

DuPont Fuel Cells

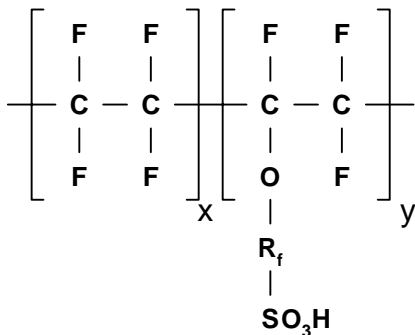
Safe Handling and Use of Perfluorosulfonic Acid Products

Introduction

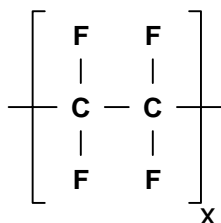
The purpose of this brochure is to provide guidelines for the safe handling and use of DuPont™ Nafion® PFSA products. The complete contents should be reviewed before Nafion® PFSA products are processed or used at elevated temperatures. Refer to the "Fluoropolymers Safe Handling Guide" published by The Society of the Plastics Industry, for general background on fluoropolymer resins.

Nafion® PFSA products are fabricated from a copolymer of tetrafluoroethylene and perfluorinated monomers containing sulfonic acid groups. The safety considerations for these membranes are based on the thermal and combustion decomposition products of the copolymer.

The perfluorinated products are composed of a carbon-fluorine backbone with perfluoro side chains containing sulfonic acid groups. The chemical structure is shown below:



The analogous structure for Teflon® PTFE Fluoropolymer resins is:



The Nafion® PFSA products have the extraordinary chemical and thermal stability of DuPont™ Teflon® fluoropolymer resins. While Teflon® resin is one of the most hydrophobic substances known, Nafion® perfluorosulfonic polymers is one of the most hydrophilic. It will absorb water and some polar organics rapidly, even at room temperature, in amounts dependent upon the number of sulfonic acid groups. Whereas Teflon® resin is chemically inert, the Nafion® PFSA polymer is a strong polymeric acid, which reacts with organic and inorganic bases. However, the sulfonic acid groups in the polymer are essentially immobile and immersed in a fluoropolymer matrix. Consequently, membranes can contact the skin without producing irritation.

Since the development of Nafion® PFSA polymer, several thousand kilograms have been used in many applications. During this time, there have been no reported cases of injury resulting from handling or exposure to these products.

Ingestion

The perfluorosulfonic acid copolymers used in Nafion® membranes exhibit very low acute toxicity when administered in oral doses to rats. The LD50s are greater than 20,000 mg/kg of body weight.

Skin Contact

When tested on rabbits, perfluorinated sulfonic acid copolymers used in Nafion® membranes were not irritating to the skin. Tests designed to determine the skin irritation and sensitization potential of these materials was also conducted with human volunteers. The results indicated that no unusual dermatitis hazard could be expected in the normal use of membranes for non-apparel industrial applications. Prolonged contact, however, may be irritating to the skin of certain individuals.

Nafion® at High Temperatures

Almost without exception, the fumes from decomposing materials, such as Nafion®, Teflon®, and other plastics in high-temperature environments are objectionable from the standpoint of health and safety. However, Nafion® PFSA polymer and other fluoropolymers are more resistant to decomposition at higher temperatures than most other thermoplastics. The maximum continuous operating temperature of Nafion® perfluorinated sulfonic acid copolymer is about 175°C in anhydrous systems. In aqueous and organic systems with proton-donating solvents, the maximum temperature is higher; for example, stability in aqueous systems at 220° to 240°C has been demonstrated for several days.

Polymer Fume Fever

Exposure to thermal decomposition products of Nafion® PFSA polymer may cause a temporary flu-like condition. The symptoms do not ordinarily occur until several hours after exposure, and pass within 24 to 48 hours, even in the absence of treatment. Observations indicate that for other fluoropolymer resins these attacks have no lasting effect, and the effects are not cumulative. These attacks would be expected to occur after exposure to vapors evolved from the polymer at temperatures above 250°C or from smoking cigarettes or tobacco contaminated with the polymer.

Thermal Degradation Products

Using the standard Infrared Analysis of Thermal Effluents (IRATE) technique developed by DuPont, the composition of the effluent from perfluorinated sulfonic acid copolymer was determined at the following conditions: the atmosphere was air, flow rate 13 ml/min, sample size 0.5 g. The sample heated in a stainless steel tube a 10°C/min to 200°C, and then 5°C/min to 400°C and held for an additional 20 minutes, giving a total run time of about 75 minutes. The results are shown below:

Degradation Products of Perfluorosulfonic Acid Copolymer

Compound	Evolution Temp., °C	Mg/g Sample
SO ₂	280	15
CO ₂	300	30
HF	400	— *
CO	400	3
R _f COF	400	10 **
COF ₂	400	3
COS	400	Trace
R _f OH	400	Trace

* Significant level but could not calculate because HF reacts with and absorbs on cell walls.

** Mixture of products.

Repetitive IR scans of the effluent gave the approximate evolution temperature for each product while amounts were determined by collecting air in a 1-meter IR cell and examining its spectrum.

Ventilation Recommendations When Heating Nafion® PFSA Membranes

Nafion® PFSA membranes are not suitable for melt processing. Thermal decomposition begins before the membranes become fluid enough for shaping. However, at times it is desirable to heat seal films and laminates to form tubes, pockets, etc. In heat sealing, temperatures in the range of 300°C are encountered for brief intervals, and only a small amount of material is exposed to the decomposition temperature.

When Nafion® PFSA membranes are exposed or used at elevated temperatures, good safety practice requires the use of adequate ventilation to prevent inhalation of irritating and toxic fumes and gases that may evolve. Normal ventilation required for personnel in work areas may not be sufficient for all operations.

Therefore, it is recommended that a local exhaust ventilation system, in addition to normal ventilation, be used whenever Nafion® PFSA membranes are heated above 150°C in the work area. Strict adherence to this practice will prevent discomfort or injury to personnel.

Flammability

Nafion® PFSA membranes will not burn in air but will burn in environments that are highly oxygen-enriched. The limiting oxygen index (LOI), as measured by the "candle test" (ASTM D2863-77), is 95%.

As a fuel, Nafion® PFSA membranes have a comparatively low rating. Heat of combustion is about 5.8 MJ/kg (2,500 Btu/lb) compared to 46 MJ/kg (20,000 Btu/lb) for polyethylene.

Questions may arise concerning fire hazards associated with the storage of Nafion® PFSA membranes. In essentially all situations, whether in storage or use, the quantity of Nafion® PFSA polymer involved is so small in proportion to other materials that its presence is unlikely to add appreciably to other hazards attendant to a fire. Bulk quantities (over 50 kg) should be stored away from flammable materials.

In the event of fire, temperatures may rise above the decomposition temperature of Nafion[®] PFSA polymer, thus liberating hydrogen fluoride and other volatile fluoropolymers. Under these conditions, personnel entering the storage or use area should wear self-contained breathing apparatus and full protective equipment to minimize contact with the skin. This type of equipment is standard in fighting many types of fires. All types of chemical extinguishers may be used to fight fires involving Nafion[®] PFSA polymer. Large quantities of water may also be used to cool and extinguish the fire.

Additional Safety Information

The following information should be reviewed before handling and processing Nafion[®] PFSA products:

- DuPont Material Safety Data Sheet for the specific product.
- "Guide to Safe Handling of Fluoropolymer Resins", Fourth Edition, November 2005, Published by the Fluoropolymers Division of the Society of the Plastics Industry, Inc.

Waste Disposal

The preferred method of waste disposal of Nafion[®] PFSA polymer is landfill in compliance with government regulations. Nafion[®] PFSA polymer is not biodegradable, contains no extractable material, and is unaffected by exposure to sunlight, seawater or fresh water.

An alternative method is incineration. Small quantities of Nafion[®] PFSA polymer, up to ten pounds at a time, can be incinerated along with general plant refuse if special precautions are followed. Incineration of Nafion[®] PFSA polymer above 800°C in the presence of normal organic refuse produces sulfur dioxide, hydrogen fluoride, and carbon dioxide. Hydrogen fluoride causes eye and nose irritation before approaching systemic toxic levels, and may also affect certain vegetation. Therefore, to reduce hydrogen fluoride concentration to an acceptable amount (less than 1 part per billion at ground level), the incinerator should have alkaline scrubbing facilities.

For information about product offerings from DuPont Fuel Cells, contact:

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The data listed here fall within the normal range of product properties, but they should not be used to establish specification limits nor used alone as the basis of design. This information is based on technical data that DuPont believes to be reliable. It is intended for use by persons having technical skill and at their own discretion and risk. This information is given with the understanding that those using it will satisfy themselves that their particular conditions of use present no health or safety hazards. Because conditions of product use are outside our control, DuPont makes no warranties, express or implied, and assumes no obligation or liability in connection with any use of this information or for results obtained in reliance thereon. The disclosure of the information is not a license to operate under or a recommendation to infringe any patent of DuPont or others.

Caution: Do not use in medical applications involving permanent implantation in the human body. For other medical applications, see "DuPont Medical Caution Statement", H-50102.