NOTES

The Toxicity of Thermolysis Products of Spacecraft Elastomers

The polymer industry has developed a variety of fluorocarbon elastomers to fulfill the rigid specifications set forth by the needs of the space program. Although noncombustible, the fluorocarbons will degrade at elevated temperatures, producing the monomer, water, some CO, CO_2, and various toxic gases, among which are carbonyl fluoride and perfluoroisobutylene. Information on the toxicity of the complex mixture of thermolysis products of these elastomers is limited at ambient pressures[1-3] and practically nonexistent under spacecraft conditions (250 torr O_2). Therefore, the following study was completed to compare the relative toxicities of the thermolysis products of several of the spacecraft elastomers which have already fulfilled the physical characteristics specifications.

The toxicity of a proprietary formulation of the copolymer of vinylidene fluoride and perfluoropropylene, called Refset Fluorel, was compared to that of raw Fluorel (containing no additives), Redar Viton (a different formulation of the same copolymer), and Clear Teflon FEP Film (a copolymer of perfluoroethylene and perfluoropropylene).

The elastomer samples were thermolyzed at 600°C in a 304 stainless steel tube containing oxygen (at a pressure of 250 torr and at a flow rate of 2 liters/min). The thermolysis products were introduced directly into a 142-liter Bethlehem exposure chamber containing ten 140- to 160-g Manor Farm rats. A small fan was used to facilitate mixing. Twenty-three controlled exposures were completed. Table I depicts the results of the 30-min exposures to the thermolysis products of each of the various elastomers. Deaths were counted at three days. Initial trials had shown that no acute deaths occurred in 30 animals after a three-day period (held for 14 days).

The cause of death in all cases was asphyxia, which resulted directly from an immediate or delayed edema in the lung. The amount of lung edema was, in general, found to be dose dependent. In serial sacrifices done on 40 rats at higher doses, edema was found immediately following exposure. At lower doses, edema formation was delayed 4 to 20 hr after exposure. Histological findings correlated well with observations made at autopsy. The tissue damage found was in the bronchi, bronchioles, and alveoli, in every case. No abnormal conditions were found in muscle, brain, gastrointestinal tract.

The characteristic perivascular "cuffing" of the lymphatic vessels in the lung was seen in all animals, even when the animal was sacrificed three days after exposure. Cellular

TABLE I
Toxicity Results

Elastomer tested	Largest dose which caused no death, g	Lowest dose which caused 10/10 deaths, g
Refset Fluorel	22.5 (10 exposures)	30
Raw Fluorel	5 (6 exposures)	7
Redar Viton	2 (5 exposures)	5
Clear Teflon Film (FEP)	2 (5 exposures)	5

damage in the liver and the kidneys was also observed following the Clear Teflon Film thermolysis exposures, but was not seen following Fluorel or Viton exposures. The damage seen was not considered sufficient to be the cause of death in any case, however.

In order to examine the role of carbon monoxide, ten rats were exposed to each of the four elastomers in Table I at the lowest dose which caused 10/10 deaths. The animals were immediately sacrificed and blood carboxy hemoglobins determined on the cooximeter. The per cent carboxy hemoglobin ranged from 15.1% to 20.6%, insufficient to be the cause of death from any of the elastomers under the conditions of the exposure.

When the Refset Fluorel was thermolyzed at 600°C, it produced 28% ash. Triplicate elemental analyses of the Refset Fluorel ash showed it to be approximately 40% magnesium (as the metal of the salt). If the salt is assumed to be magnesium oxide, this would account for approximately 70% of the total ash from Fluorel. Viton ash contained approximately 0.02% magnesium. Teflon and Raw Fluorel samples left less than 10 mg of ash after thermolysis of 5 g of elastomer.

The disparity of toxicity of Refset Fluorel from that of raw Fluorel, Redar Viton, or Clear Teflon Film can probably be accounted for by two factors: (1) The dilution of the elastomer by the magnesium salt, leaving less pure copolymer to be thermolyzed; (2) the magnesium salt may also act as a "scavenger" of reactive fluorine species such as carbonyl fluoride and HF, thus reducing the quantity of these species in the effluent, and a consequent reduction of toxicity of the Refset formulation when compared to the pure copolymer. Regardless of the mechanism, the experiments have conclusively demonstrated the lesser toxicity of the pyrolysis products of Refset Fluorel when compared to either Redar Vitan or raw Fluorel pyrolyzed under the same conditions.

This investigation was supported by Public Health Service Research Grant No. CA-11531 from the National Cancer Institute.

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Received January 10, 1973