

AD-A044 515

NAVAL SURFACE WEAPONS CENTER WHITE OAK LAB SILVER SP--ETC F/G 7/2  
NITROGEN TRIFLUORIDE: ITS CHEMISTRY, TOXICITY, AND SAFE HANDLIN--ETC(U)  
NOV 76 F J PISACANE, E BAROODY, R ROBB  
NSWC/WOL/MP-76-24

UNCLASSIFIED

NL

| OF |  
AD  
A044 515



END  
DATE  
FILMED  
11-77  
DDC

AD A044515

NSWC/WOL MP 76-24

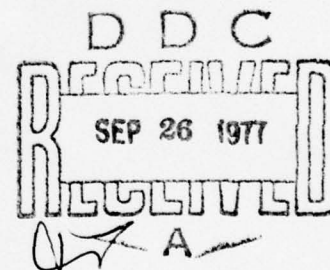
12  
B.S.

# NITROGEN TRIFLUORIDE: ITS CHEMISTRY, TOXICITY, AND SAFE HANDLING

BY FRANK J. PISACANE  
EDWARD BAROODY

RESEARCH AND TECHNOLOGY DEPARTMENT

12 NOVEMBER 1976



DDC FILE COPY



**NAVAL SURFACE WEAPONS CENTER**

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

DISTRIBUTION STATEMENT A  
Approved for public release;  
Distribution Unlimited

| REPORT DOCUMENTATION PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                 | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM                                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| 1. REPORT NUMBER<br>NSWC/WOL/MP-76-24                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 2. GOVT ACCESSION NO.                                                           | 3. RECIPIENT'S CATALOG NUMBER                                                                            |
| 4. TITLE (and Subtitle)<br>NITROGEN TRIFLUORIDE: ITS CHEMISTRY, TOXICITY,<br>AND SAFE HANDLING.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 5. TYPE OF REPORT & PERIOD COVERED<br>Summary Report,<br>Mar. 1974 - Aug. 1975. |                                                                                                          |
| 7. AUTHOR(s) Frank Pisacane, Barry Pailay,<br>Ottmar H. Dengel, William Gilligan,<br>Edward Baroody, George Wilmot,<br>Robert Robb, Anthony Rowek                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                 | 6. PERFORMING ORG. REPORT NUMBER                                                                         |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Naval Surface Weapons Center<br>White Oak Laboratory<br>White Oak, Silver Spring, Maryland 20910                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                 | 8. CONTRACT OR GRANT NUMBER(s)                                                                           |
| 11. CONTROLLING OFFICE NAME AND ADDRESS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                 | 10. PROGRAM ELEMENT, PROJECT, TASK<br>AREA & WORK UNIT NUMBERS<br>ONN; O;<br>/092-1F-SL40AA76; DN484056; |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                 | 12. REPORT DATE<br>12 November 1976                                                                      |
| 15. SECURITY CLASS. (of this report)<br>Unclassified                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                 | 13. NUMBER OF PAGES<br>25                                                                                |
| 16. DISTRIBUTION STATEMENT (of this Report)<br>Approved for public release; distribution unlimited.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                 | 15a. DECLASSIFICATION/DOWNGRADING<br>SCHEDULE                                                            |
| 17. DISTRIBUTION STATEMENT (if different from Report)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                 |                                                                                                          |
| 18. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                 |                                                                                                          |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Nitrogen trifluoride; Flammability limits; Compatibility; Corrosion;<br>Toxicity; Detection: Monitoring: Disposal: Fire-fighting                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                 |                                                                                                          |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Nitrogen trifluoride (NF <sub>3</sub> ) is the most promising near-term replacement for<br>fluorine in a DF chemical laser. Safety and compatibility characteristics<br>of NF <sub>3</sub> have been scattered through the literature since the gas was first<br>prepared by Ruff in 1928. Most of the data have been obtained to outline the<br>general chemical behavior of NF <sub>3</sub> and leave many critical safety, compatibility<br>and environmental questions unanswered. Moreover, some of the data found<br>in the literature are erroneous. As part of the Advance Reactants Program at |                                                                                 |                                                                                                          |

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

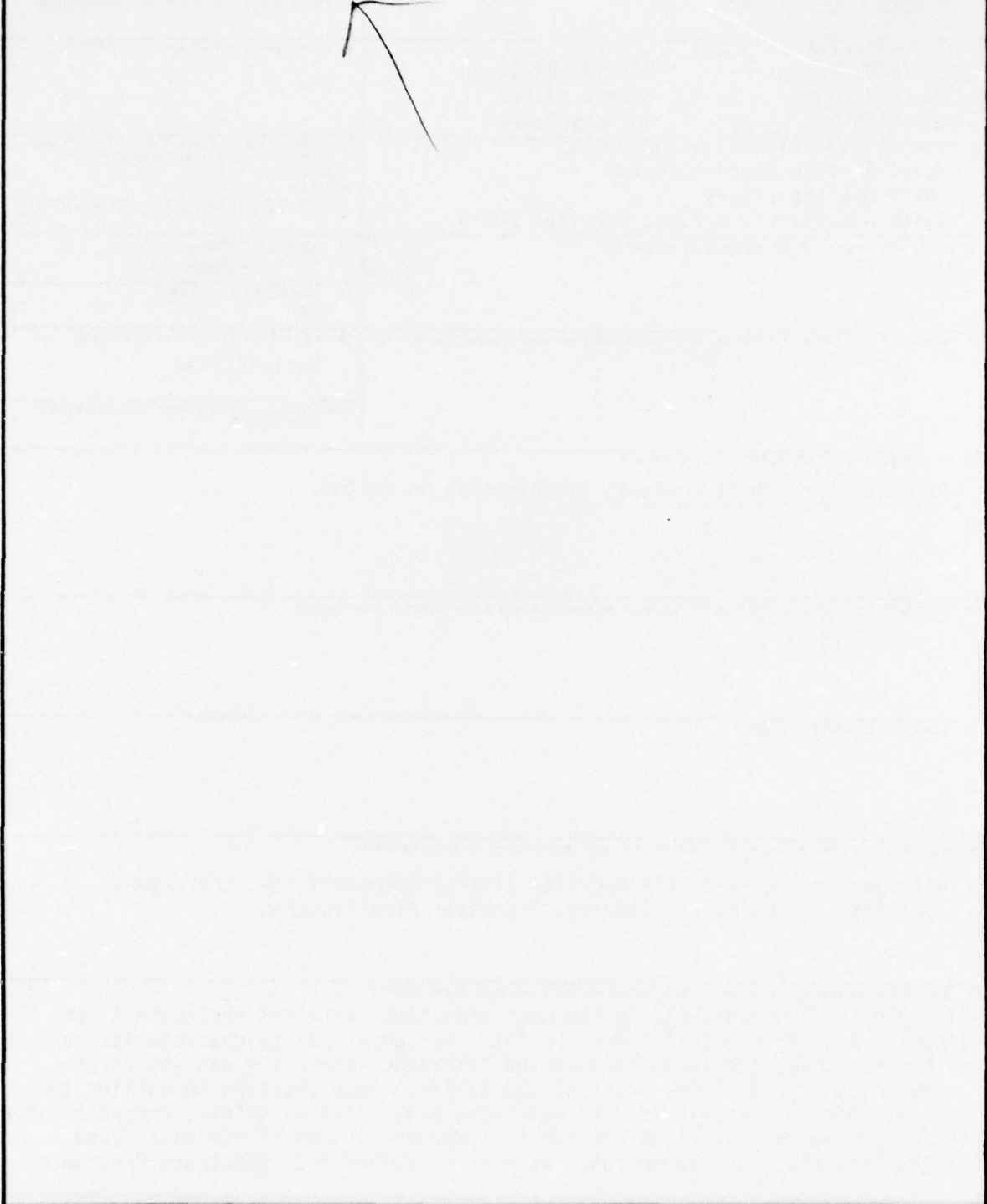
391 596

LB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

the Naval Surface Weapons Center, an experimental program was conducted to:  
(1) determine safety and compatibility characteristics of  $\text{NF}_3$  under various conditions with gases, liquids, and solids with which it might come into contact; (2) survey the available toxicity data; (3) develop adequate detection techniques; and (4) recommend safe handling, fire-fighting, and emergency disposal methods.



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

NSWC/WOL/MP 76-24

NAVSURPWPNCEN  
NITROGEN TRIFLUORIDE: ITS CHEMISTRY, TOXICITY, AND SAFE HANDLING

By  
Frank J. Pisacane  
Edward Barody  
Robert Robb  
Ottmar H. Dengel  
William Gilligan  
George Wilmot  
Anthony Rowek  
Barry Pallyay

12 November 1976

Distribution unlimited. Date statement applied 12 November 1976. Other requests for this publication must be referred to NAVSURFWPNCEN/WOL, Code WR20.

|                                 |                                                   |
|---------------------------------|---------------------------------------------------|
| ACCESSION NO.                   |                                                   |
| NTIS                            | White Section <input checked="" type="checkbox"/> |
| DOC                             | Buff Section <input type="checkbox"/>             |
| UNANNOUNCED                     | <input type="checkbox"/>                          |
| JUSTIFICATION                   |                                                   |
| BY                              |                                                   |
| DISTRIBUTION/AVAILABILITY CODES |                                                   |
| Dist.                           | AVAIL. AND/OR SPECIAL                             |
| A                               |                                                   |

NAVAL SURFACE WEAPONS CENTER  
WHITE OAK LABORATORY  
WHITE OAK, SILVER SPRING, MARYLAND 20910

CONTENTS

| <u>Heading</u>                                                                | <u>Page</u> |
|-------------------------------------------------------------------------------|-------------|
| Abstract . . . . .                                                            | iii         |
| Introduction . . . . .                                                        | 1           |
| Discussion . . . . .                                                          | 1           |
| I. Safety and Compatibility of NF <sub>3</sub> . . . . .                      | 1           |
| A. Reactions of NF <sub>3</sub> with Gases . . . . .                          | 1           |
| B. Reactions of NF <sub>3</sub> with Polymers . . . . .                       | 5           |
| C. Reactions of NF <sub>3</sub> with Metals . . . . .                         | 6           |
| II. Toxicity of NF <sub>3</sub> . . . . .                                     | 10          |
| A. Chronic Toxicity of NF <sub>3</sub> . . . . .                              | 10          |
| B. Acute Toxicity of NF <sub>3</sub> . . . . .                                | 11          |
| C. Safety Recommendations . . . . .                                           | 13          |
| III. Detectors for NF <sub>3</sub> . . . . .                                  | 14          |
| A. Non-Discriminating Detectors . . . . .                                     | 14          |
| B. Discriminating Detectors . . . . .                                         | 14          |
| IV. Fire Extinguishment . . . . .                                             | 18          |
| V. Emergency Disposal of NF <sub>3</sub> . . . . .                            | 20          |
| A. Disposal by Exhausting into Water or Venting into the Atmosphere . . . . . | 20          |
| B. Disposal by Reaction with Charcoal or Metals . . . . .                     | 20          |
| C. Disposal by Reaction with a Solid Propellant . . . . .                     | 21          |
| D. Disposal by Combustion with a Fuel . . . . .                               | 21          |
| Summary . . . . .                                                             | 22          |
| References . . . . .                                                          | 23          |

TABLES

|                                                                                            |    |
|--------------------------------------------------------------------------------------------|----|
| I. Gas Phase DTA Data for NF <sub>3</sub> Reactions . . . . .                              | 7  |
| II. Temperature (°C) Required for Metal Wires to Ignite in Oxidizing Atmospheres . . . . . | 7  |
| III. Additional Metal Ignition Temperatures . . . . .                                      | 8  |
| IV. Estimated Mass Combustion Rates (G/Sec X 10 <sup>-3</sup> ) . . . . .                  | 8  |
| V. Interfering Gases . . . . .                                                             | 17 |

FIGURES

|                                                                                                                 |    |
|-----------------------------------------------------------------------------------------------------------------|----|
| 1. Limits of Flammability of H <sub>2</sub> /NF <sub>3</sub> /N <sub>2</sub> Mixtures . . . . .                 | 3  |
| 2. Limits of Flammability of C <sub>4</sub> H <sub>10</sub> /NF <sub>3</sub> /N <sub>2</sub> Mixtures . . . . . | 3  |
| 3. Limits of Flammability of C <sub>2</sub> F <sub>6</sub> /NF <sub>3</sub> /N <sub>2</sub> Mixtures . . . . .  | 3  |
| 4. Limits of Flammability of C <sub>4</sub> H <sub>10</sub> /O <sub>2</sub> /N <sub>2</sub> Mixtures . . . . .  | 3  |
| 5. a. Absorption Band of NF <sub>3</sub> at 17.5 ppm and 1 Meter Path . . . . .                                 | 16 |
| b. Transmission of Band Pass Filter . . . . .                                                                   | 16 |
| 6. Gas Phase Infrared Detector for NF <sub>3</sub> . . . . .                                                    | 16 |
| 7. Detector Response to Various NF <sub>3</sub> Concentrations . . . . .                                        | 16 |
| 8. Intensity vs Concentration Data of Fig. 7 . . . . .                                                          | 16 |

ABSTRACT

Nitrogen trifluoride ( $\text{NF}_3$ ) is the most promising near-term replacement for fluorine in a DF chemical laser. Safety and compatibility characteristics of  $\text{NF}_3$  have been scattered through the literature since the gas was first prepared by Ruff in 1928. Most of the data have been obtained to outline the general chemical behavior of  $\text{NF}_3$  and leave many critical safety, compatibility and environmental questions unanswered. Moreover, some of the data found in the literature are erroneous. As part of the Advance Reactants Program at the Naval Surface Weapons Center, an experimental program was conducted to: (1) determine safety and compatibility characteristics of  $\text{NF}_3$  under various conditions with gases, liquids, and solids with which it might come into contact; (2) survey the available toxicity data; (3) develop adequate detection techniques; and (4) recommend safe handling, fire-fighting, and emergency disposal methods.

Approved by:

*Kurt F. Mueller*

KURT F. MUELLER  
Propellants Chemistry Branch  
Propellants Division  
Research and Technology Department  
NAVAL SURFACE WEAPONS CENTER  
WHITE OAK LABORATORY  
White Oak, Silver Spring, Maryland 20910

## INTRODUCTION

From the standpoint of safety and handling, nitrogen trifluoride ( $\text{NF}_3$ ) is the most promising near-term replacement for fluorine as a pre-combustor oxidizer in a DF chemical laser. Since  $\text{NF}_3$  was first prepared by Ruff in 1928<sup>(1)</sup>, safety and compatibility data have been scattered through the literature, but most of these data were obtained to outline the general chemical characteristics of the gas. A survey of available information on the properties and behavior of  $\text{NF}_3$  under various conditions has revealed that the reported physical and chemical data are at best incomplete. Inconsistencies exist, and some data are even incorrect. Conclusions based on these data may create hazardous situations. In addition, many critical safety, compatibility, and environmental questions remain unanswered.

As a part of the Advanced Reactants Program at the Naval Surface Weapons Center, an experimental program was undertaken to better characterize  $\text{NF}_3$  and to identify potential hazards involved in its use. Specific areas of concern were: the determination of safety and compatibility characteristics of  $\text{NF}_3$  with gases and condensed matter with which it might come into contact; the compilation and evaluation of available toxicity data; the detection and monitoring of  $\text{NF}_3$  leaks into the atmosphere; and the identification of safe handling, fire-fighting, and emergency disposal techniques.

## DISCUSSION

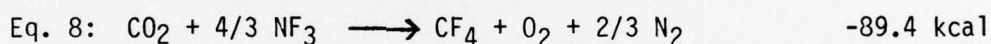
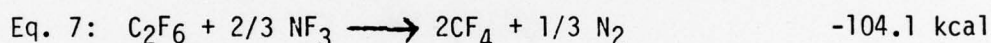
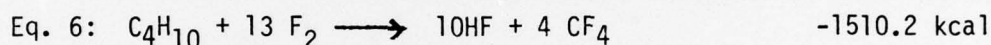
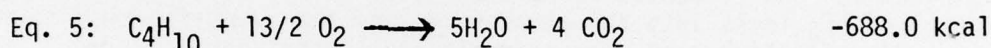
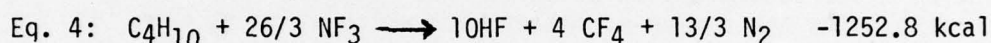
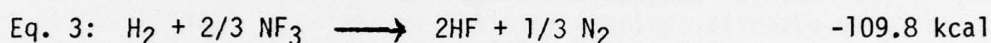
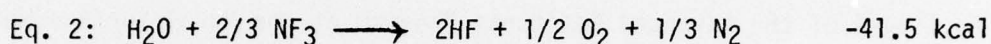
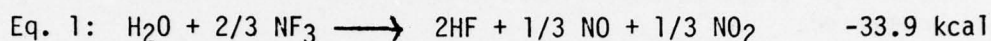
### I. Safety and Compatibility of $\text{NF}_3$

Tests were conducted to determine some of the safety and compatibility characteristics of  $\text{NF}_3$  with a variety of gases and condensed matter<sup>(2)</sup>. At room temperature  $\text{NF}_3$  appears to be relatively inert towards most materials; however, slow reactions may occur over long exposures. This relative inertness enables  $\text{NF}_3$  to mix with gaseous fuels, forming highly flammable or explosive compositions that are sensitive to spark, heat, or impact. As the temperature is increased,  $\text{NF}_3$  becomes a stronger fluorinating agent. Rapid reactions begin to occur at about 250 - 350°C. If the temperature is sufficiently high,  $\text{NF}_3$  can be expected to ignite most materials with which it comes into contact. The chemistry of its reactions is different than that of either oxygen or fluorine and caution must be taken when drawing analogies.

#### I.A. Reactions of $\text{NF}_3$ with Gases

Ruff et al<sup>(3,4)</sup> have reported that mixtures of  $\text{NF}_3$  with  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{S}$  or  $\text{NH}_3$  do not react at room temperature but explode violently when exposed to an electric discharge. Mixtures of  $\text{NF}_3$  with  $\text{ClF}$  or  $\text{SO}_2$  appeared to be inert. Water vapor and  $\text{NF}_3$  were reported to ignite when sparked and burned with a brown flame according to Equation 1; however, the reaction

shown by Equation 2 is thermodynamically more favored. Tompkins et al<sup>(5)</sup> have reported the range of flammability of NF<sub>3</sub>/H<sub>2</sub> mixtures to be from 9.4 to 95 mole percent H<sub>2</sub>. The heat released for complete fuel consumption is given in Equation 3, and the effect of adding nitrogen diluent on the flammability limits is shown in Figure 1. (In Figures 1 through 4, the shaded areas represent mixtures that will propagate combustion by either flame or explosion. The lines labeled "S" indicated stoichiometric mixtures of oxidizer and fuel.) For comparison, the range of flammability of hydrogen/oxygen mixtures and hydrogen/air mixtures are 4.0 to 96 and 4.0 to 75 mole percent hydrogen, respectively<sup>(6)</sup>. A diagram very similar to Figure 1 can be constructed for O<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> mixtures, and it is tempting to estimate that the flammability hazards of NF<sub>3</sub>/fuel mixtures are closely approximated by those of O<sub>2</sub>/fuel mixtures. Such a comparison is not valid.



At the Naval Surface Weapons Center, limits of flammability were determined for mixtures of several other gaseous fuels and NF<sub>3</sub>. The combustion chamber was a one-meter length of 10 cm I.D. clear plastic pipe, mounted vertically with a gas inlet at the top, a stirring shaft extending the length of the tube, and two 3mm diameter stainless steel electrodes at the bottom. The electrodes had a 3mm gap and were connected to a 9000 v., 13 ma power supply.

The range of flammability of n-butane/NF<sub>3</sub> mixtures was determined to be 1.5 to 75 mole percent butane and the effect of nitrogen diluent is shown in Figure 2. Most mixtures within the shaded area explode violently when sparked. The areas of flammability hazard for methane, ethane, and propane can be anticipated to lie between that of hydrogen and butane. Mixed with oxygen, butane is flammable only from 1.8 to 49 mole percent butane<sup>(6)</sup>, and the area of flammability hazard shown in Figure 4 is about two-thirds that of the area in Figure 2. Not only is butane flammable over a wider range in NF<sub>3</sub> than in O<sub>2</sub>, but as shown by Equations 4 and 5, it also releases more heat when burned in NF<sub>3</sub>. For comparison, the heat released by the combustion of butane in F<sub>2</sub> is shown in Equation 6. Thermodynamic calculations indicate that maximum combustion temperatures are produced by fuel-rich mixtures, and Allan<sup>(7)</sup> has reported that the burning velocities of NF<sub>3</sub>/hydrocarbon mixtures

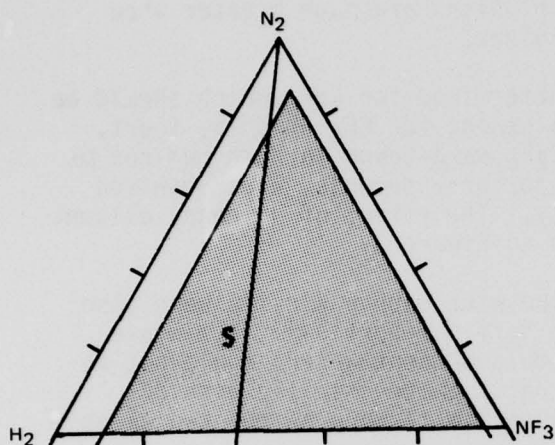


Figure 1. Limits of Flammability of  $\text{H}_2/\text{NF}_3/\text{N}_2$  Mixtures (5)

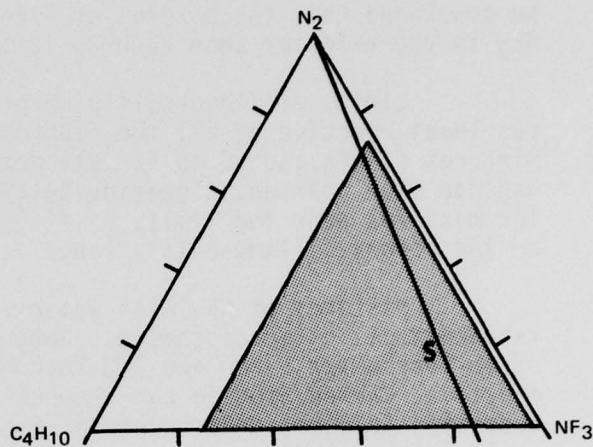


Figure 2. Limits of Flammability of  $\text{C}_4\text{H}_{10}/\text{NF}_3/\text{N}_2$  Mixtures

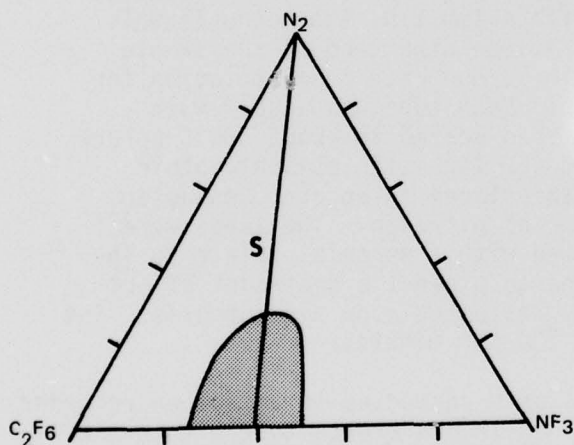


Figure 3. Limits of Flammability of  $\text{C}_2\text{F}_6/\text{NF}_3/\text{N}_2$  Mixtures

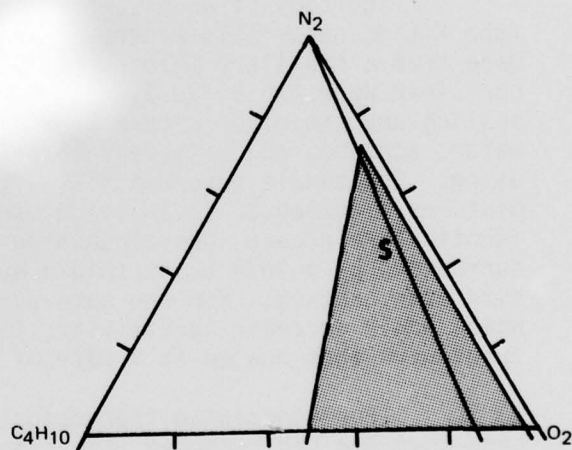


Figure 4. Limits of Flammability of  $\text{C}_4\text{H}_{10}/\text{O}_2/\text{N}_2$  Mixtures

are about three times greater than that of  $O_2$ /hydrocarbon mixtures. It can be concluded that the hazards of fire or explosions are much greater when  $NF_3$  is the oxidizer than when  $O_2$  is the oxidizer.

Limits of flammability were also determined for  $C_2F_6$  which should be the least reactive of all the fluorocarbons except for  $CF_4$  which is inert. Mixtures of  $NF_3$  and 26 to 52 mole percent  $C_2F_6$  were found to burn but not to explode when sparked. Ignition delays, up to three seconds, were observed for mixtures near the limits of flammability. The effect of nitrogen diluent on the observed flammability range is shown in Figure 3.

Mixtures of  $NF_3$  with water vapor and with carbon dioxide were also exposed to electric discharge. Contrary to Ruff's report(3,4), a mixture of 15 Torr water vapor and 740 Torr  $NF_3$  (2 mole percent water) could not be ignited. Carbon dioxide can theoretically react exothermically with  $NF_3$  according to Equation 8; however, a stoichiometric mixture of the two gases could not be ignited.

Reactions of  $NF_3$  with gaseous fuels was also examined under considerably milder conditions. A differential thermal analysis apparatus (DTA) capable of examining gaseous samples was constructed. Work to be described later had indicated that  $NF_3$  at elevated temperatures reacted with many materials. To minimize side reactions, the sample containers were fabricated entirely of glass.

The body of each sample container was made from a 16 x 150 mm test tube fitted co-axially at the closed end with a 1mm I.D. thermocouple well made from a capillary melting-point tube. At the other end of the sample container were two 10/30  $\frac{1}{8}$  ground glass joints, one with a constriction for sealing and the other with a break-seal tip. Each tube was washed with water, acetone, and methylene chloride and then heated to about 500°C before using. The sample tube was filled to about 400 Torr with stoichiometric mixtures of gases to be analyzed, sealed, and placed in an oven beside an identical reference tube containing 400 Torr of nitrogen. The tubes were surrounded by a thin brass shield and covered with a porcelain plate to insure even heating. For the same purpose and to prevent a heat-sink effect which would decrease sensitivity, the tubes rested only on pin supports. The tubes were then heated at a rate of 1.5 to 2°C per minute.

Iron-constantan thermocouple leads were connected to a two-pen recorder such that one pen recorded the temperature in the reference tube within one degree centigrade and the other pen recorded the difference in temperature between the sample and reference tubes. Reaction temperatures were taken as the initial departure of the exotherm or endotherm peaks from the base line.

The results are summarized in Table I, and the products listed were identified by gas chromatography. Nitrogen trifluoride reacted with the glass sample container at 273°C and the reactions with other gases at or above this temperature are questionable. Of the gas mixtures examined, only  $NF_3$ /trichloroethylene definitely reacted at a lower temperature, and this was also

the only endothermic reaction observed. A sample of trichloroethylene by itself exhibited only a slow exothermic decomposition beginning at 374°C. Nitrogen trifluoride/butane indicated a slow exotherm beginning at 231°C, but the heat produced was very small. Analysis of the reaction products did support the initiation of a reaction at this temperature. One reaction product was a relatively large amount of carbon, and Allan<sup>(7)</sup> has also reported the formulation of copious amounts of carbon in the combustion of butane with  $\text{NF}_3$ .

Benzene/ $\text{NF}_3$  showed an exothermic reaction at the same temperature as did  $\text{NF}_3$  alone, but the two components did not necessarily react directly with one another. The products contained a large amount of  $\text{CO}$ , and it is believed that the  $\text{NF}_3$  first reacted with the glass, producing nitrogen oxides which in turn reacted with the benzene.

Carbon dioxide did not react with  $\text{NF}_3$ , and the exotherm and products are attributed only to the  $\text{NF}_3$ /glass reaction. Mixtures of water vapor, ammonia, or 2-propanol with  $\text{NF}_3$  exothermed at temperatures higher than  $\text{NF}_3$  alone, and these fuels may be sufficiently adsorbed on the glass so as to passivate it until higher temperatures. Water vapor and  $\text{NF}_3$  produced a higher ratio of  $\text{NO}$  to  $\text{NO}_2$  than did the  $\text{NF}_3$ /glass reaction; however, unreacted water was recovered and it was not conclusively determined if any had been consumed. As with benzene, 2-propanol and ammonia may have reacted either directly with  $\text{NF}_3$  or with nitrogen oxides produced by an  $\text{NF}_3$ /glass reaction.

#### I. B. Reactions of $\text{NF}_3$ with Polymers

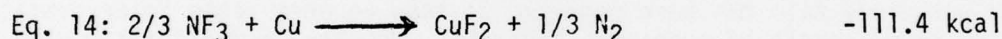
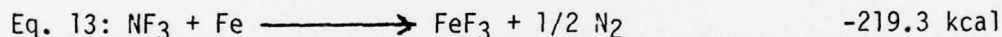
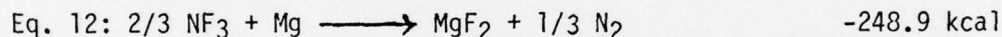
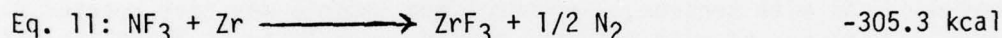
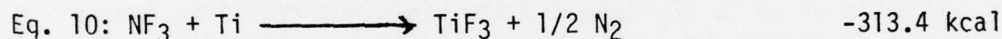
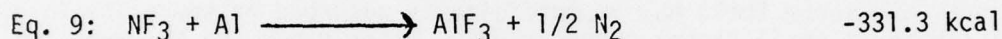
At room temperature  $\text{NF}_3$  appears to be inert towards polymers. Even polyethylene film has been reported to show no observable deterioration after more than a month of exposure to  $\text{NF}_3$ <sup>(8)</sup>. However, compatibility data at elevated temperatures are lacking. At the Naval Surface Weapons Center, samples of polyethylene, polypropylene, polystyrene, poly- $\alpha$ -methylstyrene, Lucite, and silicone grease were examined both visually and by differential scanning calorimetry after six days of exposure to five atmospheres of  $\text{NF}_3$  at 135°C. Comparisons were made with samples heated under  $\text{N}_2$ . All but Lucite and silicone grease showed a mild surface reaction.

In another study, samples of Kel-F valve packing, Teflon, Tetrafluor, Viton, Neoprene, silicone rubber, Buna-N, butyl rubber, and ethylene propylene were heated for six weeks at 150°C under 150 psi of  $\text{NF}_3$ . Similar samples were also heated under  $\text{N}_2$ . No changes were observed in the Teflon, Tetrafluor, Viton or Kel-F. Silicone rubber heated under  $\text{N}_2$  was unchanged but the sample exposed to  $\text{NF}_3$  was noticeably deteriorated. Although still flexible, it was covered with cracks, was less elastic, and appeared softer. Its shore hardness had dropped from 57 to 40. Neoprene had become considerably stiffer, harder, and brittle, and the other polymers showed extensive deterioration.

I. C. Reactions of NF<sub>3</sub> with Metals

Reactions of NF<sub>3</sub> with metals are characterized by the formation of N<sub>2</sub>, N<sub>2</sub>F<sub>4</sub>, cis and trans N<sub>2</sub>F<sub>2</sub>, and metal fluorides. In their early work, Ruff et al(3) reported that Li, Na, and K react violently with NF<sub>3</sub> when heated above their melting points. Barium and zinc were reported to ignite when heated above 200°C, Pb and Cd formed fluoride coatings at their melting point, Hg formed a scum on heating, and B and Si ignited at about 500°C. Reported as less reactive were Cu, Ag, Fe, Ca, Al, Mg, As and Sb. Observed as unreactive were Mo, Bi, Cr, Ni, Co, W, Mn, Pt, P, C, and S.

At the Naval Surface Weapons Center, tests were conducted to determine: (1) the temperature required to ignite metals in an NF<sub>3</sub> atmosphere; (2) the temperature at which metals that are rapidly heated in NF<sub>3</sub> first exhibit a noticeable reaction; and (3) the effects on metals that are exposed for long periods to NF<sub>3</sub> at ambient or moderate temperatures. The heat released by the reaction of NF<sub>3</sub> with several metals is shown in Equations 9 through 14.



To determine the temperatures required to ignite metals in an NF<sub>3</sub> atmosphere, thin wire samples were directly heated by an electric current. With only the wire at an elevated temperature, reaction of NF<sub>3</sub> with other materials was avoided. As the current was increased, the change in resistance was calculated from continuous recording of voltage and current measurements. If changes in resistance due to corrosion can be neglected, the temperature of a wire can be calculated by the equation:

$$t = \frac{\Delta R}{\alpha P} + 20$$

where t is the temperature in °C, ΔR is the change in measured resistance from that at 20°C, P is the resistance of the wire at 20°C, and α is the temperature coefficient of the metal.

Wires of pure nickel, iron, copper, and aluminum were examined. Each had a diameter of 0.127 mm and was clamped between terminals 3 cm apart in a 110 ml closed bomb. The bomb was evacuated prior to filling with NF<sub>3</sub>.

TABLE I  
GAS PHASE DTA DATA FOR  $\text{NF}_3$  REACTIONS

| Reactant                                     | Temperature, °C              | Products                                                                      |
|----------------------------------------------|------------------------------|-------------------------------------------------------------------------------|
| Glass                                        | 273 (Exo)                    | $\text{NO}$ , $\text{NO}_2$ , White Solid                                     |
| $\text{CO}_2$                                | 273 (Exo)                    | $\text{NO}$ , $\text{NO}_2$ , White Solid                                     |
| $\text{H}_2\text{O}$                         | 291 (Exo)                    | $\text{NO}$ , $\text{NO}_2$ , White Solid                                     |
| $\text{C}_6\text{H}_6$                       | 273 (Exo)                    | $\text{CO}$ , $\text{N}_2$ , $\text{CO}_2$ , Unidentified Gas, Polymeric Film |
| $\text{NH}_3$                                | 296 (Exo)                    | $\text{N}_2$ , White Solid                                                    |
| $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ | 314 (Exo)                    | $\text{CO}$ , $\text{CO}_2$ , $\text{NO}$ , Brown Solid                       |
| $\text{C}_4\text{H}_{10}$                    | 231 & 285 (Exo)              | $\text{N}_2$ , $\text{NO}$ , $\text{CO}$ , Carbon, White Solid                |
| $\text{CHCl} = \text{CCl}_2$                 | 190, 208 (Endo)<br>249 (Exo) | $\text{NO}$ , Colorless Liquid and Crystals                                   |
| $\text{CHCl} = \text{CCl}_2(\text{Alone})$   | 374 (Exo)                    | Dark Brown Oil                                                                |

TABLE II  
TEMPERATURES(°C) REQUIRED FOR METAL WIRES TO IGNITE IN OXIDIZING ATMOSPHERES

|                                                  | Al           | Cu   | Fe   | Ni         |
|--------------------------------------------------|--------------|------|------|------------|
| Melting Point                                    | 660          | 1083 | 1535 | 1455       |
| Breaking Point under $\text{N}_2$                | 550          | 1080 | 1517 | 1385       |
| Ignition Point under $\text{NF}_3$ (1 atm)       | Inconsistent | 550  | 817  | 1187       |
| Ignition Point under $\text{NF}_3$ (100 psi)     | Inconsistent | 475  | 612  | 967        |
| Ignition Point under $\text{F}_2$ (1 atm) (9)    | Above M.P.   | 692  | 672  | 1153       |
| Ignition Point under $\text{O}_2$ (1 atm) (10)   | 1750         | 1100 | 1300 | Above M.P. |
| Ignition Point under $\text{O}_2$ (100 atm) (10) | 1750         | 800  | 680  | -          |

TABLE III  
ADDITIONAL METAL IGNITION TEMPERATURES

|                 | $F_2^{(9)}$ | $O_2^{(10)}$ | $O_2(100 \text{ ATM})^{(10)}$ |
|-----------------|-------------|--------------|-------------------------------|
| Stainless Steel | 681°C       | 1400°C       | 1300°C                        |
| Monel           | 396°C       | -            | -                             |
| Molybdenum      | 205°C       | 780°C        | 700°C                         |
| Brass           | -           | 1100°C       | 800°C                         |
| Magnesium       | -           | 640°C        | 640°C                         |
| Lead            | -           | 850°C        | 850°C                         |
| Tungsten        | 283°C       | -            | -                             |
| Zinc            | -           | 940°C        | 1200°C                        |

TABLE IV  
ESTIMATED MASS COMBUSTION RATES (G/Sec X  $10^{-3}$ )

|          | $NF_3$ | $O_2$ | Air   |
|----------|--------|-------|-------|
| Iron     | 2.348  | 2.010 | 1.205 |
| Aluminum | 2.802  | 1.25  | 0.121 |
| Nickel   | 8.565  | -     | 0.194 |
| Copper   | 6.911  | 6.410 | 3.476 |

Tests were done in atmospheres of 15 psi  $\text{NF}_3$ , 100 psi  $\text{NF}_3$ , and 15 psi  $\text{N}_2$ . Data for each metal are summarized in Table II. For comparison, Tables II and III also list data for the ignition of electrically heated wires under an atmosphere of  $\text{F}_2$ <sup>(9)</sup> and of  $\text{O}_2$ <sup>(10)</sup>.

Under nitrogen atmosphere the wires broke near their melting points but none of them ignited. Under  $\text{NF}_3$  all wires ignited, and nickel which is reported in the literature to be unreactive burned brilliantly.

Pictures at 100 frames per second were taken of Al, Cu, Fe, and Ni wires ignited in  $\text{NF}_3$ ,  $\text{O}_2$  and air. From these pictures, mass burning rates were calculated, as shown in Table IV.

The temperature at which metals that are rapidly heated in an atmosphere of  $\text{NF}_3$  first exhibit a noticeable reaction was determined by differential scanning calorimetry (DSC). Powdered metal samples were heated at 20°C per minute in a DSC cell filled with an atmosphere of  $\text{NF}_3$ . Contrary to Ruff's observation<sup>(3)</sup>, zinc powder did not react with  $\text{NF}_3$  until about 300°C, and at that temperature it did not ignite. Successive heatings of the same sample rapidly eliminated the reaction at 300°C but a strong endotherm remained at the melting point of zinc, 418°C, suggesting that the surface of the metal had been passivated. Similarly, nickel powder appeared to become passivated at about 330°C, aluminum at 300-325°C, copper at 270-340°C, and silver at 350°C.

For comparison and in conflict with Ruff's observations, Glemser<sup>(11)</sup> has reported that Mo powder reacts with  $\text{NF}_3$  at 280°C. Colburn and Kennedy<sup>(12)</sup> have reported the preparation of  $\text{N}_2\text{F}_4$  in 62 - 71% yield from the reaction of  $\text{NF}_3$  with Cu, Bi, As, Sb, or stainless steel in a flow reactor at 375°C and a residence time of about three minutes contradicting Ruff's observation that Bi is unreactive. Also contrary to Ruff's observation, Gould and Smith<sup>(13)</sup> found C to be readily reactive with  $\text{NF}_3$  and have reported 75% conversion of  $\text{NF}_3$  to  $\text{N}_2\text{F}_4$  in a fluidized bed of carbon at about 440°C and a reaction time of only a few seconds. Dresden et al<sup>(14)</sup> have reported that  $\text{NF}_3$  reacts with liquid Hg at 320 - 333°C in a flow system. About 60% of the  $\text{NF}_3$  is converted to  $\text{N}_2\text{F}_4$  and a small amount to cis  $\text{N}_2\text{F}_2$ . Others have reported that Hg vapor reacts readily with  $\text{NF}_3$  in an electric discharge.

To determine the effects on metals after prolonged exposure to  $\text{NF}_3$  at moderate temperatures, samples of the twelve metals listed below were exposed for 72 hours to 160 psi of  $\text{NF}_3$  at 115°C and a second set of samples was exposed for 48 days to 225 psi of  $\text{NF}_3$  at 25°C.

|                     |                     |
|---------------------|---------------------|
| Aluminum 6061       | Stainless Steel 347 |
| Aluminum 5052       | Monel 400           |
| Aluminum 1100       | Nickel 200          |
| Aluminum 2024       | Copper              |
| Stainless Steel 321 | Aluminum Brass      |
| Stainless Steel 304 | Admiralty Brass     |

After the exposure at 25°C, all of the samples except for aluminum alloys showed slight corrosion under examination with a scanning electron microscope. After the exposure at 115°C, all samples except the aluminum alloys exhibited visible tarnishing and weight increases. Under the scanning electron microscope, extensive crystal growth was observed on all except the aluminum alloys which showed only slight corrosion. Detailed studies of metallographic copper surfaces indicated that the corrosion by  $\text{NF}_3$  occurred indiscriminately, suggesting a passivating reaction. There was no evidence of preferential attack at crystal boundaries. Some of the alloys, particularly aluminum alloys, may react more along the grain boundaries but the data presently available are not conclusive.

## II. Toxicity of $\text{NF}_3$

The first toxicity studies on nitrogen trifluoride were performed in 1931<sup>(15)</sup>. Concentrations of 10,000ppm were fatal to mice after 40 minutes and to a cat after four hours. The deaths were caused by anoxia as a result of methemoglobin formation. In 1956, Jarry and Miller<sup>(16)</sup> reported that incompletely purified (90 percent) nitrogen trifluoride caused irritation of lung tissue comparable to that from nitrogen oxides but required much higher concentrations. However, the use of impure nitrogen trifluoride in these early experiments largely invalidates the results.

### II. A. Chronic Toxicity of $\text{NF}_3$

The only available data on the chronic effects of  $\text{NF}_3$  exposure were reported by Torkelson et al<sup>(17)</sup> at the Dow Chemical Company in 1962. They exposed rats to 100 ppm of nitrogen trifluoride for seven hours a day, five days a week over a period of 4-1/2 months. The rats at the end of this period appeared normal. There were no changes in behavior, heart, lungs, blood and no appearance of fluorosis. However, microscopic examination showed definite degenerative changes in the livers and kidneys of both male and female rats, with damage being more pronounced in the females.

The Dow group also reported good qualitative agreement in the results obtained by intraperitoneal injection and acute inhalation studies. Single exposures to greater than 1000 ppm caused deaths after four hours. Exposure to higher concentrations caused deaths in shorter periods of time. Enlarged spleens were found in many of the surviving rats. After intraperitoneal injection of 10 ml of undiluted nitrogen trifluoride, the rats appeared normal in behavior and activity. Autopsies revealed, however, gross enlargement of the spleen, damage to liver and spleen, myocardial degeneration and an increase in the fluoride content of blood, bones, and teeth. These results were taken to indicate there is a different mode of toxic behavior in acute as opposed to chronic exposures.

The Dow group concluded that their data were not sufficient to set a "No-effect" concentration level. They felt that additional experiments involving repeated exposures of several species for seven to eight hours at levels of 50 ppm or less were needed.

## II. B. Acute Toxicity of NF<sub>3</sub>

In 1968, a group at Oregon State University, Corvallis, Oregon investigated the pharmacology and metabolism of NF<sub>3</sub><sup>(18)</sup>. They found that a concentration of 10,000 ppm of NF<sub>3</sub> was lethal to rats after exposure times of 60 to 70 minutes. At this concentration, 60 to 70 percent of the available hemoglobin had been converted to methemoglobin. The formation of methemoglobin, however, is reversible and the level in rats exposed to sub-lethal concentrations rapidly returned to near-normal. They found that dogs exposed to 2500 ppm of NF<sub>3</sub> could reduce methemoglobin faster than it was formed and presumably could survive indefinitely or until chronic effects became paramount. They also state that at a concentration of 500 ppm the uptake of NF<sub>3</sub> in dogs ceased, but this conclusion is at variance with the data of Torkelson and should be viewed with suspicion. Other findings indicated a possible effect upon filtration or secretion mechanisms may be caused by acute exposure.

Other studies<sup>(19,20)</sup> by the Oregon State University group showed that NF<sub>3</sub> is almost innocuous to nonmammalian organisms.

A SysteMed Corp. Group<sup>(21,22,23)</sup> determined the LC<sub>50</sub> values for NF<sub>3</sub> at 60, 30, and 15 minute exposure times. The LC<sub>50</sub> values at 50 minutes for mice, rats, dogs and monkeys are respectively 7500, 6700, 9600 and 10,000 ppm. They also found that no detectable physiological changes occurred in dogs and monkeys at exposure levels of 1000 ppm for 30 minutes and 500 ppm for one hour. They proposed that the Emergency Exposure Limit (EEL) set by The National Academy of Sciences, National Research Council Committee on Toxicology (NAS-NRC) of 100 ppm for 30 minutes and 50 ppm for 60 minutes (3000 ppm minute) be raised to 30,000 ppm minutes. Recently, an EEL value of 22,500 ppm minutes based on Vernots<sup>(23)</sup> data has been recommended by the Naval Surface Weapons Center and established by NAS-NRC.

Foster<sup>(24)</sup> has studied the effects of NF<sub>3</sub> inhalation on the cardiovascular system of rats. After exposure for one minute to 100 percent NF<sub>3</sub>, there was a decrease in diastolic pressure, systolic pressure and heart rate. However, rats which inhaled oxygen for five minutes immediately after NF<sub>3</sub> exposure showed a temporary increase in diastolic pressure, systolic pressure and heart rate.

Coppoc and Leger<sup>(25)</sup> studied the effects of NF<sub>3</sub> of plasma concentrations of lactate and certain enzymes. They found a six-fold increase in blood lactate of rats exposed to 10,000 ppm of NF<sub>3</sub> for 45 minutes. This quickly returned to normal within four hours. Serum isocitric dehydrogenase did not change. Serum glutamic oxalacetic transaminase was unchanged at one hour but increased two to three times by six hours and remained elevated for as long as 24 hours. They, too, concluded that the toxicity of NF<sub>3</sub> cannot be explained solely on the basis of methemoglobin formation.

To sum up, exposure to large concentrations of nitrogen trifluoride can cause a rapid production of methemoglobin which returns to baseline levels five to ten hours after exposure. There is a slower increase of Heinz bodies which reaches a maximum a day or two after exposure. A gradual decrease in total hemoglobin occurs shortly after exposure and reaches a minimum in five days to two weeks. There is a similar decrease in red blood cells and hemotocrit with a six percent increase in reticulocytes after three weeks. The symptoms are typical of Heinz body anemia. Dogs and monkeys almost always died within one hour after exposure to lethal concentrations. Many mice, however, survived for several hours, a few for one day, and one for three days. Those dying after one day showed extensive pneumonia<sup>(23)</sup>.

Unfortunately a number of erroneous conclusions regarding the toxicity of  $\text{NF}_3$  have entered the literature. These appear to be the results of "better safe than sorry" precautions taken at a time when the properties of  $\text{NF}_3$  were poorly defined. It seems the tendency was to equate  $\text{NF}_3$  with fluorine and/or HF or perhaps tetrafluorohydrazine. Fluorine and HF are corrosive gases while tetrafluorohydrazine is easily hydrolyzed giving rise to HF. On the contrary,  $\text{NF}_3$  is only hydrolyzed with difficulty at elevated temperatures over relatively long periods of time. Thus,  $\text{NF}_3$  should be innocuous insofar as skin contact is concerned. Butressing this conclusion is the fact that there is no mention whatsoever of any skin damage occurring during any of the acute or chronic toxicity study carried out to date.

Nevertheless, it has been stated that skin contact must be avoided<sup>(26)</sup>. This is apparently based upon a Stauffer Chemical Company Technical Bulletin<sup>(27)</sup>. Recently, this same warning based upon these references has again been duly reported<sup>(29,30,31,32)</sup>. Thus, a Technical Data Sheet<sup>(29)</sup> by Air Products and Chemicals, Inc., Allentown, Pennsylvania states that first aid for  $\text{NF}_3$  exposure is similar to treatment for HF. For skin contact they recommend: (a) a drenching shower of water, (b) removal of clothing while in the shower, (c) flushing of the exposed areas with a two to three percent aqueous ammonia solution followed by liberal rinses of water, (d) followed by an ice-cold saturated solution of magnesium sulfate or iced 70 percent alcohol, for 30 minutes, and (e) call a physician. Since skin and eye contact will necessarily occur upon inhalation, it is not quite clear how immediate oxygen administration in conjunction with eye irrigation can be carried out simultaneously with the above procedures for skin contact.

An October 1973 study by the J. J. Henry Company<sup>(30)</sup> recommends similar but somewhat more stringent first aid treatment. For skin contact they recommend a drenching cool shower for as long as two hours, the application of an iced solution of hyamine or other high molecular weight quaternary compounds (unspecified), and finally a generous quantity of thick paste made from magnesium oxide and glycerin. It should be noted that untrained personnel could unwittingly use a quaternary ammonium hydroxide, a highly corrosive chemical, without violating the above instructions.

The Air Products Bulletin also states that the moldy, pungent odor of  $\text{NF}_3$  is the best means of detection<sup>(29)</sup>. However, it has been determined that only one person of five tested could detect  $\text{NF}_3$  by odor at a concentration of 500 ppm, a level at which physiological damage could occur. A statement in the same bulletin that "prolonged absorption of nitrogen trifluoride may cause mottling of the teeth and skeletal changes of osteosclerosis" is bemusing. The reference given in justification for this statement is the Merck Index<sup>(33)</sup>, wherein it is stated "for chronic effects, see sodium fluoride". Again there is no experimental basis for equating  $\text{NF}_3$  with sodium fluoride but while perhaps innocuous, it is illustrative of the types of unjustified comparisons that have been made and which still persist.

Warnings and treatment procedures for skin contact are coupled with similar warnings concerning eye contact. There are a number of observations in the literature that  $\text{NF}_3$  can cause eye irritation<sup>(23,34)</sup>, but irritation is said to be slight<sup>(35)</sup> without follow-up complications.

## II. C. Safety Recommendations

The above references include the most reliable data on the toxicity of  $\text{NF}_3$  available at this time<sup>(36)</sup>. Concurrence has been expressed by others with experience in the  $\text{NF}_3$  field<sup>(35,37,38)</sup>. On this basis, in January 1975, the Naval Surface Weapons Center recommended revision of the EEL's for  $\text{NF}_3$ . The recommended revisions are applicable to military or space personnel and have since been established by the National Academy of Sciences - National Research Council, Committee on Toxicology as follows: 2250 ppm for ten minutes, 750 ppm for 30 minutes, and 375 ppm for 60 minutes.

A threshold limit value of 10 ppm, one-tenth of the concentration at which demonstrable histologic change has occurred<sup>(17)</sup> has been recommended by the American Conference of Governmental Industrial Hygienists<sup>(39)</sup>. This recommendation is however arbitrary, based on analogy with other oxidant gases, and should be retained only until more definitive data is available. It is recommended that chronic toxicity studies be carried out at a number of concentrations lower than 100 ppm to determine an accurate threshold limit value.

Instrumental monitoring of  $\text{NF}_3$  levels is mandatory, preferably coupled with an automatic alarm system. Self-contained breathing apparatus should be present and readily accessible in working areas. The working areas should also be equipped with vacuum exhaust systems.

An individual exposed to massive concentrations of nitrogen trifluoride should be removed from the contaminated area as quickly as possible. Oxygen therapy should be begun at once by trained personnel preferably, if at all possible, under the direct supervision of a physician. Oxygen therapy should be continued for periods of up to six hours. The patient then should be allowed to rest under close supervision until all possibility of secondary complications

such as pneumonia can be discounted. Under no circumstances should the patient be placed in a situation where additional exposure to nitrogen trifluoride could occur until clinical symptoms of anemia have returned to normal. Treatment of secondary symptoms such as eye irritation should not be of primary consideration, but if bothersome to the patient, probably could be treated by the applications of a topical anesthetic during oxygen therapy.

### III. Detectors for NF<sub>3</sub>

The possible large-scale use of NF<sub>3</sub> has caused a need for an instrument to measure low concentrations of the gas in the atmosphere. Two types of applications arise: leak detection and long-term monitoring of storage and work areas. In most environments, NF<sub>3</sub> leak detectors need not be very discriminating against other gases. The main requirements are rapid response and good sensitivity to NF<sub>3</sub>. On the other hand, long-term monitors should have good discrimination between NF<sub>3</sub> and other atmospheric contaminants. They can have a relatively slow response to low levels of NF<sub>3</sub> but do require good sensitivity and long-term stability.

#### III. A. Non-Discriminating Detectors

Leak detection of NF<sub>3</sub> can be readily accomplished with commercially available halogen leak detectors that have been designed for refrigeration repair work. Such instruments have sensitivities to NF<sub>3</sub> in the order of about one ppm or better. A small battery powered unit is available from TIF Instrument Company for about seventy-five dollars<sup>(40)</sup>. Several more sophisticated halogen detectors such as General Electric's "Feret" are more sensitive and can be calibrated for quantitative leak detections; however, they are considerably more expensive, less portable, and require more maintenance. These instruments detect many halogenated gases without discrimination, and they should not be used in explosive atmospheres.

#### III. B. Discriminating Detectors

Discriminating and quantitative techniques that have been studied for NF<sub>3</sub> detection are quadrupole mass spectrometry, electron capture gas chromatography, and laser or infrared spectral absorption. At the Naval Surface Weapons Center, an infrared detection method for NF<sub>3</sub> has been explored for both leak detection and long-term monitoring applications. Such a method measures at a spectral absorption frequency of NF<sub>3</sub>, the intensity of infrared radiation passing through a sample of air. The decrease in intensity caused by the presence of NF<sub>3</sub> is a measure of its concentration. Figure 5 shows the absorption of NF<sub>3</sub> gas in the 900 cm<sup>-1</sup> (27432 ft.<sup>-1</sup>) region at a concentration of 17.5 ppm in a one meter (3.28ft.) path as measured by a Model 421 infrared spectrophotometer. Since an absorption of this same intensity would be obtained from one ppm of NF<sub>3</sub> in a 17.5 meter (57.4 ft.) path, it is evident that sensitivities well below one ppm can be achieved in a long path cell.

Since, in the infrared absorption method, any other gaseous contaminant which absorbs in the same spectral region as the gas being measured

will also give a signal, the identification of such interfering gases and the application of methods to eliminate or reduce their influence are an important aspect of the development of a useful infrared detector. A consideration of the intensities and frequencies of the  $\text{NF}_3$  infrared absorption bands and of possible interfering gases, indicated that the  $908\text{ cm}^{-1}$  (27676 ft. $^{-1}$ ) band of  $\text{NF}_3$  was best suited for the detector application. An examination of possible interfering gases suggested that detection of  $\text{NF}_3$  would be least subject to interferences if detected at  $900\text{ cm}^{-1}$  rather than at the  $908\text{ cm}^{-1}$  band center. Table V lists gases which were found to absorb significantly at  $900\text{ cm}^{-1}$ . The absorption coefficient,  $k$ , is defined by the equation.

$$\ln(I/I_0) = -k c l$$

where  $I_0$  and  $I$  are the incident and transmitted intensities, respectively,  $c$  is the concentration and  $l$  is the path length. The sensitivity ratio is the sensitivity for the detection of  $\text{NF}_3$ , as compared to that of the interfering gas. This ratio also listed in Table V can be considered the parts per million of the interfering gas required to give the same absorption intensity as one ppm of  $\text{NF}_3$ .

The cis isomer of  $\text{N}_2\text{F}_2$  also absorbs strongly at  $900\text{ cm}^{-1}$  but its concentration can be expected to be low with respect to that of  $\text{NF}_3$ . In general, aliphatic and aromatic hydrocarbons do not absorb strongly at  $900\text{ cm}^{-1}$ . Of the interfering compounds of Table V, the freons and cleaning solvents are expected to be most likely in the areas where  $\text{NF}_3$  is to be stored or used. Ammonia may also be a likely contaminant. Fortunately, the  $\text{NF}_3$  band exactly coincides with none of the  $900\text{ cm}^{-1}$  region bands of these compounds. Therefore, further decreases in the sensitivity of the instrument to these contaminants can then be achieved by double-beam subtraction techniques if it should prove necessary.

In order to determine the sensitivity of infrared detection of  $\text{NF}_3$  at  $900\text{ cm}^{-1}$ , an existing infrared monitor, designed for Otto Fuel II vapor detection was modified for use in the  $900\text{ cm}^{-1}$  region. The optical layout of the modified instrument is shown in Figure 6. An  $f/4$  beam from the heated ceramic rod S is transformed into an  $f/8$  beam by mirror  $M_1$  and directed into a long path cell. Multiple passes back and forth in the cell give path lengths from 3.25 to 20 meters (10.7 to 65.6 ft.). A path of 17.2 meters (56.4 ft.) was used in this work. Upon leaving the long path cell at a lower level, the beam is deflected by plane mirrors  $M_4$  and  $M_5$  and passes through a 13 Hz chopper to mirror  $M_7$  which transforms the beam back to  $f/4$ . The beam is then further condensed by the optical lens, passes through the narrow-band filter F and is focused onto a pyroelectric radiation detector D. The detector output is amplified, demodulated and filtered by a lock-in amplifier and then displayed on a strip chart recorder. A considerable reduction in instrumental noise was achieved when the constant voltage ac supply which powered the infrared source was replaced by a highly stabilized dc supply.

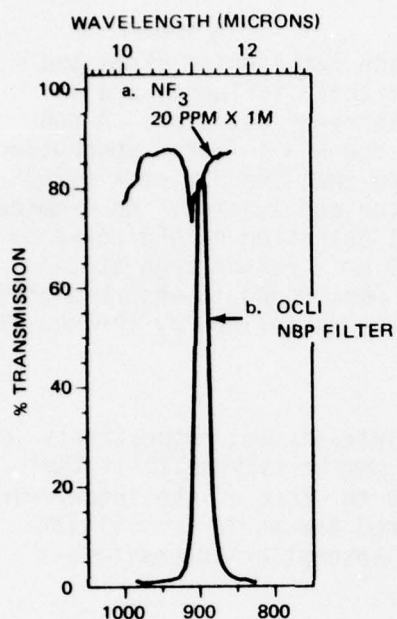


FIG. 5a ABSORPTION BAND OF  $\text{NF}_3$  AT 17.5 PPM AND 1 METER PATH

5b TRANSMISSION OF BAND PASS FILTER

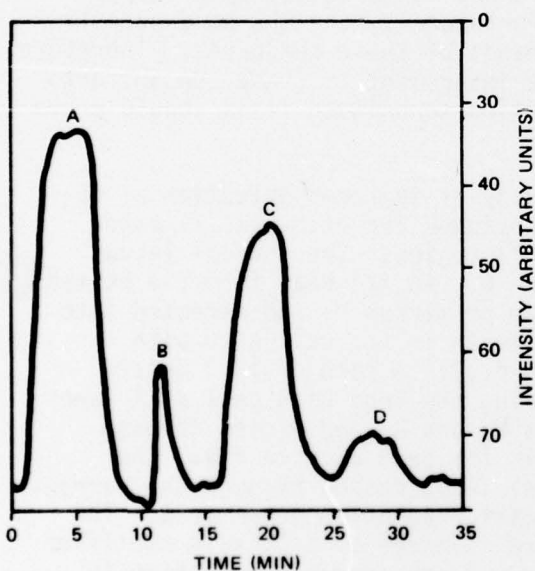


FIG. 7 DETECTOR RESPONSE TO VARIOUS  $\text{NF}_3$  CONCENTRATIONS

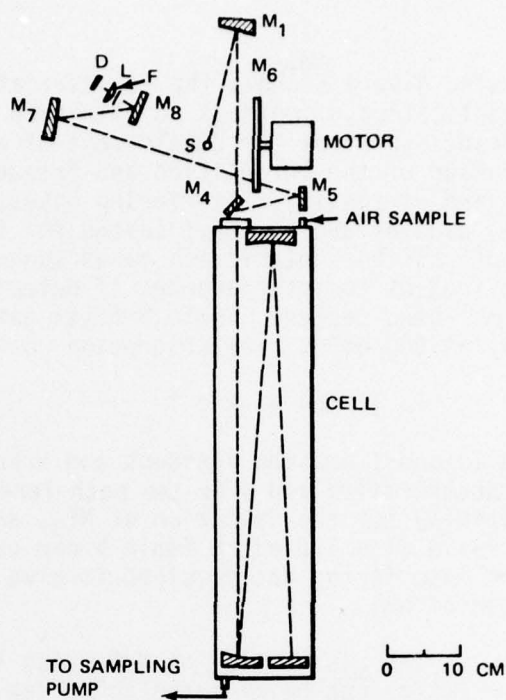


FIG. 6 GAS PHASE INFRARED DETECTOR FOR  $\text{NF}_3$

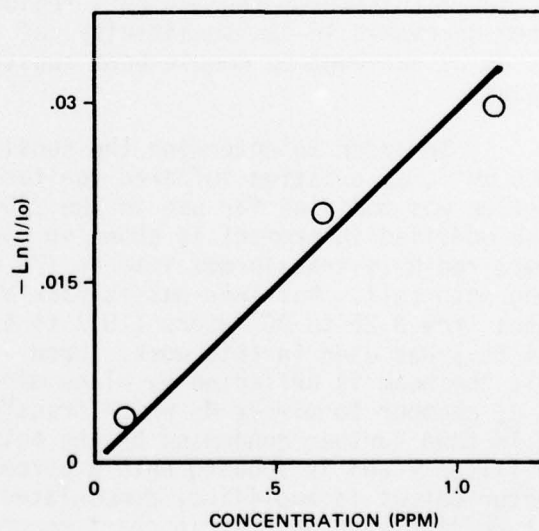


FIG. 8 INTENSITY VS CONCENTRATION - DATA OF FIG. 7

Table V

## INTERFERING GASES

| Gas                    | Absorption Coefficient at<br>900 $\text{cm}^{-1}$ , $k(\text{m}^{-1}\text{ppm}^{-1}) \times 10^3$ | Sensitivity<br>Ratio, $k\text{NF}_3/k$ |
|------------------------|---------------------------------------------------------------------------------------------------|----------------------------------------|
| $\text{NF}_3$          | 5.9                                                                                               | 1                                      |
| Nitric Acid            | 6.9                                                                                               | 0.85                                   |
| Freon 12               | 1.1                                                                                               | 5.2                                    |
| 1,1-Dimethyl Hydrazine | 0.90                                                                                              | 6.5                                    |
| 2-Methoxyethanol       | 0.47                                                                                              | 12                                     |
| Hydrazine              | 0.46                                                                                              | 13                                     |
| 1,3-Butadiene          | 0.39                                                                                              | 15                                     |
| Tetrachloroethylene    | 0.38                                                                                              | 16                                     |
| Freon 114              | 0.36                                                                                              | 17                                     |
| t-Butyl Alcohol        | 0.35                                                                                              | 17                                     |
| Tetrahydrofuran        | 0.26                                                                                              | 23                                     |
| 1,4-Dioxane            | 0.23                                                                                              | 26                                     |
| Vinyl Chloride         | 0.21                                                                                              | 28                                     |
| Ethylene Oxide         | 0.18                                                                                              | 32                                     |
| Ammonia                | 0.12                                                                                              | 50                                     |
| Ethanol                | 0.075                                                                                             | 79                                     |
| Acetone                | 0.054                                                                                             | 109                                    |

Discrimination against other atmospheric contaminants is realized in the instrument described here by a narrow band pass interference filter which transmits only radiation in a narrow band of frequencies, the center of which should be optimized both with respect to the band of  $\text{NF}_3$  and to the bands of the possible interfering gases. The filter obtained for this study was an off-the-shelf item and not optimum for  $\text{NF}_3$ . Its spectral transmission curve is displayed in Figure 5. As was pointed out above in the discussion of interfering gases, a filter peaking in the range of  $900\text{--}905\text{ cm}^{-1}$  would give both greater sensitivity to  $\text{NF}_3$  and less to several of the interfering gases, particularly Freon 12.

A mixing system was set up to produce air samples with  $\text{NF}_3$  concentration in the range of 0.01 to 10 ppm. The signals obtained with various mixtures in this range are shown in Figure 7. Peaks A, C, and D are responses to concentrations of 1.1 ppm, 0.6 ppm and 0.08 ppm, respectively flowing at 12-20 l/min. for periods of 2-4 minutes. The signal rises to a steady state and then returns to zero when the  $\text{NF}_3$  injection into the sampled air is stopped. Peak B shows the response to a concentration of about 20 ppm for a few seconds. The rise time for this signal is characteristic of the electronic response of the instrument while the decay is chiefly determined by the flushing time of the long path cell volume (8 liters,  $0.28\text{ ft}^3$ ). The peak heights of signals A, C, and D were used to calculate the absorbances at these three concentrations and the results are plotted in Figure 8. The deviations from a straight line are measures of the errors involved and include errors of mixing the various concentrations as well as errors in the measurement.

Measurement of the sensitivity of the instrument to Freon 12, showed that the sensitivity to Freon 12 is about 1/4 that to  $\text{NF}_3$ . The use of a band pass filter with a peak transmission at about  $900\text{ cm}^{-1}$  would both increase sensitivity to  $\text{NF}_3$  and decrease sensitivity to Freon 12 and give an estimated 5:1 sensitivity ratio (Table V). Further improvements can be realized by double-beam techniques.

From the results obtained, it is evident that an infrared detector for  $\text{NF}_3$  operating at  $900\text{ cm}^{-1}$  can reliably detect  $\text{NF}_3$  to 50 ppb or less. In fact, a commercially available instrument, the Miran ambient gas analyzer, has been applied by commercial vendors to the detection of  $\text{NF}_3$  in the one ppm range. This instrument is not sufficiently stable for long-term monitoring applications since it is a single-beam, direct-recording type. The Miran II infrared gas analyzer achieves long-term stability by using a ratio recording system. In the Miran II system, an intensity ratio is formed between radiation at the absorption frequency of the gas to be measured and radiation at a nearby frequency. The use of a separate reference frequency unfortunately doubles the problem of interference since absorption by another gas at either frequency will produce a false signal.

In order to achieve long-term stability, any system using spectral absorption techniques (uv, visible, laser, infrared, or microwave) must use ratio recording in order to eliminate variations in source intensity, window transmission, detector response and amplifier gain. A method that ratios between two paths, one containing the air to be sampled, the other  $\text{NF}_3$ -free air, at a single frequency ( $900\text{ cm}^{-1}$  for  $\text{NF}_3$ ) offers some advantages over the Miran II frequency ratioing technique. In the two-path (double-beam) method, the problem of interfering gases is confined to a single frequency. With two paths available, the effects of interfering gases can be eliminated if the absorption frequencies of the interfering gases do not exactly coincide with those of the gas being measured. This is achieved by placing relatively high concentrations of the interfering gas in both beams, thus effectively removing radiation at those particular frequencies.

#### IV. Fire Extinguishment

When dealing with  $\text{NF}_3$  propagated or initiated fires, it should be recalled that a high temperature  $\text{NF}_3$  is a vigorously reactive oxidizer. Fire containment and extinguishment techniques suitable for  $\text{F}_2$  fires can be used. One major difference must be stressed;  $\text{NF}_3$  fires can be expected to generate more toxic gaseous products than  $\text{F}_2$  fires. The source of  $\text{NF}_3$  should be positively removed if at all possible, and personnel should be supplied with portable breathing units, not chemical cartridge respirators.

The energy released on combustion of fuels with  $\text{NF}_3$  is much greater than with  $\text{O}_2$ , and Allan et al (41,42,43) have reported that  $\text{NF}_3$ /hydrocarbon mixtures burn about three times faster than the corresponding  $\text{O}_2$ /hydrocarbon mixtures. It should be recalled, however, that like  $\text{O}_2$  at room temperature  $\text{NF}_3$  can form mixtures with gaseous fuels. In the event of fire, excessive heat or sparks, areas which might contain  $\text{NF}_3$ /fuel mixtures would present a hazard of explosion and appropriate precautions are necessary. Fuels mixed with  $\text{NF}_3$  would present a fire or

explosion hazard over a much broader range of concentrations than with  $O_2$ . In contrast,  $F_2$  would generally not present this hazard as it would react with most fuels on contact too rapidly to form potentially explosive mixtures.

Perhaps the most effective extinguisher for fires involving massive quantities of  $NF_3$  would be liquid nitrogen. It is completely inert, would present a large heat sink, and should not damage most equipment. The probable storage of  $NF_3$  as a cryogenic liquid would necessitate its ready availability.

Carbon dioxide fire extinguishers have been recommended for areas where  $NF_3$  is stored, moved or used. Gas phase DTA studies in this laboratory have indicated  $CO_2$  to be inert towards  $NF_3$  up to  $400^\circ C$ ; however,  $CO_2$  can theoretically react with  $NF_3$  to generate considerable heat and produce toxic nitrogen oxides. As data indicating the minimum energy to initiate this reaction are not presently available, we cannot at this time recommend unconditionally the use of  $CO_2$  as an extinguisher for fires involving massive quantities of  $NF_3$ . If the amount of  $NF_3$  is small,  $CO_2$  should be acceptable.

As a fire extinguisher, water can be delivered rapidly in large volumes but may damage otherwise salvagable equipment. The use of water may pose an additional hazard. At relatively low temperatures, near  $300^\circ C$ , water vapor reacts with  $NF_3$  to produce  $HF$ ,  $NO$ , and  $NO_2$ . The extent of this hazard may be substantially reduced in that all of these highly toxic gaseous products are water soluble and may be at least partially washed away with the bulk of the water. It would seem that water cannot be eliminated as a candidate fire extinguisher.

Dry ammonium phosphate or bicarbonate type fire extinguishers might generate hazardous quantities of  $HF$  and nitrogen oxides when subjected to  $NF_3$  under fire conditions. They probably should not be used to extinguish  $NF_3$  fires. However, aqueous solutions would be no more hazardous than plain water and might be better fire extinguishers.

Bromotrifluoromethane, Halon 1301, might generate highly toxic gaseous products and might react vigorously with burning metals. While it may in some situations be a useful fire extinguisher, it cannot be recommended at this time for use with  $NF_3$  fires.

To inhibit propagation of  $NF_3$  initiated fires, supply lines should be equipped with heat sinks or other flame and explosion arrestors. Analogous to  $F_2$ , once ignited,  $NF_3$  supply lines might be expected to burn relatively slowly but explosions may occur and propagate through the lines. Valves can be automatically actuated by a burglar-alarm type device, i.e., wires wrapped around the supply lines.

To reduce fire and explosion hazards, cleaning procedures should be suitable for systems handling  $O_2$  or  $F_2$ . Soft fluorocarbon valve seats and packings are generally not reliable for  $F_2$  but should present less of a problem with  $NF_3$ . A line fire might, however, propagate back through a soft valve seat and back-up metal seated valves should be used.

#### V. Emergency Disposal of $NF_3$

Shipboard storage of  $NF_3$  presents the potential of serious health, fire, and explosion hazards if the tanks rupture or leak. Development of emergency disposal methods for  $NF_3$  are essential. This is not to be confused with the laser exhaust scrubber and ejector systems currently being developed, which deal mainly with disposal of  $HF$ ,  $DF$ , and  $F_2$  and which operate under a different set of constraints.

For a first approximation, the constraints for emergency disposal of  $NF_3$  can be considered to be:

- a. Quantity of  $NF_3$  to be disposed: 420 kg (924 lbs.)
- b. Time limitation for disposal: 5 to 10 minutes
- c. Acceptable exhaust level for toxic gases: present EEL values for 30 minutes exposure
- d. Acceptable disposal unit volume: less than  $2 \text{ m}^3$  ( $70 \text{ ft}^3$ )
- e. Limitations of shipboard facilities, with respect to power, water, etc.: none

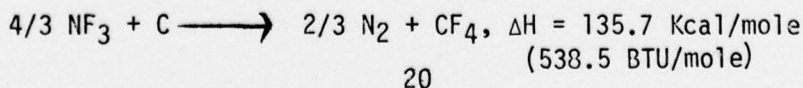
These are based in part on an NSRDC Shipboard study.

#### V. A. Disposal by Exhausting into Water or Venting into the Atmosphere

Disposal of  $NF_3$  by exhausting it into water is impractical because it hydrolyzes extremely slowly and has very low solubility in water. Venting into the atmosphere is also impractical. Since  $NF_3$  is approximately three times as dense as air, it can settle out and cause local areas to have  $NF_3$  concentrations higher than the acceptable EEL value. To dilute the  $NF_3$  below hazardous levels before venting would require a very large volume of air. For a five minute disposal time, the mass flow rate of  $NF_3$  necessary for complete disposal is approximately 1400 g/sec. (3.09 lb/sec.). At  $23^\circ\text{C}$  ( $73.4^\circ\text{F}$ ), the density of  $NF_3$  is 0.003 g/cc (0.187 lb/ft<sup>3</sup>) and the density of air is 0.001 g/cc (0.069 lb/ft<sup>3</sup>). The volumetric flow rate of air required to achieve an  $NF_3$  concentration of 750 ppm (30 min. EEL) is  $6 \times 10^5 \text{ l/sec.}$  ( $2.1 \times 10^4 \text{ ft}^3/\text{sec.}$ ). This large air flow could be achieved but the mechanical blowers needed would be much larger than the acceptable disposal unit volume of  $2 \text{ m}^3$  ( $70 \text{ ft}^3$ ).

#### V. B. Disposal by Reaction with Charcoal or Metals

The reaction of  $NF_3$  with charcoal can be represented by the equation:



Disposal of  $\text{NF}_3$  via this reaction is highly exothermic but could be done in a fluidized bed where the heat transfer is excellent. Such a technique has been demonstrated for fluorine disposal<sup>(44)</sup>. A significant problem, however, is that the reaction of  $\text{NF}_3$  and carbon can produce the highly toxic and hazardous intermediate  $\text{N}_2\text{F}_4$ . Gould and Smith<sup>(45)</sup> have reported a 75 percent conversion of  $\text{NF}_3$  to  $\text{N}_2\text{F}_4$  at  $400^\circ\text{C}$  ( $752^\circ\text{F}$ ) in a fluidized charcoal bed. Raising the temperature to  $500\text{--}600^\circ\text{C}$  ( $932\text{--}1112^\circ\text{F}$ ) should shift the reaction more towards  $\text{N}_2$  formation, but the production of  $\text{N}_2\text{F}_4$  could still be expected. Methods do exist to neutralize  $\text{N}_2\text{F}_4$  but would result in a much more elaborate disposal system. Increasing the residence time in the bed should also decrease the intermediate  $\text{N}_2\text{F}_4$ , but a much larger bed and lower gas flow rate would be required. The system constraints could not be met.

For arguments very similar to those given above, disposal of  $\text{NF}_3$  in a fluidized bed of metal particles also seems impractical.

#### V. C. Disposal by Reaction with a Solid Propellant

An ejector-scrubber for DF chemical lasers is currently being developed by Atlantic Research Corporation. The device consists of a solid propellant (ejector) impregnated with particles of Mg and  $\text{MgO}$  (scrubbers). Such a unit might conceivably serve also for  $\text{NF}_3$  disposal. In principle, ignition of the solid grain would generate gases sufficiently hot to dissociate any  $\text{NF}_3$  fed into the unit. The fluorine produced would react with Mg vapor, forming  $\text{MgF}_2$ . Addition of water to the product gases would shift the reaction equilibrium so that the remaining  $\text{F}_2$  would then react with  $\text{MgO}$ . At present, sufficient data are not yet available to determine the feasibility of this approach to  $\text{NF}_3$  disposal.

#### V. D. Disposal by Combustion with a Fuel

Emergency disposal of  $\text{NF}_3$  by reaction with the laser fuel may be the simplest and most feasible method available if the present laser combustor can be modified to also serve as a disposal combustor. Both hydrocarbons and fluorocarbons are being considered as fuels. In principle, their combustion with  $\text{NF}_3$  is essentially the same except for the formation of HF by hydrocarbons. Disposal of HF can be readily achieved with the laser scrubber or by exhausting the highly water soluble gas directly into the ocean.

In normal laser operation, excess oxidizer is used and the combustion products contain considerable elemental or atomic fluorine. If instead a fuel-rich mixture were used, the fluorine would be consumed. For example, a number of  $\text{C}_6\text{F}_6/\text{NF}_3$  mixtures containing 15 weight percent He as a diluent have been reacted. This work has been conducted by TRW under Navy contract. A mixture containing 56 weight percent  $\text{NF}_3$ , 29 weight percent  $\text{C}_6\text{F}_6$ , 15 weight percent He (approximately 3 weight percent fuel-rich) gave a combustion temperature of  $2082^\circ\text{K}$  ( $3288^\circ\text{F}$ ) and produced 1900 ppm of unreacted fluorine, which is well above the 30 minute EEL value of 10 ppm. By cooling the combustion products to  $1500^\circ\text{K}$  ( $2241^\circ\text{F}$ ), the equilibrium is shifted and

the fluorine concentration is reduced to two ppm. The major gaseous species produced are all inert materials. A fuel-rich combustion also produces carbon which is not toxic but may contaminate much of the equipment.

Flow conditions necessary to dispose of all of the  $\text{NF}_3$  in five minutes is about one-half of the reactant flow conditions under normal laser operation, and the effluent gas stream would be flowing at approximately 2.4 kg/sec. (5.3 lb/sec.).

Modification of the present DF chemical laser combustor to serve also as a disposal combustor would require programming the combustor to change the fuel/oxidizer ratio on command. The remaining portion of the laser would then be used to cool the combustion products. If modification of the combustor is not feasible, a separate unit can be used. Even a water-cooled pipe might serve as an acceptable reaction chamber. Such a separate device can be programmed to burn any readily available fuel, even diesel oil.

#### SUMMARY

Many literature sources contain erroneous information on the toxicity of  $\text{NF}_3$  and on the proper treatment for exposure to it. A new EEL value of 22,500 ppm-minute has recently been established and the present TLV should be examined for validity.

Commercially available halogen leak detectors can detect  $\text{NF}_3$  at concentrations of one ppm or less but cannot distinguish it from other halogenated gases. An improved IR detector for  $\text{NF}_3$  operating at  $900\text{ cm}^{-1}$  has been assembled. The device can detect  $\text{NF}_3$  to 50 ppb or less with little or no interference from other atmospheric contaminants.

The reactivity and the fire or explosion hazards of  $\text{NF}_3$  at room temperature appear to be similar to that of oxygen but become more like that of fluorine as the temperature is increased. Nitrogen trifluoride can form readily ignitable explosive mixtures with many gaseous fuels and appropriate caution must be exercised in handling, storage and fire-fighting procedures.

Of the techniques that have been evaluated for the emergency disposal of  $\text{NF}_3$ , the most promising one appears to be combustion with excess of either a hydrocarbon or fluorocarbon fuel, and the present laser combustor might serve also as the disposal unit.

#### REFERENCES

1. Ruff, O., J. Fischer, F. Luft, Z anorg u allgem chem, 72, 417, 1928.
2. Pisacane, F. J., E. Baroody, R. Robb and O. H. Dengel, Twelfth JANNAF Combustion Meeting, Newport, RI, Aug. 1974, CPIA Publication #273,585.

3. Ruff, O., Z. anorg. Chem., 197, 273, 1931.
4. Ruff, O., Berl. Ber., 69A, 181, 1936.
5. Tompkins, J. F., et al, U. S. Pat. 3,235,474, 14 Feb 1966.
6. Zabetakis, M. G., "Flammability Characteristics of Combustible Gases and Vapors", Bulletin 627, Bureau of Mines, U. S. Department of the Interior, 1965.
7. Allan, B. D., Thesis, University of Alabama, 1964.
8. Dost, F. N. et al, "Inorganic Fluoride Propellant Oxidizers", Aerospace Medical Research Laboratories Technical Report 66-187 (Vol. II).
9. Lorenz, C. F., and T. W. Godwin, Lewis Flight Propulsion Laboratory, Cleveland, Ohio.
10. Schmidt, Harold, Private Communication, Lewis Flight Propulsion Laboratory, Cleveland, Ohio.
11. Glenser, O., Paper No. 38, 4th International Symposium on Fluorine Chemistry, July 1967.
12. Colburn, C., and A. Kennedy, J. Amer. Chem. Soc., 80, 5004, 1958.
13. Gould and Smith, Stauffer Chem. Co., Chem. & Eng. News, 38, 85, 1960.
14. Dresdner, R. D. et al, J. Inorg. Nucl. Chem., 14, 299, 1960.
15. Ruff, O., Z. anorg. u allgem. Chem., 197, 273, 1931.
16. Jarry, R. L., and H. C. Miller, J. Phys. Chem., 60, 1412, 1956.
17. Torkelson, T. R., F. Oyen. S. E., Sadek, V. K. Rowe, Tox. and Appl. Pharm. 4, 770, 1962.
18. Dost, F. N., D. J. Reed, A. Finch and C. Wang, "Metabolism and Pharmacology of Inorganic and Fluorine Containing Compounds", AMRL-TR-67-200. Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, Nov 1968.
19. Reed, D. J., F. N. Dost and C. H. Wang, AMRL-TR-66-187, Vol. I. Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, 1967.
20. Dost, F. N., D. J. Reed, and C. H. Wang, AMRL-TR-66-187, Vol. II. Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, Nov 1968.
21. Vernot, E. H., and C. C. Haun, AMRL-TR-69-130. Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, Dec 1969.

22. MacEiven, J. D., and E. H. Vernot, AMRL-TR-69-84. Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, May 1969.
23. Vernot, E. H., D. C. Haun, J. D. MacEiven, G. F. Egan, Tox. and Appl. Pharm., 26, 1973.
24. Foster, L. L, SAM-TR-70-8. USAF School of Aerospace Medicine, Brooks AFB, Texas, Feb 1970.
25. Coppoc, G. L., and S. J. Leger, SAM-TR-70-42. USAF School of Aerospace Medicine, Brooks AFB, Texas, Jul 1970.
26. Liquid Propellant Manual: CPIA - Johns Hopkins University. LPAI-LMP-1, Nov 1961.
27. Stauffer Chemical Co. Technical Bulletin. "Nitrogen Trifluoride and Tetrafluorohydrazine". Market Development Dept., Feb 1960.
28. Reference 28 has been deleted, and is not necessary to this document.
29. Air Products and Chemicals, Inc., Technical Bulletin, "Nitrogen Trifluoride", SG-101-65.
30. J. J. Henry Co., Study, 12 Oct 1973. Contract N00600-72-D-0308 with NSRDC.
31. TRW "NF<sub>3</sub> Pilot Plant Operating Procedure", Jan 11, 1974.
32. Rockwell International, "Nitrogen Trifluoride Hazards Data", Oct 30, 1973.
33. The Merck Index of Chemicals and Drugs, Merck and Co., Inc., p. 727, 1960.
34. Cianko, G. M., "Range Find Tests on Nitrogen Trifluoride", Rocketdyne Report No. 6, 1962.
35. Back, Kenneth, Dr., Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, Private Communication.
36. Pisacane, F. J. et al, 1975 JANNAF Propulsion Meeting, Anaheim, CA., Oct 1975, CPIA Publication No. 266, 459.
37. Roberts, Frank, Dr., and Capt. Opray, AFRPL, Edwards AFB, Private Communication.
38. Allan, Barry, Dr., Huntsville, AL., Private Communication.

39. Documentation of the Threshold Limit Values for Substances in Workroom Air. American Conference of Governmental Industrial Hygienists. Third Edition, 1971.
40. "TIF Tector", TIF Instrument Co., 3661 N. W., 74th St., Miami, FL 33147.
41. Research Laboratory Quarterly, Army Missile Command, Redstone Arsenal, Alabama, No. 28, January 1961.
42. Ibid, No. 29, April 1961.
43. Ibid, No. 30, July 1961.
44. Schmidt, H. W., "Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems", National Aeronautics and Space Administration, Washington, DC, 1967.
45. Gould, J. R., and R. A. Smith, Abstracts of Papers Presented at the 138Th Meeting of the American Chemical Society, New York City, NY, p. 7M, Sep. 1960.

## DISTRIBUTION

|                                                                                                                                                |    |                                                                                                                            |   |
|------------------------------------------------------------------------------------------------------------------------------------------------|----|----------------------------------------------------------------------------------------------------------------------------|---|
| Central Intelligence Agency<br>Attn: CRS/ADD<br>Washington, DC 20505                                                                           | 1  | AF Rocket Propulsion Lab.<br>Attn: DOZ<br>For: DY<br>Edwards, CA 93523                                                     | 1 |
| Assistant Director(Eng. Technology)<br>Office of Director of Defense<br>Research and Engineering<br>Pentagon, 3D1085<br>Washington, DC 20301   | 1  | AF Rocket Propulsion Lab.<br>Attn: Technical Library<br>For: LK<br>Edwards, CA 93523                                       | 1 |
| NASA, Lewis Research Center<br>Attn: Librarian<br>21000 Brookpart Road<br>Cleveland, OH 44135                                                  | 1  | AF Rocket Propulsion Lab.<br>Attn: DOZ<br>For: MK<br>Edwards, CA 93523                                                     | 1 |
| NASA, Kennedy Space Center<br>Attn: NWSI-D<br>For Library<br>John F. Kennedy Space Ctr.<br>Kennedy Space Ctr. FL 32899                         | 1  | AF Office of Scientific Research<br>Attn: NA<br>For: Dr. Joseph F. Masi, Bldg. 410<br>Bolling AFB<br>DC 20332              | 1 |
| NASA, Johnson Space Ctr.<br>Attn: JM5, Tech. Library<br>Houston, TX 77058                                                                      | 1  | Army Ballistic Res. Labs.<br>Attn: AMXBR-SS, Mrs. Smith<br>For: AMXBR-IB, J. Hurban<br>Aberdeen Proving Ground<br>MD 21005 | 1 |
| NASA, Langley Research Ctr.<br>Attn: MS-185 Tech. Library<br>Hampton, VA 23665                                                                 | 2  | Thiokol Chemical Corp.<br>Elkton Division<br>Attn: Scty Ofc., J. E. Dwyer<br>P. O. Box 241<br>Elkton, MD 21921             | 1 |
| NASA, Scientific & Tech. Info.<br>Office - Ind. Affairs<br>Tech. Util. Office<br>Attn: KSS-10-Lib. Br.<br>For: Code RP<br>Washington, DC 20546 | 1  | Thiokol Chemical Corp.<br>Wasatch Division<br>Attn: Technical Library<br>P. O. Box 524<br>Brigham City, UT 84302           | 2 |
| Defense Documentation Center<br>Attn: TCA<br>Cameron Station, Bldg. 5<br>Alexandria, VA 22314                                                  | 12 | United Technologies Corp.<br>Attn: Acquisitions Library<br>400 Main Street<br>East Hartford, CT 06108                      | 1 |
| AF Systems Command<br>Attn: (DLXL) Maj. H. G. Hock<br>Andrews AFB<br>Washington, DC 20331                                                      | 1  | AF Armament Lab<br>Attn: DLOS-STINFO<br>Eglin AFB, FL 32542                                                                | 1 |

## DISTRIBUTION (Continued)

|                                                                                                                                                                          |   |                                                                                                                    |   |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|--------------------------------------------------------------------------------------------------------------------|---|
| United Technologies Corp.<br>Pratt & Whitney Aircraft Div.<br>Florida Research & Development Ctr.<br>Attn: Head Librarian<br>P. O. Box 2691<br>West Palm Beach, FL 33402 | 1 | Naval Postgraduate School<br>Attn: Library, Tech. Repts.<br>Section 2124<br>Monterey, CA 93940                     | 2 |
| Frankford Arsenal<br>Attn: K2400 Library B51-2<br>For Propellant Div. Br.<br>Bridge & Taconny St.<br>Philadelphia, PA 19137                                              | 1 | Naval Research Branch Office<br>Attn: DEP DIR-CH Aci.<br>1030 East Green Street<br>Pasadena, CA 91106              | 1 |
| Army Missile Command<br>Redstone Scientific Info. Ctr.<br>Attn: Chief, Document Section<br>Redstone Arsenal, AL 35809                                                    | 2 | Office of Naval Research<br>Attn: Code 473, Power Branch<br>800 N. Quincy St.<br>Arlington, VA 22217               | 1 |
| White Sands Missile Range<br>Attn: Technical Library<br>White Sands MR, NM 88002                                                                                         | 1 | Naval Sea Systems Command<br>Attn: SEA-09G32<br>Tech. Library<br>Washington, DC 20362                              | 2 |
| Naval Air Systems Command<br>Attn: AIR-954, Tech. Library<br>Washington, DC 20361                                                                                        | 2 | Naval Research Laboratory<br>Attn: Code 5117<br>Washington, DC 20390                                               | 1 |
| Naval Air Systems Command<br>Attn: AIR-53664<br>Washington, DC 20361                                                                                                     | 1 | Navy Strategic Systems Project Ofc.<br>Attn: Tech. Library<br>Washington, DC 20360                                 | 1 |
| Naval Sea Systems Command<br>Attn: SEA-0624<br>Washington, DC 20362                                                                                                      | 1 |                                                                                                                    |   |
| Naval Sea Systems Command<br>Attn: SEA-0331<br>Washington, DC 20362                                                                                                      | 2 |                                                                                                                    |   |
| Naval Sea Systems Command<br>Attn: SEA-0331B<br>Washington, DC 20362                                                                                                     | 1 | Naval Ordnance Station<br>Attn: Tech. Library, Code 613<br>Indian Head, MD 20640                                   | 3 |
| Naval Air Systems Command<br>Attn: AIR-330<br>Washington, DC 20361                                                                                                       | 2 | Naval Intelligence Support Center<br>Attn: NISC<br>For: Doc. Library<br>4301 Suitland Road<br>Washington, DC 20390 | 1 |
| Naval Weapons Center<br>Attn: Code 753, Tech. Library<br>China Lake, CA 93555                                                                                            | 2 |                                                                                                                    |   |

## DISTRIBUTION (Continued)

|                                                                                                                                                         |   |                                                                                                                                         |   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|---|-----------------------------------------------------------------------------------------------------------------------------------------|---|
| Aerojet Solid Propulsion Co., DIV.<br>Attn: Library<br>P. O. Box 13400<br>Sacramento, CA 95813                                                          | 1 | Lockheed Missile Space Co., Inc.<br>Attn: Tech. Info. Ctr.<br>For: DCS-M-5252, Rpts. Acq.<br>3251 Hanover Street<br>Palo Alto, CA 94304 | 1 |
| Aerojet Liquid Rocket Co.<br>Attn: Tech. Info. Ctr.<br>P. O. Box 13222<br>Sacramento, CA 95813                                                          | 1 | Exxon Research & Engineering Co.<br>Gov't. Research Lab.<br>Attn: Defense Security Officer<br>P. O. Box 8<br>Linden, NJ 07036           | 1 |
| Aerospace Corporation<br>Attn: Lib. Acq. Group<br>P. O. Box 92957<br>Los Angeles, CA 90009                                                              | 1 | Hercules, Inc.<br>Allegany Ballistics Lab.<br>Attn: Technical Library<br>P. O. Box 210<br>Cumberland, MD 21502                          | 1 |
| Hercules, Inc.<br>Hercules Research Center<br>Attn: Technical Info. Lib.<br>Wilmington, DE 19899                                                        | 1 | The Marquardt Company<br>Attn: Library<br>P. O. Box 2013<br>Van Nuys, CA 91409                                                          | 1 |
| California Inst. of Technology<br>Jet Propulsion Laboratory<br>Attn: Lib. Op. GP-Acq.<br>For: Winston Gin<br>4800 Oak Grove Drive<br>Pasadena, CA 91103 | 1 | Martin-Marietta Corporation<br>Attn: MP-30, Engineering Lib.<br>P. O. Box 5837<br>Orlando, FL 32805                                     | 1 |
| Altantic Research Corporation<br>Attn: Library<br>5390 Cherokee Avenue<br>Alexandria, VA 22314                                                          | 1 | Rockwell International Corp.<br>Space Division<br>Attn: Tech. Info. Ctr.<br>12214 Lakewood Blvd.<br>Downey, CA 90241                    | 1 |
| Textron, Inc.<br>Bell Aerosystems Co., Div.<br>Attn: Library<br>P. O. Box 1<br>Buffalo, NY 14240                                                        | 1 | Rocket Research Corporation<br>Attn: Tech. Library<br>11441 Willow Road, NE<br>Redmond, WA 93052                                        | 1 |
| Boeing Company, Kent Library<br>Attn: 87-67<br>Library Processing Supr.<br>P. O. Box 3707<br>Seattle, WA 98124                                          | 1 | Rockwell International Corp.<br>Rocketdyne Division<br>Attn: Library Dept. 086-306<br>6633 Canoga Avenue<br>Canoga Park, CA 91304       | 1 |
| The Johns Hopkins University/APL<br>Chemical Propulsion Info. Agency<br>1100 Johns Hopkins Road<br>Laurel, MD 20810                                     | 2 | Army Research Office, Info. Proj. Ofc.<br>Attn: RDRD-IPL-CH<br>Box CM, Duke Station<br>Durham, NC 27706                                 | 1 |

## DISTRIBUTION (Continued)

|                                                                                                                       |   |                                                                                                                                                          |   |
|-----------------------------------------------------------------------------------------------------------------------|---|----------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| TRW, Inc.<br>TRW Systems Group-Tech. Info. Ctr.<br>Attn: Superv.<br>One Space Park<br>Redondo Beach, CA 90278         | 2 | The Trustees of Princeton University<br>Forrestal Campus Library<br>Attn: Librarian<br>P. O. Box 710<br>Princeton, NJ 08540                              | 1 |
| Thiokol Corporation<br>Huntsville Division<br>Attn: Tech. Library<br>Huntsville, AL 35807                             | 1 | Stanford Research Institute<br>Attn: Document Center<br>Classified Document Services<br>For: M. E. Hill<br>333 Ravenswood Avenue<br>Menlo Park, CA 94025 | 1 |
| United Technologies Corp.<br>Chemical Systems Division<br>Attn: Library<br>1050 E. Arques Ave.<br>Sunnyvale, CA 94088 |   | LTV Aerospace Corporation<br>Wright Division<br>Attn: CH. Lib.<br>P. O. Box 5907<br>Dallas, TX 75222                                                     | 1 |
|                                                                                                                       |   | McDonnell Douglas Corp.<br>Attn: A3-339 Library<br>5301 Bolsa Avenue<br>Huntington Beach, CA 92647                                                       | 1 |