Nafion™
Ion Exchange Materials

Safety in Handling and Use

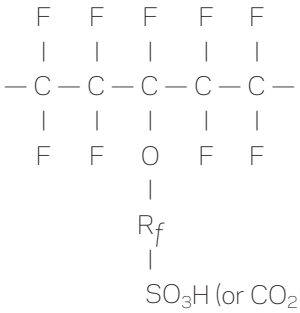
Technical Information

Introduction

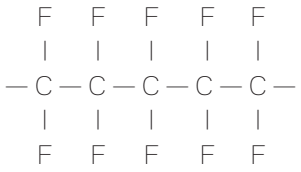
The purpose of this technical bulletin is to provide guidelines for the safe handling and use of Nafion™ perfluorinated membranes from Chemours. The complete contents should be reviewed before Nafion™ membranes are processed or used at elevated temperatures. For general background on fluoropolymer resins, reference can be made to the "Fluoropolymers Safe Handling Guide" —published by The Society of the Plastics Industry.

Nafion™ perfluorinated membranes are fabricated from copolymers of tetrafluoroethylene and perfluorinated monomers containing sulfonic acid end groups or from copolymers containing both sulfonic acid and carboxylic acid groups. The safety considerations for these membranes are based on the thermal and combustion decomposition products of the copolymers.

The perfluorinated membranes are composed of carbon-fluorine backbone chains 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™ perfluorinated membranes have the extraordinary chemical and thermal stability of Teflon™ resins. While Teflon™ resin is one of the most hydrophobic substances known, Nafion™ membranes are one of the most hydrophilic. They absorb water and some polar organics rapidly, even at room temperature, in amounts dependent upon the number of sulfonic and carboxylic groups. Whereas Teflon™ resin is chemically inert, the Nafion™ membranes are strong polymeric acids, which react with organic and inorganic bases. However, the sulfonic and carboxylic 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 perfluorinated membranes, 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 perfluorinated sulfonic 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™ 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 (347 °F) in anhydrous systems. In aqueous and organic systems with proton-donating solvents, the maximum temperature is higher; for example, stability in aqueous systems at 220–240 °C (428–464 °F) has been demonstrated for several days.

The perfluorinated carboxylic acid copolymer, as used in the Nafion™ 900/2000 series, is less resistant to elevated temperatures; however, Nafion™ membranes containing perfluorinated carboxylic acid copolymer are intended primarily for use below 120 °C (248 °F).

Fumes should present no problems, except during heat sealing operations.

Polymer Fume Fever

Exposure to thermal decomposition products of Nafion™ perfluorinated membranes 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 (482 °F) or from smoking cigarettes and/or tobacco contaminated with the polymer.

Thermal Degradation Products

Using a standard Infrared Analysis of Thermal Effluents (IRATE) technique, 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 at 10 °C (18 °F)/min to 200 °C (392 °F), and then 5 °C (9 °F)/min to 400 °C (752 °F) and held for an additional 20 min, giving a total run time of about 75 min. The results are shown below:

Degradation Products of Sulfonic Acid Copolymer

Compound	Evolution Temperature, °C (°F)	Mg/g Sample
SO_2	280 (536)	15
CO_2	300 (572)	30
HF	400 (752)	*
CO	400 (752)	3
R_fCOF	400 (752)	10**
COF_2	400 (752)	3
COS	400 (752)	Trace
R_fOH	400 (752)	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. The perfluorinated carboxylic copolymer used in the Nafion™ 900/2000 series was studied by IRATE using an atmosphere of nitrogen and heating from 250–450 °C (482–842 °F) at 5 °C (9 °F)/min. Decomposition began at approximately 320 °C (608 °F) and yielded mainly CO_2 plus some CO, tetrafluoroethlyene, hexafluoropropylene, and hydrogen fluoride. Stability is reduced, however, in air. Differential thermal analysis detects decomposition in air at 150 °C (302 °F), yielding a product identified by mass spectroscopy as CO_2 (decarboxylation).

Ventilation Recommendations When Heating Nafion™ Perfluorinated Membranes

Nafion™ perfluorinated 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 (572 °F) are

encountered for brief intervals, and only a small amount of material is exposed to the decomposition temperature.

When Nafion™ perfluorinated membranes are exposed or used at elevated temperatures, good safety practice requires the use of adequate ventilation to prevent inhalation of irritating, 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™ is heated above 150 °C (302 °F) in the work area. Strict adherence to this practice will prevent discomfort or injury to personnel.

Flammability

Nafion™ perfluorinated 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™ perfluorinated 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™ perfluorinated membranes. In essentially all situations, whether in storage or use, the quantity of Nafion™ material 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™; 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™. Large quantities of water may also be used to cool and extinguish the fire.

Waste Disposal

The preferred method of waste disposal of Nafion™ perfluorinated products is landfill in compliance with government regulations. Nafion™ materials are not biodegradable, contain no extractable material, and are unaffected by exposure to sunlight, seawater, or fresh water. An alternative method is incineration. Small quantities of Nafion™ materials, up to 10 lb at a time, can be incinerated along with general plant refuse, if special precautions are followed. Incineration of Nafion™ materials above 800 °C (1472 °F) 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.