# DuPont™ Zyron®
electronic gases

# DuPont™ Zyron® $NF_3$ Semiconductor Process Gas

## Properties, Uses, Storage, and Handling

### Background

As part of DuPont's new generation of environmentally friendly alternatives for CVD chamber clean, DuPont™ Zyron® $NF_3$ is available commercially for semiconductor and electronic applications. $NF_3$ is available in a variety of grades and purity levels.

Nitrogen Trifluoride or $NF_3$ is a toxic, compressed gas without color or odor. It is not flammable, but is a strong oxidizer.

This fluorinating agent is used extensively in the semiconductor and electronics industries due to its higher etch rates, cleaner processing, and lower PFC emissions. $NF_3$ can be handled more easily relative to Fluorine gas. **Table 1** lists the physical and chemical properties of $NF_3$.

### Safety

Users of Zyron® $NF_3$ should read and understand the DuPont Material Safety Data Sheet (MSDS). Copies of a Zyron® $NF_3$ MSDS can be obtained from DuPont Customer Service or DuPont Zyron® web (see last page of this document for detailed information)

#### *Skin and Eye Contact*

At room temperature, $NF_3$ vapors have little or no effect on the skin or eyes. However, under different circumstances, $NF_3$ may fluorinate skin oils, thereby increasing the potential for dermal absorption. If contact does occur, thorough cleansing of the skin is advisable.

Always wear protective gear such as leather gloves and face shield whenever there is a risk of exposure to $NF_3$.

**Table 1. Chemical and Physical Properties**

| | |
|---|---|
| Chemical name | Nitrogen Trifluoride |
| CAS No. | 7783-54-2 |
| Molecular Wt. | 71.002 |
| Triple Point °C (°F) | –206.69 (–340.0) |
| Boiling Point, 1 atm, °C (°F) | –129.06 (–200.3) |
| Melting Point °C (°F) | –206.69 (–340.0) |
| Flammable limits in Air (1 atm) | none |
| Critical Temperature °C (°F) | –39.15 (–38.5) |
| Critical Pressure, kPa (psia) | 4461 (647) |
| Critical Density, Kg/m$^3$ (lb/ft$^3$) | 597.9 (37.3) |
| Specific Gravity (70°F; 14.7 psia; Air=1) | 2.42 |
| Specific Volume (70°F) m$^3$/Kg (ft$^3$/lb) | 0.339 (5.43) |
| Liquid Density @ –135 °C (–211°F) Kg/m$^3$ (lb/ft$^3$) | 1583.53 (98.86) |
| Vapor Density @ 21°C, 1 atm, Kg/m$^3$ (lb/ft$^3$) | 2.95 (0.18) |
| Specific Heat, Liquid (Cp) @ –135°C (–211°F), Kj/Kg K (Btu/lb °F) | 1.148 (0.274) |
| Specific Heat, Vapor (Cp) @ 21°C (70°F) 1 atm, Kj/Kg K (Btu/lb °F) | 0.746 (0.178) |
| Thermal conductivity, vapor @ 21°C (70°F), W/m-K (Btu/hr-ft °F) | 0.018 (0.0102) |
| Ozone Depletion Potential | none |
| Global Warming Potential, GWP (100 yr ITH, for $CO_2$, GWP=1) | 10800 |
| Atmospheric Lifetime, years** | 740 |
| TSCA–Reported/Included** | Yes |
| Toxicity, AEL* vol/ppm | 2 |

*AEL (Acceptable Exposure Limit) is the inhalation exposure limit assessment established by DuPont continuous exposure, 8-to 12- hour day

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### *Inhalation Toxicity*

Zyron® $NF_3$ is safe when used in accordance with DuPont's recommendations. However, exposure to excessive amounts of $NF_3$ through inhalation can lead to the conversion of hemoglobin to methemoglobin. Since hemoglobin is needed to transport oxygen to tissues, the shortage of hemoglobin will induce headache, weakness, development of a bluish skin color, and other typical effects associated with lack of oxygen. Destruction of red blood cells and chemical asphyxiation may occur after prolonged exposure to high concentrations of this gas, with secondary effects that may include hemolytic anemia, enlargement of the spleen, and pathologic changes in the liver, kidneys, and heart.

A person experiencing any of the initial symptoms should be moved to fresh air and kept calm. Oxygen should be administered as soon as possible to victims of acute $NF_3$ poisoning. Only trained personnel should administer supplemental oxygen and resuscitation. A physician should administer a follow-up examination.

Once an overexposed person breaths fresh air, methemoglobin reverts back to hemoglobin, but monitoring should be done for possible secondary effects of anemia and impaired kidney function.

### *Toxicity Data*

**Table 2. Exposure Limits for $NF_3$**

| | |
|---|---|
| PEL (OSHA) : | 10 ppm, 29 mg/m³, 8 Hr. TWA |
| TLV (ACGIH) : | 10 ppm, 29 mg/m³, 8 Hr. TWA |
| AEL* (DuPont) : | 2 ppm, 8 & 12 Hr. TWA |

* AEL is DuPont's Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence.

Differences in acceptable $NF_3$ workplace exposure standards have not yet been reconciled. The differences are not based on the source or manufacture of $NF_3$; rather, They are based on the fact that the DuPont 2 ppm level was set using recently generated toxicity testing data, which was not available at the time the 10 ppm level was established. In the recent tests, toxicity was observed at the 50 ppm (90-day) exposure level and no toxicity was observed at the 20 ppm level. In light of the newly generated $NF_3$ toxicity data, the DuPont Company established a 2 ppm allowable exposure level to protect $NF_3$ workers from adverse effects.

**Table 3. DuPont's Emergency Exposure Limits (EEL) for $NF_3$ in air.**

| Time of Exposure (min) | Concentration (ppm) |
|---|---|
| 0-1 | 1600 |
| 2-10 | 800 |
| 11-60 | 400 |

Emergency Exposure Limits are to be used for emergency planning purposes only. They should not be confused with AEL or ACGIH TLV values that are designed for repeated, safe exposures. If an EEL is exceeded at any time, evacuation, sheltering in place, or other mitigating steps should be taken.

The $NF_3$ 1-hr inhalation LC50 in rats is 6,700 ppm. Tests have shown that $NF_3$ does not cause genetic damage in bacterial or mammalian cell cultures. It has not produced genetic damage in laboratory animals. $NF_3$ did not produce developmental toxicity in a pilot rat developmental toxicity test. No adverse reproductive organ effects were observed after a 90-day exposure to 100 ppm $NF_3$. No data are available to define the carcinogenic hazards of $NF_3$.

## Flammability

$NF_3$ is non-flammable, but it will vigorously support combustion of other materials. $NF_3$ increasingly acts as a strong oxidizer at elevated temperatures. Some of the hazardous combustion products include hydrogen fluoride and other toxic fluoride compounds.

The U.S. Department of Transportation labels $NF_3$ 2.2, 5.1 with an identification number UN2451. The 5.1 label defines $NF_3$ as an oxidizer, a material that may cause or enhance the combustion of other materials. Label 2.2 defines the substance as a non-flammable, nonpoisonous compressed gas. The US Department of Transportation uses the ASTM method to test and classify the flammability of substances.

Do not use Halon 1301, dry ammonium phosphate, or bicarbonate on $NF_3$ fires because they produce toxic by-products.

When fighting a small $NF_3$ fires, use carbon dioxide extinguishers. When extinguishing fires covering a large area, use copious amounts of water. Either water or carbon dioxide may help cool area and limit formation of reactive thermal breakdown products such as fluorine

## Stability and Reactivity

At room temperature and atmospheric pressure, $NF_3$ is slightly, if at all, reactive. Temperatures above 200°C (392°F) should be avoided for any process, since the oxidizing capability of nitrogen trifluoride is greatly enhanced at these temperatures. This dissociation into reactive fluorine species can lead to uncontrolled reactions with polymers, metals, and other materials.

Conditions where inadvertent heating of $NF_3$ could occur should be avoided. Such heating can, for example, occur from adiabatic compression. Adiabatic compression occurs when high pressure $NF_3$ is rapidly introduced into a low pressure space. The rapid recompression of $NF_3$ can produce a rise in temperature sufficient to dissociate $NF_3$.

$NF_3$ is often used in concert with other gases in the processing of semiconductors. Potential interactions between $NF_3$ and any such process gases/materials need to be considered prior to use. For example, $NF_3$ and silane can form a flammable and potentially explosive mixture.

$NF_3$ is not compatible with other hydrocarbons, oil, grease and plastics.

## Environmental Matters

$NF_3$ is a non-ozone depleting perfluorocompound.

$NF_3$ has a Global Warning Potential ($CO_2$=1) of 10800 (100yr ITH) and a short atmospheric lifetime of 740 years.

$NF_3$ does not react with water under normal conditions, so the environmental hazard of a leak at sea or bodies of water is minimal. It is not listed as a marine pollutant by DOT in proposed rulemaking (49 CFR, HM-211.)

## User Safety and Handling

Users should provide ventilation and/or local exhaust to prevent accumulation of nitrogen trifluoride in excess of allowable workplace exposure limits.

When handling this gas, wear safety glasses. A SCBA or positive pressure airline with mask in areas should be worn whenever the $NF_3$ concentration is above allowable workplace exposure limits. Avoid contact with eyes and inhalation of vapors in excess of allowable workplace exposure limits. Keep away from heat, sparks and flame.

Leather work gloves and safety shoes should be worn when handling cylinders. Leather gloves and face shield should always be used when connecting, disconnecting, or opening cylinders, or whenever the possibility for contact exists.

Leaks occurring at the cylinder valve's pressure relief device, diaphragms, valve to the cylinder, etc cannot be repaired while the cylinder still contains material under pressure. Attempts to repair such leaks on cylinders under pressure may result in catastrophic failure of the container or fittings.

## Material Compatibility

Nitrogen trifluoride is incompatible with plastics, oil, grease, other hydrocarbons and organic materials.

Nitrogen trifluoride is compatible with metals such as stainless steel and Monel®

Most metals will react with $NF_3$ at temperatures in excess of 300°C. Temperatures above 300°C (575°F) should be avoided for any process, since the oxidizing capability of nitrogen trifluoride is greatly enhanced at these temperatures. All components in a system should be free of water, grease, oil, and other contaminants. These can significantly affect the corrosion resistance and compatibility of many metals. Any equipment that uses nitrogen trifluoride should be thoroughly cleaned, rinsed with solvent, and purged dry with an inert gas.

Nitrogen trifluoride is compatible with Teflon®, Viton®, Kel-F®, and Neoflon®. It is not compatible with hydrocarbon lubricants.

## Monitors

DuPont recommends $NF_3$ specific detectors since $NF_3$ has no discernible odor. As previous sections on toxicity issues states, prolonged or acute $NF_3$ exposure should be avoided. Vendors provide monitors using different technologies to detect $NF_3$ concentrations down to 2 ppm volume percent.

Vendors of these instruments include:

ATMI Life Safety
P.O. Box 4284
Portsmouth, NH 03802
Tel: (603) 433-0905

CEA Instruments, Inc.
16 Chestnut Street
Emerson, NJ 07630
Tel: (201) 967-5660

Scott Instrument c/o
North East Technical Sales
402 Gordon Drive
Exton, PA 19341

Thermo Environmental Instruments
8 West Forge Parkway,
Franklin, MA 02038
Tel: (508) 520-0430

Zellweger Analytics, Inc.
405 Barclay Blvd
Lincolnshire, IL 60069
Tel: (800) 323-2000

## Containers and Cylinders

Use DuPont specified cylinders only. Follow the cylinder return instructions. Contact DuPont Customer Service for detailed information (refer to the last page of this document for contact information)

## General Safeguards

Handlers of $NF_3$ should follow these guidelines:

- Wear safety glasses, leather work gloves, and safety shoes when handling cylinders.
- Cylinders may contain pressure as high as 1500 psig. Secure the cylinder at all times while in use and always open valve slowly.
- Storage area temperatures should not exceed 52°C (125°F) and should be free of combustible materials.
- Avoid conditions that can result in high temperatures, such as adiabatic compression of any kind.
- Fast opening of valves can potentially cause adiabatic compression, raising the temperature dangerously. Rapid-opening valves such as ball valves should not be used in a $NF_3$ closed system. They should only be used as isolation valves.
- Valves used for $NF_3$ should be opened slowly to prevent adiabatic compression.
- Cylinders should be secured in an upright position and stored in a well-ventilated area protected from the weather. Cylinder connections should be protected from straining and movement.
- Do not heat $NF_3$ cylinders with any source of heat.
- Storage should be away from heavily traveled areas and emergency exits.
- Avoid areas where salt or other corrosive materials are present. Valve protection caps and valve outlet seals should remain on cylinders not connected for use. Separate full from empty cylinders. Avoid excessive inventory and storage time.
- Use a first-in first-out system. Keep accurate inventory records. Always store and handle compressed gases in accordance with Compressed Gas Association (phone: 703-412-0900).

**CAUTION**: Compressed gas cylinders should not be refilled except by qualified producers of compressed gases. Shipment of a compressed gas cylinder which has not been filled by the owner or with the owner's written consent is a violation of federal law.

- Do not attempt purification of $NF_3$ via adsorption.
- Stainless steel is recommended for low-pressure applications.
- Teflon® and Kel-F® materials are acceptable for $NF_3$ service.
- Grease, oil, and other contaminants must not be present on any surface in contact with $NF_3$.
- High-pressure systems should be managed remotely and by personnel wearing appropriate personal protective equipment.
- When high gas temperatures are expected, fabs should avoid the use of plastics or polymers in contact with $NF_3$.

**For further information:**

DuPont Fluorochemicals
Wilmington, DE 19880-0711
www.dupont.com/zyron

**Emergency Response:**

Within US: +1 800-441-3637
Outside US: (302)-774-1000

**Product Safety Information:**

+1 (800) 441-7515

**Customer Service:**

+1 (800) 969-4758



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