather.	Instant flash on liquid contact and leather shriveling.
Glove, Smooth Leather – Used	Not tested.	Flashes and flames were more intense and glove shriveled significantly.
Glove, Rough Heavy Leather – New	Orange flame that went out when flow stopped. Exposure burned hole through leather.	Liquid immediately flashed on the surface and the second drop charred leather.
Glove, Rough Heavy Leather – Oil Film Contamination	Intense flame at oil spots and charring of general area.	Not tested.
Suit, Acid Resistant	First test produced intense flame and burn through of material. Second test had no reaction.	Explosion upon contact that left charred material where liquid impacted.
Suit, Acid Resistant – Oil Film Contamination	No reaction.	Not tested.
Suit, CPF4® Material	No reaction.	No initial reaction with small strips which then ignited when liquid flowed underneath. Using a full suit, liquid ClF_3 puddled and evaporated. No reaction with slight discoloration of material.
Suit, Kappler Responder®	No reaction.	No initial reaction with small strips which then ignited when liquid flowed underneath.
Suit, Kappler Light Material	No reaction.	No initial reaction with small strips which then ignited when liquid flowed underneath.
Suit, Neoprene Material	No reaction.	No immediate reaction but liquid appeared to contact a contaminant that ignited material.
Suit, Nomex	Smooth and intense burning at the point of contact. Burned completely through suit in two seconds. Same result for three tests.	Instant and intense flash with flame extinguishing after liquid totally reacted.

Personal Protective Equipment		
Material	**Vapor Exposure**	**Liquid Exposure**
Suit, Tychem®	No reaction.	Liquid had no reaction and collected as a puddle. Droplets of water created small flashes and reaction was sufficient to ignite material which continued to burn.
Suit, Tyvek®	Vapor traces remaining in discharge tube immediately burned Tyvek® as it was moved around the tube outlet.	Liquid exposure on material had no reaction. Liquid soaked into the Tyvek® fibrous material. A drop of water introduced onto the saturated material triggered a major detonation.

Table 2: Metals Exposure Test Results

Metals		
Material	**Vapor Exposure**	**Liquid Exposure**
Aluminum Chips	Not tested.	No reaction. Test chips were displaced by liquid contact.
Aluminum Plate	Not tested.	No visible reaction or discoloration. Liquid ClF_3 just bubbled and evaporated.
Aluminum Plate – Water on Surface	Not tested.	Slight brown fuming and white deposit left on surface.
Brass Chips	Not tested.	No reaction. One chip did ignite but could have been due to oil contamination on test stand.
Brass Fitting	Not tested.	No reaction.
Carbon Steel Plate – Epoxy Painted	Slight browning of the paint surface.	No significant reaction. Liquid just puddled and evaporated, and paint appeared to bubble.
Carbon Steel Wool	Vapor traces remaining in discharge tubing were enough to burn material as it was moved around tube outlet.	Immediate intense flash totally reacting material with very little residue remaining.
Copper Chips	Not tested.	No reaction. One chip did ignite but could have been due to oil contamination on test stand.
Copper Tube	Not tested.	No reaction. Copper tube was used for all the liquid drip tests and the tube after 40+ tests had no evidence of reaction.
Stainless Steel Chips	Not tested.	Immediate flash with the second drop causing a more intense flash.
Stainless Steel Plate	No reaction.	No reaction.

Table 3: Plastics / Elastomers Exposure Test Results

Plastics / Elastomers		
Material	**Vapor Exposure**	**Liquid Exposure**
FRP, Derakane 470	No reaction.	Immediate flash on surface – liquid appeared to be reacting with plasticizer.
Gasket, Red Rubber	Not tested.	Muffled pop and orange flame.
Gasket, Teflon-Filled – New	No reaction.	Not tested.
Gasket, Teflon-Filled – Old	Not tested.	No reaction.
Gasket Teflon-Filled – Oil Film Contamination	No reaction.	No reaction.
Polyethylene Bag – Emergency Response Item	No reaction during direct impingement or filling of bag with vapor.	No reaction after six seconds of liquid contact until liquid flowed underneath Teflon block on test stand. Then bag ignited and burned.
Polyethylene Netting – Cylinder Wall Shipping Protection	Not tested.	Material did not react until liquid contacted a contaminant which initiated reaction and fire.
Polyethylene Tubing – New	Not tested.	No reaction as the liquid dripped through the tube.
Polyethylene Tubing – Used	Not tested.	Immediate bright orange flame entire tubing length which continued to burn with intense yellow flame. Same result for two tests.
PVC	Intense burning at the point of contact, similar to wood. Burned circular hole in test piece.	Immediate surface flash and charring.
Teflon Block	Not tested.	No reaction.

Table 4: Building Materials Exposure Test Results

Building Materials		
Material	**Vapor Exposure**	**Liquid Exposure**
Asphalt	Intense burning at point of contact.	Small pieces totally exploded in both tests. Larger piece flared intensely with yellow flames.
Cinder Block	Not tested.	Surface sparking with no visible damage.
Concrete	No reaction.	No reaction.
Concrete – Wet	No visible reaction other than lightening of area where sample was wetted.	Not tested.
Duct Tape	No reaction.	Delayed reaction when liquid flowed underneath and contacted adhesive that ignited sample.
Wood, Large Timber	Intense burning with sparks ejected at point of contact, similar to welding torch. Burned circular hole in test piece.	Immediate surface flashing reactions. Then volatile compounds exploded above the wood sample.

Table 5: Miscellaneous Materials Exposure Test Results

Miscellaneous Materials		
Material	**Vapor Exposure**	**Liquid Exposure**
Chicken, Raw Piece	Immediately flared intensely during entire vapor exposure. Generated three large flares radially outward from point of contact.	Liquid drops hitting skin immediately exploded with any unreacted splattered drops resulting in vigorous sparks and pops. Fat appeared to vaporize and volatile compounds exploded above skin.
Cotton Rag	Not tested.	Cotton burned immediately and vigorously. Became more intense when second drop impacted charred material.
Manila Tag	Burned with yellow flame at point of contact and ignited remainder of tag.	Not tested.
Oil Film on Epoxy Painted Metal	Not tested.	Instant explosion when liquid contacted sample. Circular char pattern created which traced the liquid droplet splashes.
Paper Towel	Paper burned immediately on contact and continued burning after vapor flow stopped. Not a vigorous reaction.	Paper immediately burst into flames but was not a vigorous reaction.
Soda Ash	No reaction. Solids were displaced by vapor contact.	Not tested.
Water, Ice	Rapid melting of ice with no fuming or noise evident.	Rapid melting of ice with no fuming or noise evident.
Water, Liquid	Introduced above water surface. Loud popping and bubbling but no sparking flames.	Dripped into water with immediate aggressive popping and heating. Water was ejected from container with some sparking.
Water, Spray	No reaction.	Not tested.
Water Film on Concrete	No reaction.	Not tested.
Water Film on Aluminum Plate	No reaction.	Not tested.

6. EXPOSURE TESTING CONCLUSIONS

As expected the exposure test results confirmed much of the industry reactivity knowledge for ClF$_3$, however, they did refute certain expected behaviors. Some of the general conclusions were:

- The ClF$_3$ vapors were colorless and there was no fuming as reported in some literature. This result occurred even when the vapor or liquid was contacted onto water, onto ice, and sprayed with water.
- Liquid ClF$_3$ does not evaporate readily, even at an ambient temperature of 26.7°C (80°F).
- The PPE had to be tested with large pieces since small pieces ignited when liquid ClF$_3$ contacted the uncoated underside of the sample.

6.1 Importance of Maintaining Cleanliness

One of the most significant findings was how reactive chlorine trifluoride can be with common contaminants such as water or hydrocarbon (e.g., oil). In some cases where there was no reaction between liquid ClF$_3$ and the sample, if liquid contacted water or oil contamination near the test sample, the reaction heat was sufficient to ignite the sample material. This phenomenon was very evident in liquid exposure testing on contaminated nitrile gloves, used polyethylene tubing (Figures 4 and 5), and oil contaminated surfaces. Therefore, maintaining cleanliness with any materials that may come into contact with ClF$_3$, and especially PPE, is of paramount importance.

Figure 4: Vapor ClF$_3$ Exposure to Nitrile Gloves, Clean and Oil Contaminated

Figure 5: Vapor ClF$_3$ Exposure to Polyethylene Tubing, Clean and Used

6.2 Most Violent Test Result – "Bunny Suit" Explosion

The most severe reaction occurred with the Tyvek® suit material. Tyvek® is routinely employed as the material for cleanroom garments at semiconductor facilities, which is sometimes referred to as a "bunny suit". The liquid ClF$_3$ did not react to Tyvek®, however, it started to soak into the material forming a well-mixed fuel-oxidizer explosive mixture. A simple drop of water caused the saturated material to detonate and damage the liquid testing rig. This explosion result was of great concern to Air Products since it is feasible a worker handling ClF$_3$ could accidentally spill some liquid onto their PPE which would permeate into the material. This would cause the worker to feel an immediate irritation/burning in the exposed area and workers are typically trained to immediately go under a safety shower.

However, to protect workers exposed to liquid ClF$_3$ spills from serious reactions and chemical burns they must be trained to first remove exposed clothing before stepping into a safety shower.

6.3 Exposure Results with Water

As expected, the reaction of ClF$_3$ with water was vigorous, producing considerable heat. In one test where liquid ClF$_3$ is dripped onto a small pool of water there was no sound, just the immediate disappearance of the water puddle. Vapor ClF$_3$ that was passed above the liquid water surface actually reacted with a prominent sound.

6.4 Importance of System Purging

Even trace amounts of chlorine trifluoride remaining in a tube that was not purged properly were sufficient to cause immediate reactions. Samples of steel wool, Tyvek®, and paper were against the end of a tube containing residual traces of ClF$_3$ vapor and the gas diffusing from the tubing caused an immediate reaction (Figure 6). This was also

evident in the chicken tests where brief flashes were noticed in the tubing outlet, probably due to vaporized chicken fat severely reacting with the residual ClF_3 vapor.

Figure 6: Residual Vapor Exposure on Steel Wool and Tyvek® Suit

6.5 Vapor Versus Liquid Reactivity

As expected, liquid ClF_3 exposure was much more reactive than gas exposure. Chlorine trifluoride is a low pressure, liquefied gas which can easily condense in a system. If a system leak should then develop, the resulting liquid drip onto clothing or another surface can cause an immediate and violent reaction.

6.6 Exposure Test Results on Fuels

As a powerful oxidizer, liquid ClF_3 reacts immediately with any fuel, such as oil or fat. The most visually dramatic test was the liquid chlorine trifluoride exposure onto a piece of raw chicken. This test was conducted to observe the approximate reaction of ClF_3 contact on exposed skin. In slow motion on the video you can see the liquid contact the skin and immediately react dispersing smaller ClF_3 droplets around the point of contact area in a donut pattern. Even the gas release onto a piece of raw chicken created a very loud and intense flame (Figure 7).

Figure 7: Vapor and Liquid Release on Raw Chicken

Vapor Exposure

Liquid Drop First Contact

Liquid Splatter and Sparking

The reaction with asphalt was as expected. Two of the three liquid tests produced detonation of the asphalt sample. Operators who have worked with ClF_3 have reported that leaking cylinders can sometimes sound like firecrackers going off every few minutes due to the liquid drops contacting the ground. In the design of a ClF_3 system, one must insure that there are no combustible materials on the floor surface in the vicinity of the system.

6.7 Exposure Tests with No Reaction

The testing team was surprised to find no significant reaction with the concrete or cinder block samples, even when they were wetted with water. These results are in conflict with what is reported in certain literature. However, just because a reaction did not occur with certain materials (especially some organics), the same materials may ignite and react vigorously given enough energy or quantity of exposed liquid. For

example, the clean polyethylene bag did not immediately react with liquid exposure until some of the puddled liquid contacted a contaminant on the Teflon block securing the bag. Once ignited, the bag burned intensely and completely. Also, if the drop height for liquid contact was much higher, more energy would be imparted to the surface and an immediate reaction might have initiated with certain organic samples.

6.8 Final Exposure Testing Conclusions

In conclusion, the Air Products' testing has demonstrated and confirmed that chlorine trifluoride is a very reactive material in both vapor and liquid phases. Manufacturers, consumers, and emergency responders working with ClF_3 should make absolutely sure that the systems and PPE they use are meticulously clean and that all personnel are very familiar with the hazards of ClF_3.

As a direct result of this testing, Air Products has made significant changes to our Chlorine Trifluoride MSDS. Also, Air Products has developed and conducted a special two-hour training session for all of our employees and customers handling ClF_3.

7. ACKNOWLEDGEMENTS

8. REFERENCES

[1] *Advances in Fluorine Chemistry, Volume 1*, Butterworth's Scientific Publication, 1960.

[2] *Handling Hazardous Materials, Technology Survey SP-5032*, Washington, D.C.: National Aeronautics and Space Administration, Technology Utilization Division.

[3] Clark, John D., *Ignition! An Informal History of Liquid Rocket Propellants*, New Brunswick, NJ: Rutgers University Press.

[4] Gugliemini, Carmen J., *Chlorine Trifluoride Technical Data, Safety and Handling*, Allentown, PA: Air Products and Chemicals, Inc., 1997.

[5] Gugliemini, Carmen J. and Johnson, Andrew D., *Properties and Reactivity of Chlorine Trifluoride*, Semiconductor International Journal, June 1999.

[6] *Loss Prevention Data 7-7, Semiconductor Fabrication Facilities 17-12*, Factory Mutual Engineering Corp., 1997.