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FLUORINE SYSTEMS HANDBOOK

by

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FLUORINE SYSTEMS HANDBOOK

ABSTRACT

This Handbook contains criteria for the design of airborne fluorine feed systems and associated components. Two types of information are presented: 1) philosophical information defining general methods, and 2) detailed specifications and procedures. Although the major emphasis has been upon criteria for components exposed to elemental fluorine, the information is general applicable to systems utilizing other cryogenic oxidizers which contain fluorine as a constituent.

ACKNOWLEDGMENT

The works of other organizations and individuals has been used extensively in the preparation of this handbook. It has been the intent to give credit for these works by the use of references. The handbook is the result of the efforts of many individuals of the Missile and Space Systems Divisions of the Douglas Aircraft Company. Members of the Advance Propulsion Staff who were contributing authors are as follows: W. C. Robinson, C. Melton, D. P. Behrns, and B. R. Heckman. Specific acknowledgment is made to the individuals of the following industrial organizations who contributed time and effort to produce background information for inclusion herein.

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W. C. Robinson
Editor

FLUORINE SYSTEMS HANDBOOK

ABSTRACT FOR FIRST REVISION

The original program covering the "Development and Demonstration of Criteria for Liquid Fluorine Feed System Components," (Contract NASw-1351) which forms the basis for this handbook was continued on a separate supplementary contract (NAS 3-11195) under the same title. The results of the work on the supplemental program included comprehensive investigations in the design of fluorine shutoff valves and feed line filters suitable for fluorine service. This first revision to the basic handbook consists of the addition of the new information on these two subjects.

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pg 25 Sect V

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Table of Contents

Abstract

Section I SUMMARY/INTRODUCTION 1.0-1

1.0 SUMMARY 1.0-1

1.1 Section II--Design Methods for Airborne Fluorine Feed Systems 1.0-1

1.2 Section III--Manufacturing and Material Processes for Airborne Fluorine Feed Systems 1.0-2

1.3 Section IV--Operational Procedures and Safety in the Testing of Airborne Fluorine Feed Systems 1.0-2

2.0 INTRODUCTION

2.1 Scope 2.0-1

2.2 Handbook Format 2.0-2

2.3 Figures, Tables and Equations 2.0-2

2.4 Page Format 2.0-3

2.5 References and Bibliography 2.0-3

Section II DESIGN METHODS FOR AIRBORNE FLUORINE FEED SYSTEMS 1.0-1

1.0 GENERAL CONSIDERATIONS

1.1 Fluorine Properties 1.0-1

1.2 Contaminants 1.0-52

1.2.1 Passivation of Metals 1.0-54

1.2.2 Contaminant Removal from Nonmetals 1.0-55

1.2.2.1 Nitric Acid Cleaning 1.0-56

1.2.2.2 Fluorine Cleaning 1.0-56

1.2.2.3 Proof Test 1.0-56

2.0 MATERIAL SELECTION 2.0-1

2.1 Introduction 2.0-1

2.2 Metals 2.0-1

2.3 Non Metals 2.0-2

2.4 Moisture Contamination 2.0-3

2.5 Summary Conclusions 2.0-4

2.6 Metals 2.0-5

2.6.1 Static Environment 2.0-5

2.6.1.1 Metals Summary 2.0-10

2.6.1.1.1 Nickel and Nickel Alloys 2.0-10

2.6.1.1.2 Low Alloy Steel 2.0-11

2.6.1.1.3 Stainless Steel 2.0-11

2.6.1.1.4 Aluminum and Aluminum Alloys 2.0-12

2.6.1.1.5 Copper and Copper Alloys 2.0-13

2.6.1.1.6 Magnesium 2.0-14

2.6.1.1.7 Titanium 2.0-14

2.6.1.1.8 Miscellaneous Metal Alloys 2.0-14

(continued)

2.6.2 Dynamic Environment	2.0-16
2.6.2.1 Metals	2.0-17
2.7 Non-Metals	2.0-18
2.7.1 Static Environment	2.0-18
2.7.1.1 Lubricants	2.0-18
2.7.1.2 Polymerics	2.0-21
2.7.2 Dynamic Environment	2.0-22
2.7.2.1 Polymerics	2.0-22
3.0 COMPONENT CONSIDERATIONS	3.0-1
3.1 Valves	3.0-1
3.1.1 Poppet Valves	3.0-1
3.1.2 Butterfly Valves	3.0-4
3.1.3 Check Valves	3.0-5
3.2 Connections	3.0-6
3.2.1 Importance	3.0-6
3.2.2 Primary Considerations	3.0-7
3.2.3 Thermal Cycling	3.0-8
3.2.4 Selection	3.0-9
3.2.5 Line Taps	3.0-10
3.2.6 Conclusions	3.0-11
3.3 Tankage	3.0-11
3.3.1 Conclusions	3.0-13
3.4 Insulation	3.0-13
3.4.1 Conclusions	3.0-18
3.5 Instrumentation	3.0-20
3.5.1 Pressure Sensors	3.0-20
3.5.2 Temperature Sensors	3.0-21
3.5.2.1 Thermocouples	3.0-21
3.5.3 Level Sensing Devices	3.0-22
3.5.3.1 Capacitance Probe	3.0-22
3.5.3.2 Differential Pressure	3.0-22
3.5.3.3 Magnetic	3.0-23
3.5.3.4 Sonic Devices	3.0-23
3.5.4 Flowmeters	3.0-23
3.5.4.1 Differential Pressure	3.0-24
3.5.4.2 Rotometers	3.0-24
3.5.5 Feed Throughs	3.0-24
3.5.6 Conclusions	3.0-25
3.6 Boost Pumps	3.0-26
3.6.1 Application	3.0-26
3.6.2 Design Options	3.0-26
3.6.3 Mechanical Design	3.0-27
3.6.3.1 Housing	3.0-27
3.6.3.2 Impeller and Shaft	3.0-27
3.6.3.3 Bearings	3.0-28
3.6.3.4 Dynamic Seals	3.0-29
3.6.4 Drive Systems	3.0-31
3.7 Quick Disconnect Couplings	3.0-32

(continued)

3.8 Flexible Joints 3.0-35
3.8.1 Bellows 3.0-36

4.0 LEAKAGE CONSIDERATIONS AND CALCULATION METHODS 4.0-1

4.1 Nomenclature 4.0-1
4.2 Background: Analytical, Empirical 4.0-2
4.2.1 Zero Leakage 4.0-2
4.2.2 Analytical 4.0-3
4.2.3 Empirical 4.0-5
4.3 Analysis 4.0-5
4.3.1 Geometric Model 4.0-5
4.3.2 Deformation 4.0-7
4.3.3 Leakage 4.0-11
4.3.3.1 Theoretical Leakage 4.0-11
4.3.3.2 Physical Constraints on Leakage 4.0-13
4.3.4 Solution of Leakage Equations by Computer 4.0-14
4.3.4.1 Absolute Leakage 4.0-14
4.3.4.2 Relative Leakage 4.0-16
4.4 Empirical 4.0-17
4.4.1 Stress-Strain Data 4.0-17
4.4.2 Valve Leakage Correlation 4.0-18
4.4.3 Surface Fracture 4.0-18

5.0 ENERGY SENSITIVITY 5.0-1

5.1 External Heating 5.0-1
5.2 Chemical Reaction 5.0-1
5.3 Component Impacting 5.0-2
5.4 Fluid Impact 5.0-5
5.5 Conclusions 5.0-6

6.0 GALLING AND WEAR OF UNLUBRICATED SURFACES 6.0-1

6.1 Adhesive-Wear Theory 6.0-1
6.2 Surface Chemistry and Crystal Structure 6.0-2
6.3 Surface Films and Friction 6.0-4
6.4 Friction and Wear 6.0-6
6.5 Behavior of Polished Surfaces 6.0-7
6.6 Design Considerations 6.0-7
6.7 Non-Metallic Surfaces 6.0-8
6.8 Self-Lubricating Surfaces 6.0-9
6.9 Summary 6.0-11
6.10 Criteria for Wear Resistance in Fluorine 6.0-12
6.10.1 Conclusions 6.0-16

APPENDIX II-1 PROPELLANT, FLUORINE, GASEOUS AND LIQUID 1

Section III MANUFACTURING AND MATERIAL PROCESSES FOR AIRBORNE FLUORINE FEED SYSTEMS 1.0-1

1.0 MATERIAL HANDLING AND PROCESS CONTROL 1.0-1

(continued)

2.0 FABRICATION TECHNIQUES 2.0-1

2.1 Coolants and Preservatives 2.0-1
2.2 Cutting and Forming Tools 2.0-3
2.3 Welding 2.0-3
2.3.1 Techniques 2.0-3
2.3.2 Inspection 2.0-3
2.4 Polytetrafluoroethylene 2.0-4
2.4.1 Sheet, Rod, Tube, Billet 2.0-4
2.4.2 Sprayed 2.0-4
2.5 Electroplating 2.0-5

3.0 CLEANING AND PASSIVATION 3.0-1

3.1 Cleaning 3.0-1
3.2 Passivation 3.0-3

4.0 ASSEMBLY AND FUNCTIONAL TESTING 4.0-1

5.0 IDENTIFICATION 5.0-1

6.0 PACKAGING 6.0-1

7.0 INSPECTION 7.0-1

8.0 DOCUMENTATION AND TRACEABILITY 8.0-1

8.1 Documentation 8.0-1
8.1.1 Raw Material (Including Weldments and Castings) 8.0-1
8.1.2 Receiving and Inspection 8.0-1
8.1.3 Manufacturing 8.0-2
8.1.4 Post Manufacture 8.0-2
8.1.5 System 8.0-2
8.2 Traceability 8.0-3

APPENDIX III-1 POLYTETRAFLUOROETHYLENE, MOLDED ENERGETIC PROPELLANT SERVICE 1

APPENDIX III-2 POLYTETRAFLUOROETHYLENE, MOLDED CRYOGENIC, ULTRA-PURE FOR FLUORINE SERVICE 1

APPENDIX III-3 PROCEDURE FOR SPRAY COATING POLYTETRAFLUOROETHYLENE ON METALS 1

APPENDIX III-4 FLUORINE SERVICE CLEANING PROCEDURE 1

APPENDIX III-5 FLUORINE PASSIVATION PROCEDURE 1

(continued)

Section IV OPERATIONAL PROCEDURES AND SAFETY IN THE TESTING OF AIRBORNE FLUORINE FEED SYSTEMS 1.0-1

1.0 INTRODUCTION 1.0-1

2.0 PROCUREMENT AND TRANSPORTATION 2.0-1

2.1 Procurement 2.0-1
2.2 Transportation 2.0-1

3.0 SAFETY 3.0-1

4.0 TOXICOLOGY 4.0-1

4.1 General 4.0-1
4.2 Governmental Regulation of Maximum Allowable Concentration 4.0-1

5.0 LEAK DETECTION AND MEASUREMENT 5.0-1

5.1 Gross Detection 5.0-1
5.2 Trace Detection and Measurement 5.0-1
5.2.1 General 5.0-1
5.2.2 Commercially Available Instruments 5.0-2
5.2.3 Noncommercial Methods for Detection of F_2 and F_2 Compounds 5.0-4
5.2.3.1 Methods Based on Direct F_2 Measurement 5.0-4
5.2.3.1.1 Spectrophotometric (Ultraviolet Absorption) 5.0-4
5.2.3.1.2 Radiochemical Exchange by Use of Kryptonates 5.0-4
5.2.3.1.3 Electrochemical 5.0-5
5.2.3.1.4 Mercury Reaction 5.0-6
5.2.3.1.5 Chemical Fluorine and Fluoride Dosimeter 5.0-7
5.2.3.1.6 Gas Titration Analyzer (Continuous Monitor) 5.0-8
5.2.3.1.7 Thin Film Sensor 5.0-9
5.2.3.2 Methods Based on Replacement of Fluorine with Chlorine and Its Subsequent Detection 5.0-10
5.2.3.2.1 Thermoconductivity Measurement 5.0-10
5.2.3.2.2 Photometric 5.0-10
5.2.3.3 Methods 5.0-11
5.2.3.3.1 Gas Chromatography 5.0-11
5.2.3.3.2 Radioactive Cl-36 5.0-12
5.2.3.3.3 Infrared Absorption 5.0-12
5.2.3.3.4 Microwave Detectors 5.0-12
5.2.4 Summary 5.0-12

6.0 METHODS OF ANALYSIS 6.0-1

7.0 METEOROLOGICAL FACTORS IN FLUORINE HANDLING 7.0-1

7.1 Meteorological Parameters of the Toxic Hazard and Air Pollution Problem 7.0-1
7.2 Estimation of Downwind Atmospheric Pollution 7.0-2
7.2.1 Sutton's Diffusion Equations 7.0-2
7.2.2 Empirical Diffusion Equations 7.0-4
7.3 Conclusions 7.0-7

Section V BIBLIOGRAPHY 1

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LIST OF FIGURES

Figure No.	Title	Page No.
II-1.1a	DENSITY OF LIQUID FLUORINE	1.0-5
II-1.1b	DENSITY OF GASEOUS FLUORINE	1.0-7
II-1.1c	VAPOR PRESSURE OF LIQUID FLUORINE	1.0-10
II-1.1d	HEAT CAPACITY OF FLUORINE	1.0-12
II-1.1e	HEAT CAPACITY OF GASEOUS FLUORINE	1.0-15
II-1.1f	HEAT OF VAPORIZATION OF FLUORINE	1.0-18
II-1.1g	ENTHALPY OF GASEOUS FLUORINE AT ONE ATMOSPHERE	1.0-22
II-1.1h	ENTROPY OF SOLID AND LIQUID FLUORINE	1.0-24
II-1.1i	ENTROPY OF GASEOUS FLUORINE	1.0-26
II-1.1j	FREE-ENERGY FUNCTION OF SOLID AND LIQUID FLUORINE	1.0-30
II-1.1k	FREE ENERGY OF GASEOUS FLUORINE	1.0-34
II-1.1ℓ	VISCOSITY OF LIQUID FLUORINE	1.0-36
II-1.1m	VISCOSITY OF GASEOUS FLUORINE AT ONE ATMOSPHERE	1.0-38
II-1.1n	SURFACE TENSION OF LIQUID FLUORINE	1.0-40
II-1.1o	THERMAL CONDUCTIVITY OF GASEOUS FLUORINE AT ONE ATMOSPHERE	1.0-44
II-1.1p	DIELECTRIC CONSTANT OF LIQUID FLUORINE	1.0-46
II-1.1q	TEMPERATURE--ENTHALPY DIAGRAM FOR FLUORINE	1.0-51
II-2.6a	VARIATION OF FLUORINE FILM THICKNESS ON METAL POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE AT -113°F	2.0-50
II-2.6b	VARIATION OF FLUORIDE FILM THICKNESS ON METAL POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE AT +86°F	2.0-51

Figure No.	Title	Page No.
II-2.6c	VARIATION OF FLUORINE FILM THICKNESS ON METAL POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE AT +183°F	2.0-52
II-2.6d	VARIATION OF FLUORINE FILM THICKNESS ON ALUMINUM AND TITANIUM POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE	2.0-53
II-2.6e	VARIATION OF FLUORIDE FILM THICKNESS ON COPPER AND BRASS POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE AT DIFFERENT TEMPERATURES	2.0-54
II-2.6f	VARIATION OF FLUORINE FILM THICKNESS ON METAL POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE AT 86°F TOTAL RUN	2.0-55
II-2.6g	VARIATION OF FLUORINE FILM THICKNESS ON METAL POWDERS VS. TIME OF EXPOSURE TO GASEOUS FLUORINE AT 103°F TOTAL RUN	2.0-56
II-2.6h	SILICON DISPERSION IN CAST ALUMINUM ALLOY A356	2.0-57
II-2.6i	GRADE II-F A356 CAST ALUMINUM ALLOY EXPOSED TO GASEOUS FLUORINE	2.0-58
II-2.6j	GRADE III-F A356 CAST ALUMINUM ALLOY EXPOSED TO GASEOUS FLUORINE	2.0-59
II-2.7a	SOLID NONMETALLIC MATERIALS STATICALLY EXPOSED TO FLOX	2.0-60
II-2.7b	LIQUID FLOX REACTIVITY PROFILE	2.0-61
II-3.1a	FLUORINE VALVE DESIGN AND SELECTION CRITERIA	3.0-47
II-3.1b	BUTTERFLY VALVE FLOATING SEAL	3.0-48
II-3.3a	FLUORINE FEED SYSTEM TANK CONFIGURATIONS EVALUATION	3.0-49
II-3.4a	NYLON THREAD--SPECIMEN EXPOSED TO LIQUID FLUORINE AND COMPARATIVE UNEXPOSED SPECIMEN	3.0-50
II-3.4b	FIBER GLASS SPACER--SPECIMEN EXPOSED TO LIQUID FLUORINE AND COMPARATIVE UNEXPOSED SPECIMEN	3.0-51

Figure No.	Title	Page No.
II-3.4c	SPECIMENS OF PHENOLIC, TEFLON, AND LUCITE EXPOSED TO LIQUID FLUORINE	3.0-52
II-3.4d	SCOTCH 850 TAPE--SPECIMENS EXPOSED TO LIQUID FLUORINE AND COMPARATIVE UNEXPOSED SPECIMENS	3.0-53
II-3.4e	DEXIGLAS PAPER--SPECIMEN EXPOSED TO LIQUID FLUORINE AND COMPARATIVE UNEXPOSED SPECIMEN	3.0-54
II-3.4f	VELCRO FASTENER--SPECIMENS EXPOSED TO LIQUID FLUORINE AND COMPARATIVE UNEXPOSED SPECIMENS	3.0-55
II-3.6a	BOOST PUMP DYNAMIC SEAL	3.0-56
II-4.3a	AVERAGE HEIGHT VALUES FOR VARIOUS WAVE FORMS	4.0-22
II-4.3b	MODEL SURFACE GEOMETRY WITH DEFINING EQUATIONS	4.0-23
II-4.3c	SINUSOIDAL MODEL SURFACES	4.0-24
II-4.3d	EFFECT OF CONTACT ANGLE CORRECTION FACTOR ON LEAKAGE	4.0-25
II-4.3e	COMPRESSIVE STRESS-STRAIN DIAGRAM FOR 304 S.S. SHOWING THREE PHASES OF COMPRESSION	4.0-26
II-4.3f	GF_2 SEAL LEAKAGE (MONEL/MONEL)	4.0-27
II-4.3g	GF_2 SEAL LEAKAGE (STEEL/COPPER)	4.0-28
II-4.3h	GF_2 SEAL LEAKAGE (STEEL/ALUMINUM)	4.0-29
II-4.3i	LF_2 SEAL LEAKAGE (MONEL/MONEL)	4.0-30
II-4.3j	LF_2 SEAL LEAKAGE (STEEL/COPPER)	4.0-31
II-4.3k	LF_2 SEAL LEAKAGE (STEEL/ALUMINUM)	4.0-32
II-4.3ℓ	EFFECT OF ASPERITY HEIGHT ON LEAKAGE	4.0-33
II-4.3m	EFFECT OF SURFACE FINISH WAVELENGTH ON LEAKAGE	4.0-34
II-4.3n	EFFECT OF SURFACE CONTACT ANGLE ON LEAKAGE	4.0-35
II-4.3o	EFFECT OF DEFORMATION COEFFICIENT ON LEAKAGE	4.0-36
II-4.3p	EFFECT OF APPARENT SEAT STRESS ON LEAKAGE	4.0-37
II-4.3q	EFFECT OF ELASTIC MODULUS ON LEAKAGE	4.0-37.1
II-4.3r	EFFECT OF PRESSURE DIFFERENTIAL ON LEAKAGE	4.0-38

Figure No.	Title	Page No.
II-4.3s	EFFECT OF GAS TEMPERATURE ON LEAKAGE	4.0-39
II-4.3t	EFFECT OF ABSOLUTE PRESSURE ON LEAKAGE	4.0-40
II-4.3u	LEAKAGE FLOW THROUGH SEALS COMPRESSED ELASTICALLY	4.0-41
II-4.3v	LEAKAGE FLOW THROUGH SEALS COMPRESSED ELASTICALLY	4.0-41.1
II-4.3w	LEAKAGE FLOW THROUGH SEALS COMPRESSED ELASTICALLY	4.0-42
II-4.3x	SEAL CONTACT AREA IN ELASTIC COMPRESSION	4.0-42.1
II-4.3y	SEAL CONTACT AREA IN ELASTIC COMPRESSION	4.0-43
II-4.3z	SEAL CONTACT AREA IN ELASTIC COMPRESSION	4.0-43.1
II-4.4a	COMPRESSIVE STRESS-STRAIN DIAGRAMS FOR SEVERAL HEAT TREATED ALUMINUM ALLOYS	4.0-44
II-4.4b	COMPRESSIVE STRESS-STRAIN DIAGRAM COPPER, 304 SS AND K-MONEL	4.0-45
II-4.4c	SEAL LEAKAGE, GHE (MONEL/MONEL)	4.0-46
II-4.4d	FRACTOGRAPHS OF CONTACT SURFACE AREA AFTER FLUORINE TEST	4.0-47
II-4.4e	TRANSGRANULAR FRACTURE (MICROVOID COALESCENCE)	4.0-48
II-5.3a	DETAILS OF ANVIL REGION ASSEMBLY OF ABMA TYPE IMPACT TESTING DEVICE	5.0-7
II-6.10a	DESIGN COMPRESSIVE STRESS FOR SLIDING SURFACES	6.0-23
II-6.10b	DESIGN COMPRESSIVE STRESS FOR SLIDING SURFACES	6.0-24
II-6.10c	CORRECTION FACTOR FOR FIGURES 7.10a AND b	6.0-25
II-6.10d	LUBRICATING PROPERTIES IN AIR OF EUTECTIC FLUORIDE AND NICKEL-CHROMIUM ALLOY COMPOSITES	6.0-26
II-6.10e	LUBRICATING PROPERTIES IN AIR OF EUTECT FLUORIDE AND NICKEL COMPOSITES	6.0-27

LIST OF TABLES

Table No.	Title	Page No.
II-1.1a	DENSITY OF LIQUID FLUORINE	1.0-4
II-1.1b	DENSITY OF GASEOUS FLUORINE	1.0-6
II-1.1c	VAPOR PRESSURE OF LIQUID FLUORINE	1.0-8
II-1.1d	HEAT CAPACITY OF FLUORINE	1.0-11
II-1.1e	HEATS OF VAPORIZATION OF FLUORINE	1.0-17
II-1.1f	ENTHALPY OF GASEOUS FLUORINE AT ONE ATMOSPHERE	1.0-19
II-1.1g	ENTROPY OF SOLID AND LIQUID FLUORINE	1.0-23
II-1.1h	ENTROPY OF GASEOUS FLUORINE	1.0-25
II-1.1i	FREE-ENERGY FUNCTION OF SOLID AND LIQUID FLUORINE	1.0-29
II-1.1j	FREE-ENERGY FUNCTION OF GASEOUS FLUORINE	1.0-31
II-1.1k	VISCOSITY OF LIQUID FLUORINE	1.0-35
II-1.1ℓ	VISCOSITY OF GASEOUS FLUORINE	1.0-37
II-1.1m	SURFACE TENSION OF LIQUID FLUORINE	1.0-39
II-1.1n	THERMAL CONDUCTIVITY OF LIQUID FLUORINE	1.0-42
II-1.1o	THERMAL CONDUCTIVITY OF GASEOUS FLUORINE AT ONE ATMOSPHERE	1.0-43
II-1.1p	DIELECTRIC CONSTANT OF LIQUID FLUORINE	1.0-45
II-1.1q	EQUILIBRIUM CONSTANT OF DISSOCIATION AS FUNCTION OF TEMPERATURE, $F_2 \rightleftharpoons 2F$	1.0-47
II-1.1r	SUMMARY OF FLUORINE PHYSICAL AND THERMODYNAMIC PROPERTIES	1.0-48
II-2.0a	LOW MELTING ELEMENTAL FLUORIDES	2.0-27
II-2.0b	RECOMMENDED METALS FOR FLUORINE SERVICE	2.0-28
II-2.0c	MATERIALS CHEMICAL COMPOSITION	2.0-31
II-2.6a	AVERAGE CORROSION RATES OF UNSTRESSED METALS IN LIQUID FLUORINE	2.0-32

Table No.	Title	Page No.
II-2. 6b	STRESS CORROSION SAMPLES OF SELECTED METALS IN LIQUID FLUORINE	2. 0-34
II-2. 6c	MANUFACTURERS' SPECIFICATIONS GASEOUS AND LIQUID FLUORINE	2. 0-38
II-2. 6d	AVERAGE TENSILE PROPERTIES OF 1-YEAR SPECIMENS	2. 0-39
II-2. 6e	IGNITION TEMPERATURES OF SELECTED METALS IN FLUORINE	2. 0-40
II-2. 6f	CORROSION OF NICKEL AND NICKEL ALLOYS IN FLUORINE	2. 0-41
II-2. 6g	CORROSION OF IRON AND STEEL IN FLUORINE	2. 0-42
II-2. 6h	CORROSION OF ALUMINUM IN FLUORINE	2. 0-44
II-2. 6i	CORROSION OF COPPER AND COPPER ALLOYS IN FLUORINE	2. 0-46
II. 2. 6j	CORROSION OF MAGNESIUM AND MAGNESIUM ALLOYS IN FLUORINE	2. 0-47
II. 2. 6k	SILVER SOLDER COMPOSITION	2. 0-48
II-2. 7a	NONMETALS EXPOSED TO GASEOUS AND LIQUID FLUORINE	2. 0-49
II-3. 1a	FLUORINE VALVE MATERIALS	3. 0-38
II-3. 2a	MATERIAL GROUPINGS FOR INSTRUMENTATION TAPS	3. 0-39
II-3. 2b	YIELD STRENGTH OF SEAL MATERIALS	3. 0-40
II-3. 4a	EMISSIVITIES OF REFLECTIVE MATERIALS AFTER EXPOSURE TO GASEOUS FLUORINE--NITROGEN MIXTURES	3. 0-41
II-3. 4b	FLUORINE EXPOSURE RESULTS OF HPI ASSEMBLY AND INSTALLATION COMPONENTS	3. 0-43
II-3. 6a	FLUORINE BOOST PUMP DRIVE TURBINE FAILURE MODE AND EFFECT ANALYSIS	3. 0-44
II-3. 6b	LIQUID FLUORINE PUMP DYNAMIC SEAL MATERIALS	3. 0-45
II-3. 8a	FLEXIBLE JOINT SUMMARY	3. 0-46
II-4. 3a	VALUES OF C_1 FOR USE IN LEAKAGE CALCULATIONS	4. 0-20
II-4. 3b	VALUES OF C_2 FOR USE IN LEAKAGE CALCULATIONS	4. 0-20
II-4. 3c	TYPICAL ASPERITY HEIGHTS AND ANGLES FOR COMMON FINISHING TECHNIQUES	4. 0-20

Table No.	Title	Page No.
II-4. 3d	CONDITIONS FOR FLUORINE VALVE DESIGN STUDY	4. 0-21
II-4. 3e	BASELINE VALUES FOR INFLUENCE CURVES	4. 0-21
II-6. 2a	SEIZURE RESISTANCE OF PURE METALS	6. 0-18
II-6. 10a	MAXIMUM HARDNESS OF COMMON METALS AND ALLOYS	6. 0-20
II-6. 10b	SOLUBILITIES OF METAL PAIRS	6. 0-20. 1
II-6. 10c	PROPERTIES OF SELF-LUBRICATING, FLUORIDE-METAL COMPOSITES	6. 0-22
III-2. 1a	CUTTING AND FORMING COOLANTS (TYPICAL)	2. 0-6
III-5. 0a	MATERIAL GROUPINGS FOR IDENTIFICATION PURPOSES	5. 0-2
III-7. 0a	INSPECTION REQUIREMENTS	7. 0-4
IV-5. 2a	COMMERCIALLY AVAILABLE INSTRUMENTS FOR F_2 DETECTION	5. 0-3

SECTION I
SUMMARY / INTRODUCTION

Section I
SUMMARY/INTRODUCTION

1.0 Summary

The Fluorine Systems Handbook has been prepared to provide manufacturers of airborne oxidizer systems or components with a single source of basic information on fluorine and other halogenated oxidizers, and hardware technology, covering the fields of: design technique, manufacturing, material processes, operational procedures, and safety. Two types of information are presented: 1) philosophical information defining general methods and 2) detailed specifications and procedures. Although the major discussion concentrates on the handling of elemental fluorine, the techniques are usually equally applicable to other energetic oxidizers containing fluorine. The handbook has been made as complete as possible, within the confines of the contract. Only those areas which are considered unique to feed system design, production, or testing, because of the use of fluorine, have been covered. In those areas where it was felt that the clarity of the presented material would be enhanced, nonunique material has been included.

The technical information presented is contained in three sections covering the respective areas of: design, manufacturing, and testing. Each section has been presented using the vocabulary and format consistent with present practice. The three technical sections are:

1.1 Section II--Design Methods for Airborne Fluorine Feed Systems

This section contains basic engineering information of the various facets of design, analysis, selection, and specification of fluorine feed systems and components. It is intended to be used as a basic engineering reference for the design and development of airborne fluorine feed system hardware.

1.2 Section III--Manufacturing and Material Processes for Airborne Fluorine Feed Systems

Information is presented in this section to define these processes which are unique to the production of fluorine feed systems and components. Detailed specifications and procedures are included for the various processes.

1.3 Section IV--Operational Procedures and Safety in the Testing of Airborne Fluorine Feed Systems

The unique requirements for handling fluorine in the testing of airborne fluorine feed systems is presented in this section. Primary emphasis is given to the safety and health aspects of handling fluorine. The intent has been to establish procedures which fall within the Federal "Clean Air Act of 1963." Of necessity, not all facets of the subject have been included due to the sensitivity of procedures and methods to specific hardware and specific test facilities.

2.0 Introduction

2.1 Scope

The performance potential of the halogenated oxidizers has been recognized for many years. Although these energetic oxidizers have been actively investigated, the emphasis has been upon performance and engine related problems rather than the design, manufacturing, and operational usage of airborne feed systems. The present development trend is toward the use of fluorine as the oxidizer for high performance stages.

Liquid and gaseous fluorine have been produced and handled in industrial processes for many years. This usage has included the handling, transportation, and disposal of tonnage quantities of fluorine which has demonstrated that this energetic oxidizer can be handled safely over extended periods and in large quantities.

A large amount of information has been accumulated over the years on the safe handling of fluorine, and the design of fluorine systems and components. The majority of this information applies to facility or ground support systems only. The NASA, Lewis Research Center publication, HANDLING AND USE OF FLUORINE AND FLUORINE-OXYGEN MIXTURES IN ROCKET SYSTEMS, Reference 146, has summarized and reviewed much of the past work. This NASA handbook, which provides the basis for this document, clearly indicated the need for additional work to apply the available knowledge to the design of reliable flight weight feed systems. Of necessity, some of the information contained in the NASA handbook has been duplicated in the present document; however, the information has been evaluated and expanded so as to be directly applicable to airborne feed systems.

The purpose of the present work has been to assemble design criteria in the form of a FLUORINE SYSTEMS HANDBOOK, which will assist in the production of highly reliable airborne vehicles using fluorine or other halogens.

The information presented in this handbook has evolved from a comprehensive literature search, interviews with manufacturers of flight hardware and test equipment, and the Douglas Aircraft Company's own experience with fluorine

and the manufacture of airborne vehicles using cryogenic propellants. Two types of information are presented: (1) philosophical information defining general methods and recommended practices, and (2) detailed specifications and procedures.

The application of the information contained herein to the design, development, manufacturing, and testing of airborne fluorine feed systems and/or components will allow airframe and component manufacturers to produce and test hardware meeting the standards necessary to assure timely production of reliable flight hardware.

2.2 Handbook Format

The general format was designed to facilitate use and to allow for revisions as the handbook is updated and expanded. The use of looseleaf ring binding allows the individual user to incorporate pertinent information obtained from other sources. Appropriate tab dividers are provided for quick location of various sections and subsections. Each section is subdivided into subsections and sub-topics. The commonly accepted method of decimally numbering paragraphs has been adopted throughout as follows:

I. MAJOR SECTION
- 1.0 Section
- 1.1.1 Sub-Section
- 1.1.1.1 Topic
- 1.1.1.1.1 Sub-Topic

2.3 Figures, Tables and Equations

Figures, tables and equations are indexed to the lowest numbered section in which they appear, such as Figure I-1.1a, Table I-1.4a, Equation I-1.9a, etc. The letters included in the numeric designation are used to differentiate between more than one figure, table or equation within any numbered sub-division.

2.4 Page Format

Pages are numbered consecutively within each sub-section; viz., I-1.1, I-1.2, etc. Revisions are indicated by the date of issue on the respective page(s).

2.5 References and Bibliography

The complete bibliography, Section V, includes all of the references as well as the other documents which are considered germane to airborne fluorine systems design, production and test. The bibliography is listed alphabetically by document title. In those cases where the titles begin with an article, the article has been ignored in the alphabetizing. In keeping with standard practice, to assist in cross-referencing, those documents which have more than one author, only the first has been indicated.

SECTION II
DESIGN TECHNIQUES

Section II
DESIGN METHODS FOR AIRBORNE FLUORINE FEED SYSTEMS

1.0 General Considerations

1.1 Fluorine Properties

The performance potential of chemical rocket propulsive systems using fluorine as the oxidizer has long been recognized. The major obstruction to its utilization has been the high reactivity and toxicity of elemental fluorine. Fluorine is the most reactive oxidizer known, and will react with all matter which is not in its highest valence state and is not completely fluorinated. The rate of reaction is primarily a function of exposure time, temperature and pressure as with other chemical reactions. In addition, fluorine is an extremely toxic fluid and its reaction with fuels containing hydrogen produces another toxic product, hydrogen fluoride (HF).

Gaseous fluorine is yellow brown in color over a wide range of pressures and temperatures. Liquid fluorine also is yellow brown in color, with the liquid varying from yellow to light brown, dependent upon its depth or volume. Fluorine begins to solidify at 96.37°R, and is yellow in color. As the temperature is reduced below 81.99°R, the solid undergoes an allotropic crystalline structure change, with a corresponding change in color--from yellow to white.

The odor of fluorine is characteristically halogenic, being similar to ozone or chlorine. Tests have indicated that fluorine can be detected by odor at concentrations of less than one part per million.

Fluorine is chemically stable and will not decompose due to additions of energy. However, fluorine will support combustion, and if sufficient energy additions are available to reach the kindling temperature of any material in a fluorine environment, the material will burn until completely consumed, or until the fluorine is removed.

The properties of fluorine are presented in Tables II-1.1a through II-1.1r and Figures II-1.1a through II-1.1q. Table II-1.1r presents a "Summary of Fluorine Physical and Thermodynamic Properties."

Currently there is no NASA or military specification for fluorine. Presently it has been necessary to rely upon manufacturer's specification for procurement. Appendix II-1; "Propellant, Fluorine, Gaseous and Liquid;" has been prepared to fill the need for a formal procurement specification. The use of this specification is recommended for procurement of all fluorine for use in airborne vehicle systems.

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Table II-1.1a

DENSITY OF LIQUID FLUORINE

Temperature °R	Pressure, psia	Density lb/cu ft	Reference
118.40	--	102.26	95
129.17	--	99.51	95
134.87	--	98.51	95
141.46	--	96.77	95
146.10	--	95.64	95
146.11	--	95.39	95
151.81	--	94.52	95
[a]153.09	--	93.96	95
156.44	--	93.49	95
158.87	--	92.46	95
159.30	--	92.65	95
162.14	--	91.90	95
164.79	--	91.02	95
165.15	--	91.24	95
170.51	--	89.52	95
175.61	--	88.15	95
180.38	--	86.84	95
184.95	--	85.53	95

[a]Normal boiling point from ref. 52

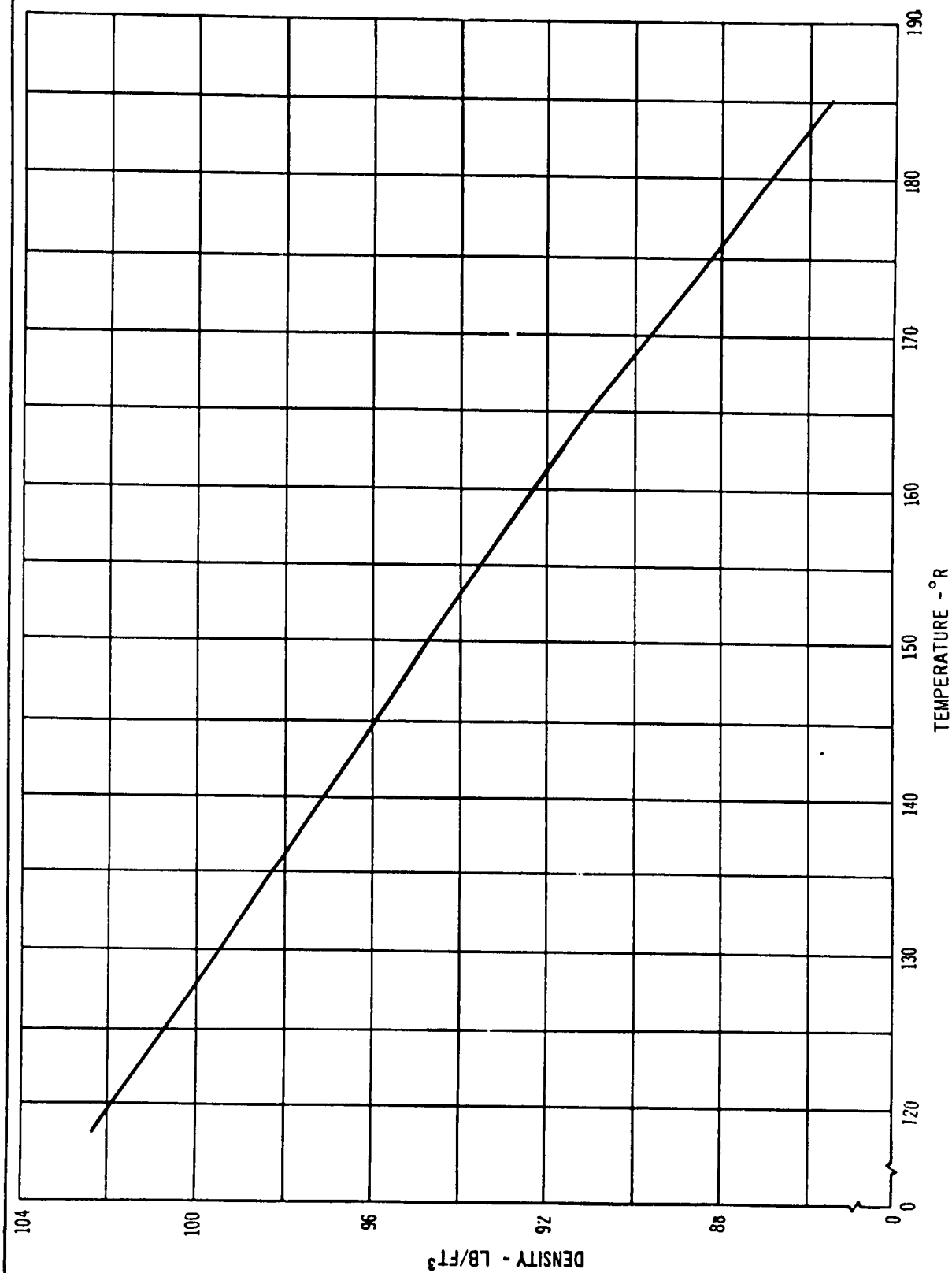

Figure II-1.1a. Density of Liquid Fluorine (Reference 95)

Table II-1.1b

DENSITY OF GASEOUS FLUORINE (Saturated Vapor)

Temperature °R	Pressure, psia	Density lb/cu ft	Reference
153.43	14.696	0.352	59
162.00	23.80	0.570	59
171.00	40.31	0.895	59
180.00	62.55	1.355	59
189.00	84.89	1.973	59
198.00	122.06	2.824	59
207.00	186.54	3.934	59
216.00	252.76	5.391	59
225.00	234.00	7.297	59
234.00	419.21	9.801	59
243.00	508.35	13.328	59
252.00	676.44	19.134	59
259.00	808.28	29.441	59

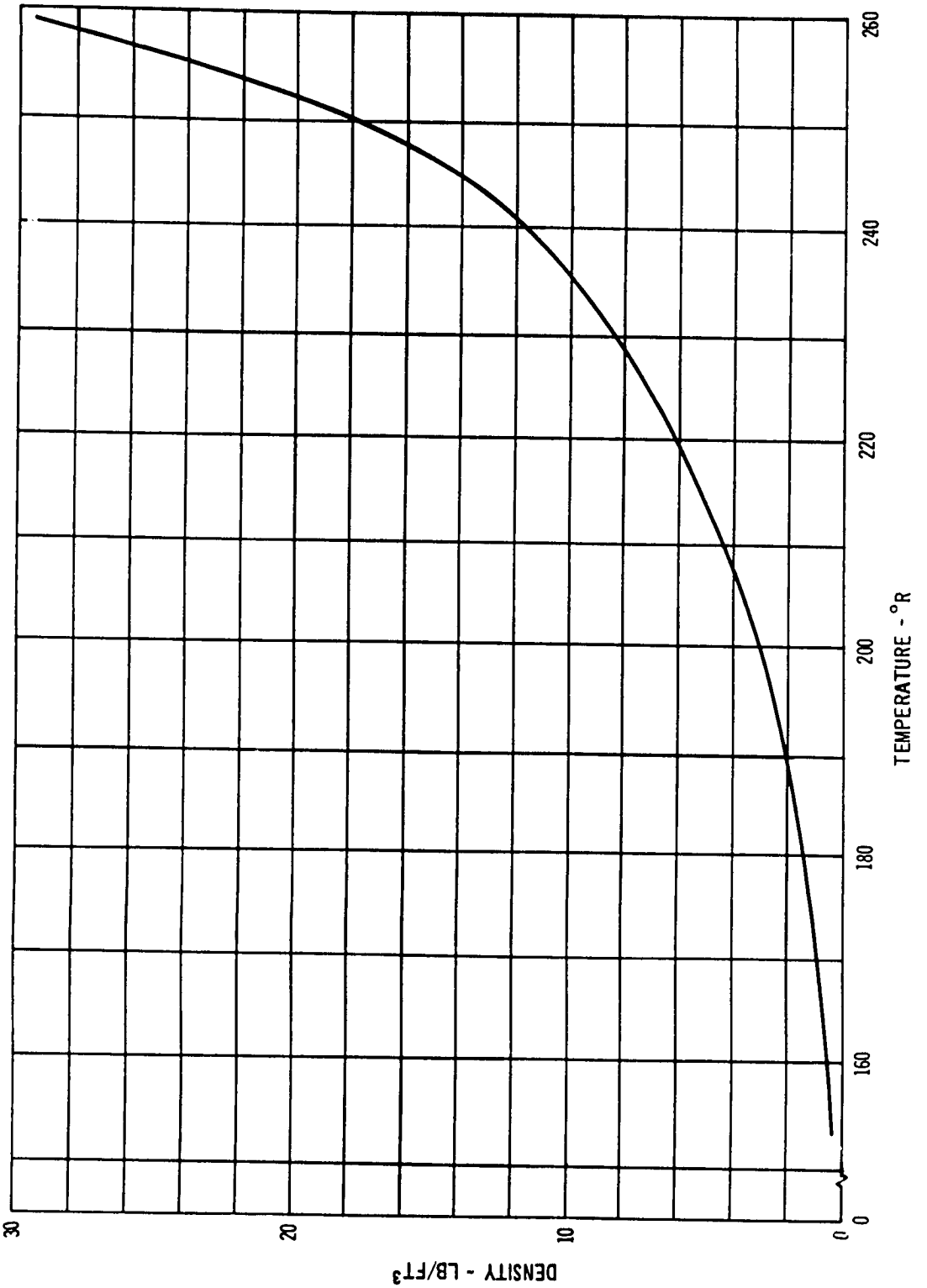

Figure II-1.1b. Density of Gaseous Fluorine (Saturated Vapor) (Reference 59)

Table II-1.1c
VAPOR PRESSURE OF LIQUID FLUORINE

Temperature °R	Vapor Pressure psia	Reference
96.41	0.032	54
98.98	0.052	54
103.61	0.115	54
107.82	0.195	268
108.90	0.249	54
114.28	0.501	54
114.50	0.509	268
117.00	0.686	268
119.74	0.930	54
120.69	1.000	163
123.66	1.261	268
125.23	1.630	54
125.98	1.780	268
130.61	2.701	54
131.13	2.772	268
135.02	4.043	268
137.70	4.999	163
138.91	5.422	54
139.52	5.598	268
142.83	7.377	268
143.96	7.780	268
144.05	7.981	54
147.69	9.997	163
149.51	11.681	54
150.17	11.758	268
152.24	13.980	54
[a]153.05	14.696	163
153.49	15.210	163
155.18	16.343	268
155.88	17.539	54
157.54	19.389	54
158.69	20.000	163
160.92	23.589	163
167.18	30.000	163
178.69	50.000	163

[a]Normal boiling point.

Table II-1.1c (page 2 of 2)
VAPOR PRESSURE OF LIQUID FLUORINE

Temperature °R	Vapor Pressure psia	Reference
186.70	70.000	163
193.70	90.000	163
196.18	100.000	163
215.69	200.00	163
228.19	300.00	163
236.68	400.00	163
243.68	500.00	163
249.70	600.00	163
254.68	700.00	163
258.70	800.00	163

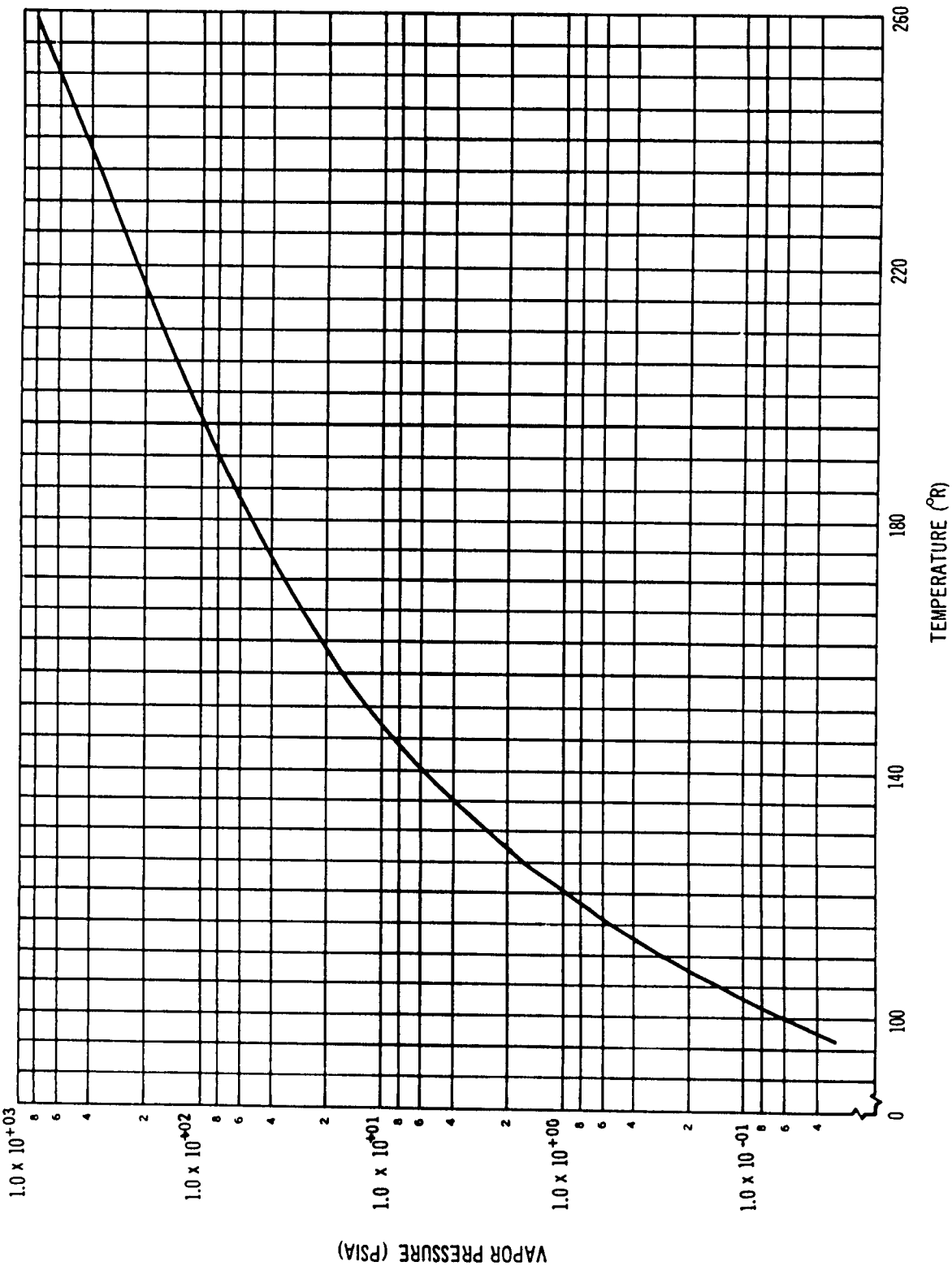

Figure II-1.1c. Vapor Pressure of Liquid Fluorine (References 54, 163 and 268)

Table II-1.1d (page 1 of 3)

HEAT CAPACITY OF FLUORINE

Temperature °R	Heat Capacity Btu/(lb)(°R)	Reference
Solid II		
27	0.0459	89
36	0.0817	89
45	0.1213	89
54	0.1587	89
63	0.1954	89
72	0.2310	89
81	0.2668	89
81.99	0.2707	89
Solid I		
81.99	0.2925	89
90	0.3102	89
96.37	0.3213	89
Liquid		
96.37	0.3604	89
99	0.3603	89
108	0.3599	89
117	0.3579	89
126	0.3566	89
135	0.3589	89
144	0.3628	89
153.04	0.3669	89
Gas		
153.04	0.1830	287
162.00	0.1830	287
171.00	0.1830	287
180	0.1831	287
360	0.1867	287

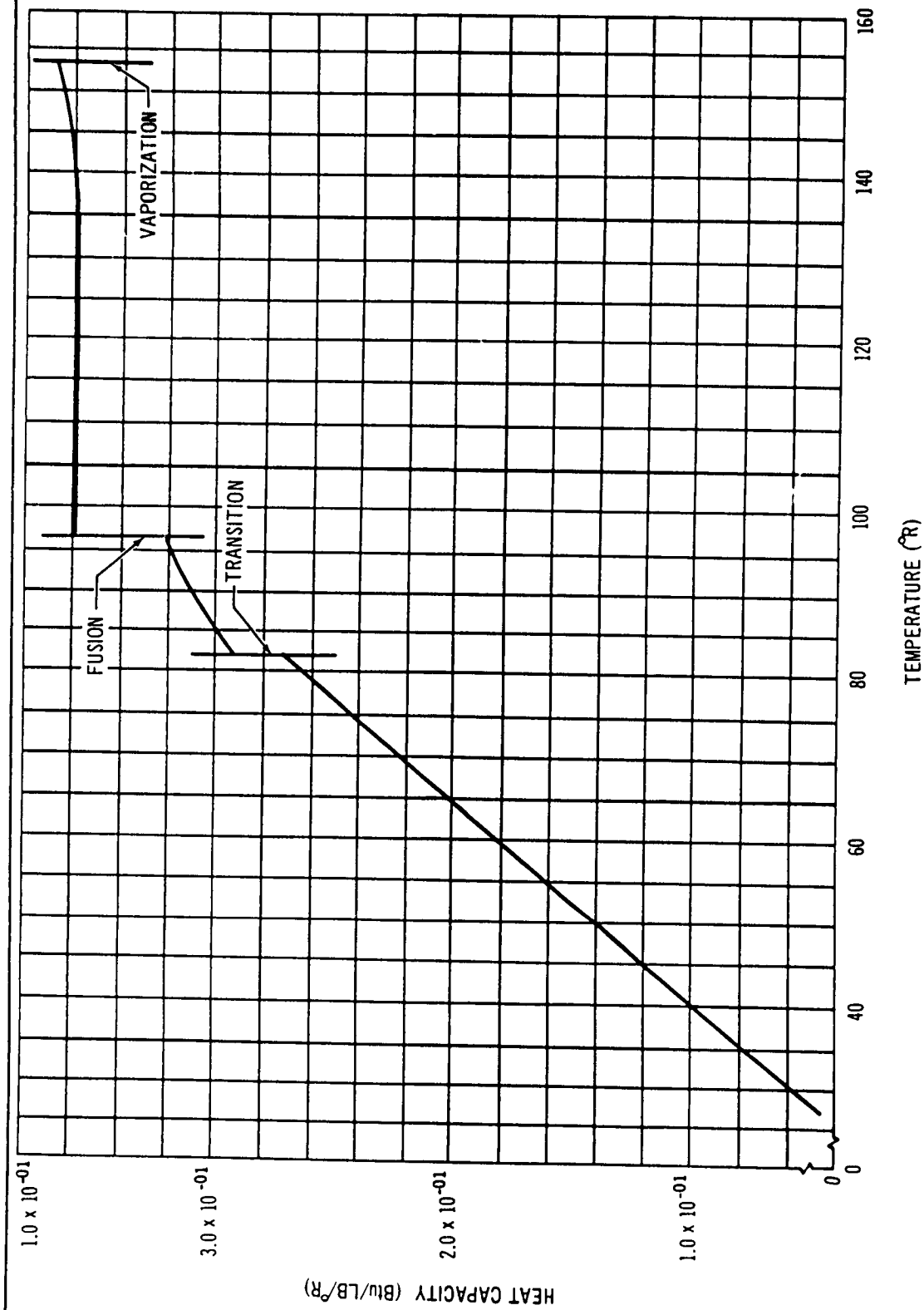

Figure II-1.1d. Heat Capacity of Fluorine (References 89 and 287)

Table II-1. 1d (page 2 of 3)

HEAT CAPACITY OF FLUORINE

Temperature °R	Heat Capacity Btu/(lb)(°R)	Reference
Gas (continued)		
536.69	0.1969	287
540	0.1972	287
720	0.2077	287
900	0.2157	287
1080	0.2214	287
1260	0.2257	287
1440	0.2288	287
1620	0.2313	287
1800	0.2332	287
1980	0.2349	287
2160	0.2363	287
2340	0.2374	287
2520	0.2385	287
2700	0.2395	287
2880	0.2403	287
3060	0.2412	287
3240	0.2419	287
3420	0.2427	287
3600	0.2434	287
3780	0.2440	287
3960	0.2447	287
4140	0.2453	287
4320	0.2459	287
4500	0.2465	287
4680	0.2471	287
4860	0.2477	287
5040	0.2483	287
5220	0.2488	287
5400	0.2494	287
5580	0.2499	287
5760	0.2505	287
5940	0.2510	287
6120	0.2516	287
6300	0.2521	287
6480	0.2526	287

Table II-1.1d (page 3 of 3)
HEAT CAPACITY OF FLUORINE

Temperature °R	Heat Capacity Btu/(lb)(°R)	Reference
Gas (concluded)		
6660	0.2532	287
6840	0.2537	287
7020	0.2542	287
7200	0.2547	287
7380	0.2553	287
7560	0.2558	287
7740	0.2563	287
7920	0.2568	287
8100	0.2563	287
8280	0.2578	287
8460	0.2584	287
8640	0.2589	287
8820	0.2594	287
9000	0.2599	287
9180	0.2604	287
9360	0.2609	287
9540	0.2614	287
9720	0.2619	287
9900	0.2624	287
10080	0.2630	287
10260	0.2635	287
10440	0.2640	287
10620	0.2645	287
10800	0.2650	287

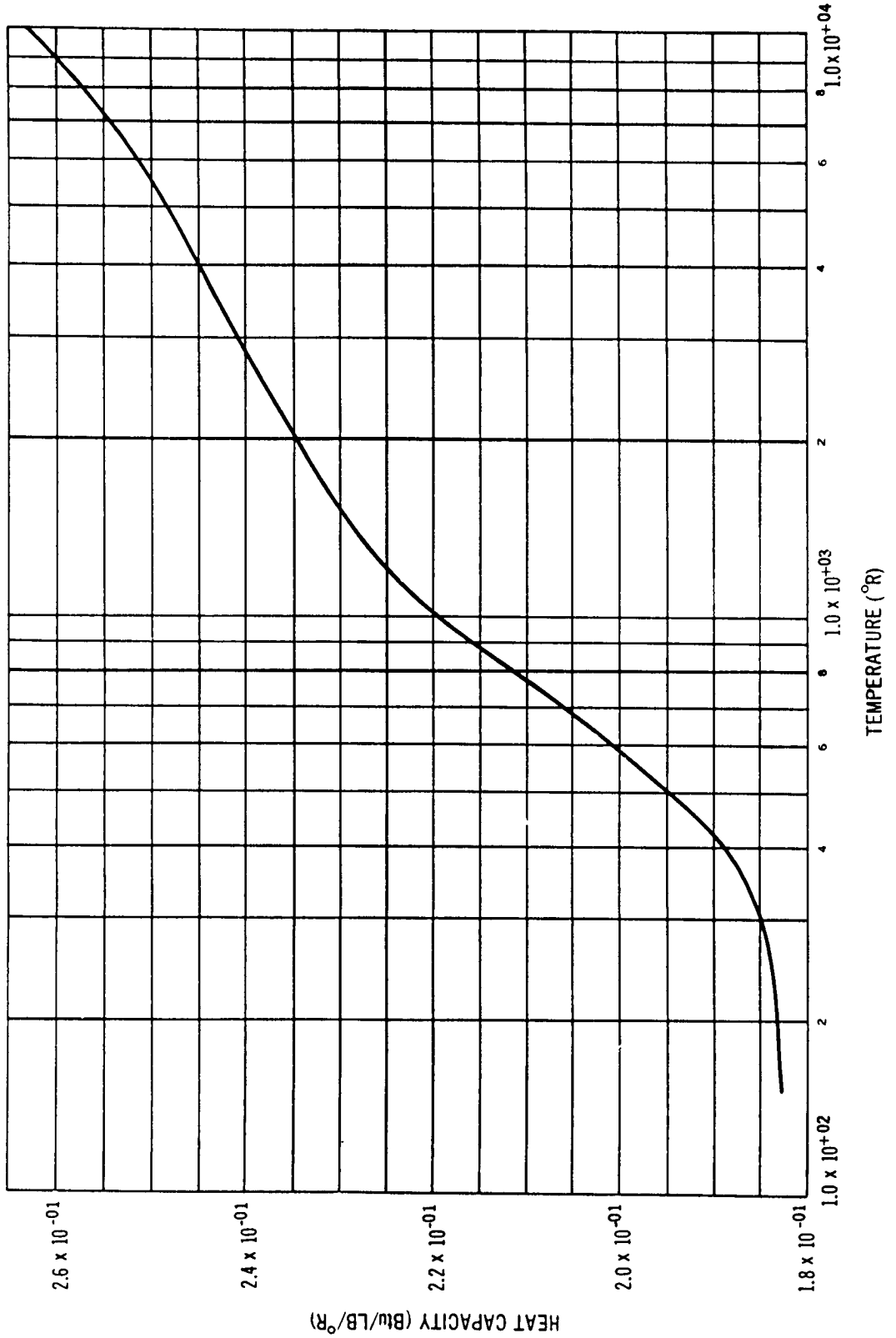

Figure II-1.1e. Heat Capacity of Gaseous Fluorine (Reference 287)

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Table II-1.1e
HEATS OF VAPORIZATION OF FLUORINE

Temperature °R	Heat of Vaporization Btu/lb	Reference
153.43	71.526	59
162.00	69.252	59
171.00	66.694	59
180.00	63.947	59
189.00	61.105	59
198.00	57.931	59
207.00	54.473	59
216.00	50.636	59
225.00	46.326	59
234.00	41.163	59
243.00	34.721	59
252.00	25.437	59
259.20	6.39	52

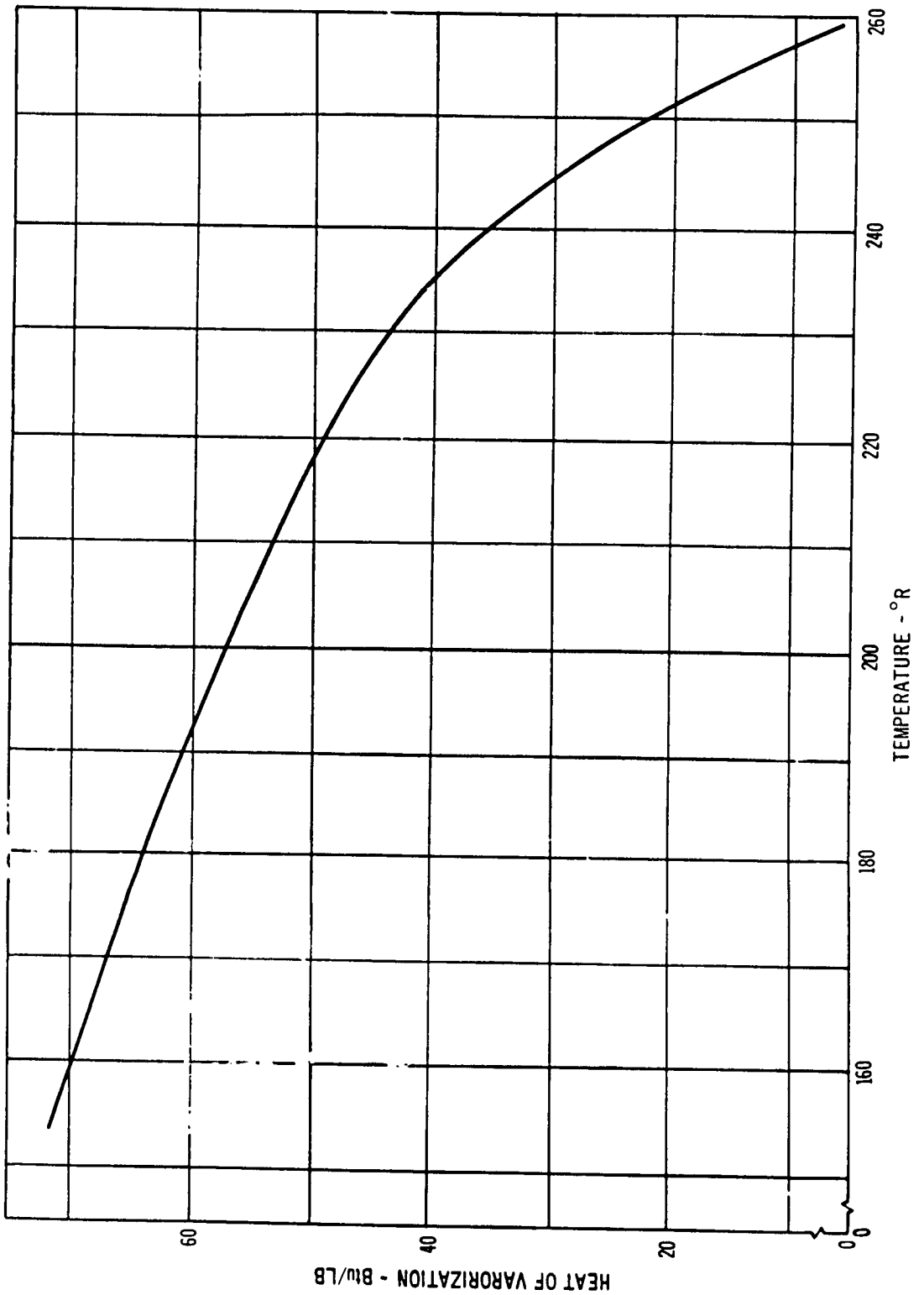

Figure II-1.1f. Heat of Vaporization of Fluorine (Reference 52 and 59)

Table II-1.1f (page 1 of 3)
ENTHALPY OF GASEOUS FLUORINE AT ONE ATMOSPHERE

Temperature °R	Enthalpy, H--$^{a}H_{O}$ Btu/lb	Reference
153.04	27.975	287
162.00	29.616	287
171.00	31.264	287
180.00	32.912	287
216.00	39.506	287
252.00	46.108	287
288.00	52.728	287
324.00	59.380	287
360.00	66.076	287
396.00	72.830	287
432.00	79.652	287
468.00	86.550	287
504.00	93.528	287
536.69	99.931	287
540.00	100.589	287
720.00	137.067	287
900.00	175.216	287
1080.00	214.602	287
1260.00	254.874	287
1440.00	295.809	287
1620.00	337.241	287
1800.00	379.071	287
1980.00	421.223	287
2160.00	463.645	287
2340.00	506.295	287
2520.00	549.148	287
2700.00	592.186	287
2880.00	635.385	287
3060.00	678.736	287
3240.00	722.233	287
3420.00	765.863	287
3600.00	809.621	287
3780.00	853.502	287
3960.00	897.265	287
4140.00	941.619	287

$^{a}H_{O}$ = 0°K.

Table II-1. 1f (page 2 of 3)

ENTHALPY OF GASEOUS FLUORINE AT ONE ATMOSPHERE

Temperature °R	Enthalpy, H--$^{a}H_{O}$ Btu/lb	Reference
4320.00	985.846	287
4500.00	1030.177	287
4680.00	1074.622	287
4860.00	1119.165	287
5040.00	1163.819	287
5220.00	1208.565	287
5400.00	1253.429	287
5580.00	1298.385	287
5760.00	1343.436	287
5940.00	1388.587	287
6120.00	1433.837	287
6300.00	1479.181	287
6480.00	1524.625	287
6660.00	1570.160	287
6840.00	1615.793	287
7020.00	1661.522	287
7200.00	1707.344	287
7380.00	1753.258	287
7560.00	1799.271	287
7740.00	1845.373	287
7920.00	1891.570	287
8100.00	1937.863	287
8280.00	1984.245	287
8460.00	2030.721	287
8640.00	2077.288	287
8820.00	2123.950	287
9000.00	2170.701	287
9180.00	2217.548	287
9360.00	2264.484	287
9540.00	2311.510	287
9720.00	2358.631	287
9900.00	2405.847	287
10080.00	2453.148	287
10260.00	2500.543	287
10440.00	2548.029	287

$^{a}H_{O}$ = 0°K.

Table II-1.1f (page 3 of 3)
ENTHALPY OF GASEOUS FLUORINE AT ONE ATMOSPHERE

Temperature °R	Enthalpy, $H - {}^{a}H_{O}$ Btu/lb	Reference
10620.00 10800.00	2595.610 2643.275	287 287
${}^{a}H_{O}$ = 0°K.		

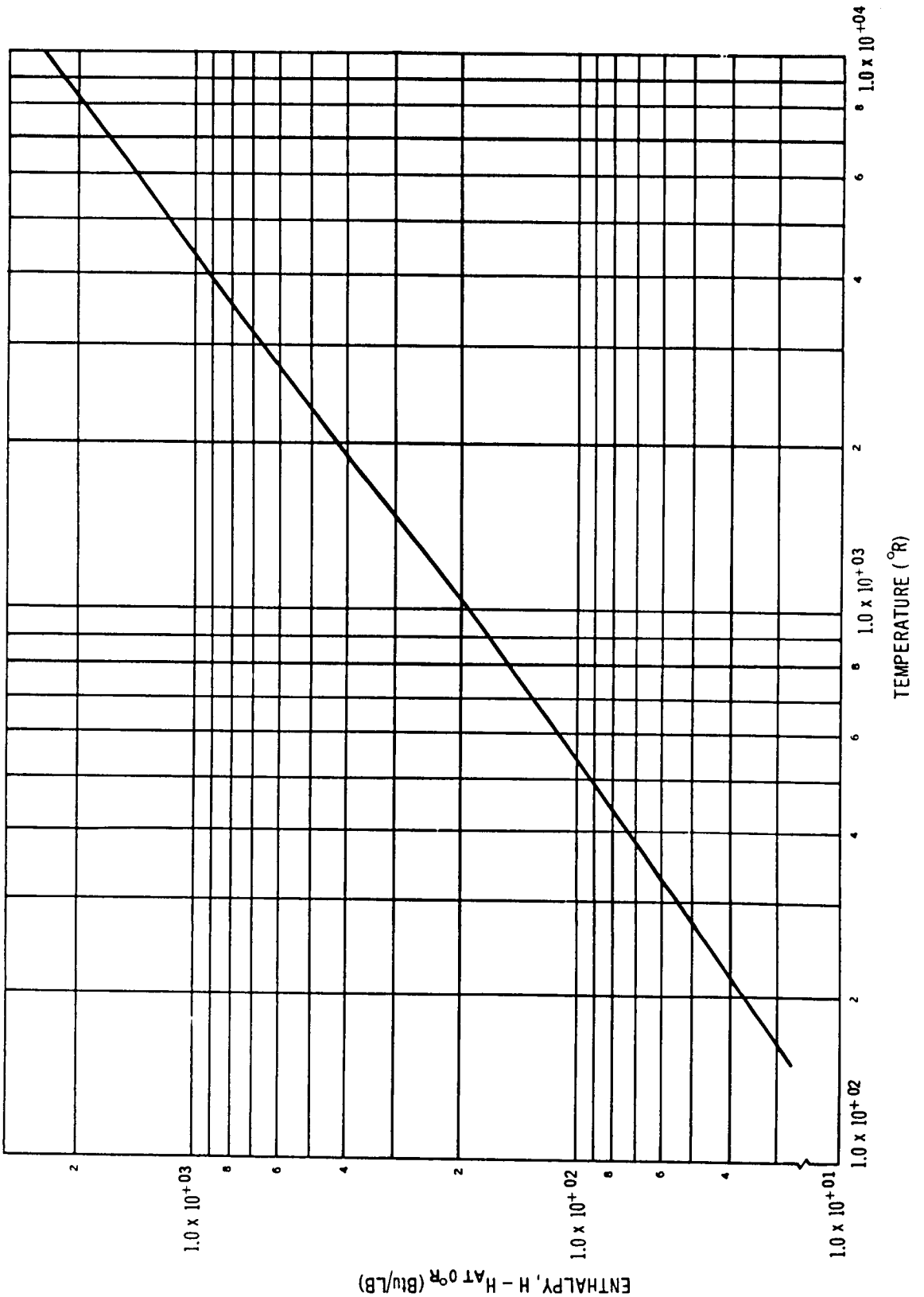

Figure II-1.1g. Enthalpy of Gaseous Fluorine at One Atmosphere (Reference 287)

Table II-1.1g
ENTROPY OF SOLID AND LIQUID FLUORINE

Temperature °R	Entropy, S Btu/(lb)(°R)	Reference
Solid II		
27	0.0195	52
36	0.0375	52
45	0.0600	52
54	0.0854	52
63	0.1126	52
72	0.1411	52
81	0.1703	52
81.99	0.1736	52
Solid I		
81.99	0.2740	54
90	0.3021	54
96.37	0.3238	54
Liquid		
96.37	0.3837	54
99	0.3934	54
108	0.4247	54
117	0.4535	54
126	0.4799	54
135	0.5046	54
144	0.5279	54
153	0.5500	54
153.036	0.5500	54
153.036	1.0334	54

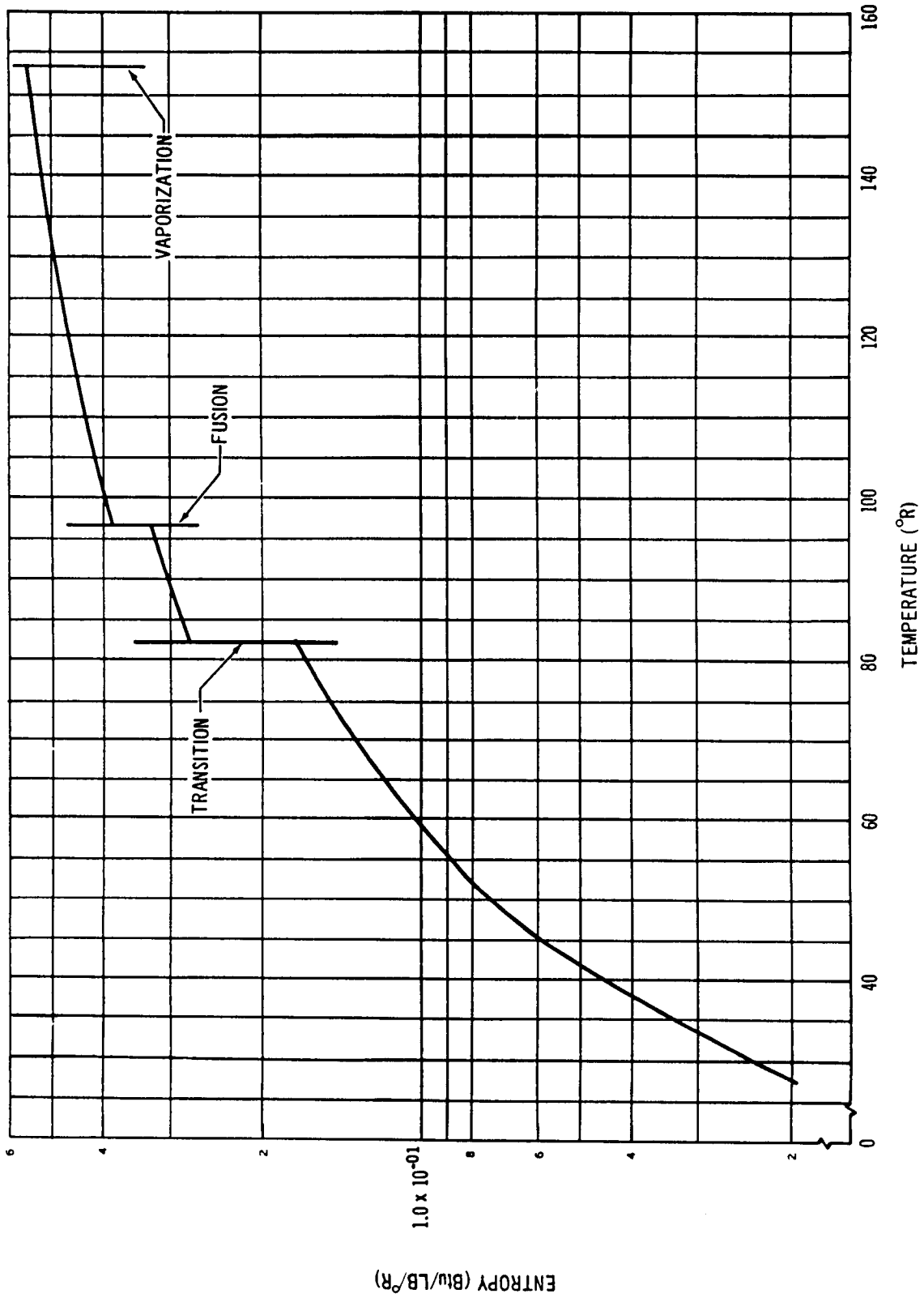

Figure II-1.1h. Entropy of Solid and Liquid Fluorine (References 52 and 54)

Table II-1.1h (page 1 of 2)
ENTROPY OF GASEOUS FLUORINE

Temperature °R	Entropy, S Btu/(lb)(°R)	Reference
Gas		
153.04	1.0408	287
162.00	1.0512	287
171.00	1.0611	287
180.00	1.0879	287
360.00	1.1980	287
536.69	1.2744	287
540.00	1.2756	287
720.00	1.3338	287
900.00	1.3810	287
1080.00	1.4209	287
1260.00	1.4554	287
1440.00	1.4857	287
1620.00	1.5128	287
1800.00	1.5373	287
1980.00	1.5600	287
2160.00	1.5801	287
2340.00	1.5990	287
2520.00	1.6167	287
2700.00	1.6332	287
2880.00	1.6487	287
3060.00	1.6632	287
3240.00	1.6771	287
3420.00	1.6902	287
3600.00	1.7026	287
3780.00	1.7145	287
3960.00	1.7259	287
4140.00	1.7368	287
4320.00	1.7472	287
4500.00	1.7573	287
4680.00	1.7669	287

Table II-1. 1h (page 2 of 2)
ENTROPY OF GASEOUS FLUORINE

Temperature °R	Entropy, S Btu/(lb)(°R)	Reference
Gas (concluded)		
4860.00	1.7763	287
5040.00	1.7853	287
5220.00	1.7940	287
5400.00	1.8025	287
5580.00	1.8107	287
5760.00	1.8186	287
5940.00	1.8263	287
6120.00	1.8338	287
6300.00	1.8411	287
6480.00	1.8482	287
6660.00	1.8552	287
6840.00	1.8619	287
7020.00	1.8685	287
7200.00	1.8749	287
7380.00	1.8812	287
7560.00	1.8874	287
7740.00	1.8934	287
7920.00	1.8993	287
8100.00	1.9051	287
8280.00	1.9108	287
8460.00	1.9163	287
8640.00	1.9218	287
8820.00	1.9271	287
9000.00	1.9323	287
9180.00	1.9375	287
9360.00	1.9423	287
9540.00	1.9475	287
9720.00	1.9524	287
9900.00	1.9572	287
10080.00	1.9620	287
10260.00	1.9666	287
10440.00	1.9712	287
10620.00	1.9757	287
10800.00	1.9802	287

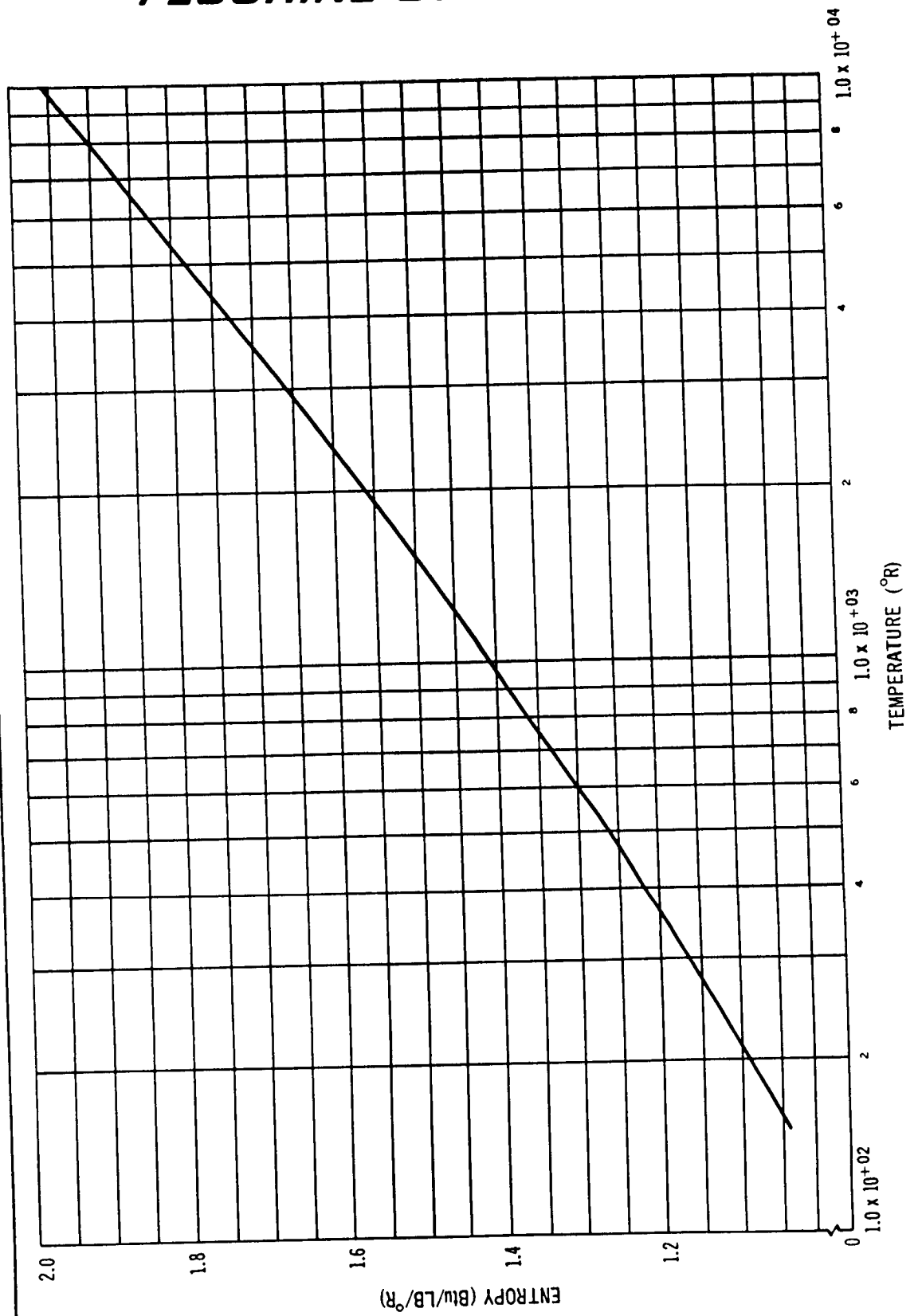

Figure II-1.1i. Entropy of Gaseous Fluorine (Reference 287)

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Table II-1.1i
FREE-ENERGY FUNCTION OF SOLID AND LIQUID FLUORINE

Temperature °R	Free-energy Function, $-(F - H_O)$[a] Btu/(lb)	Reference
Solid II		
27.00	0.155	54
36.00	0.408	54
45.00	0.843	54
54.00	1.496	54
63.00	2.386	54
72.00	3.526	54
81.00	4.926	54
81.99	5.096	54
Solid I		
81.99	5.096	54
90.00	7.406	54
96.37	9.404	54
Liquid		
96.37	9.404	54
99.00	10.423	54
108.00	14.108	54
117.00	18.064	54
126.00	22.268	54
135.00	26.701	54
144.00	31.349	54
153.00	36.200	54
153.04	36.212	54
Vapor		
153.04	36.231	54

[a] H_O = 0°K for liquid, solid phases.

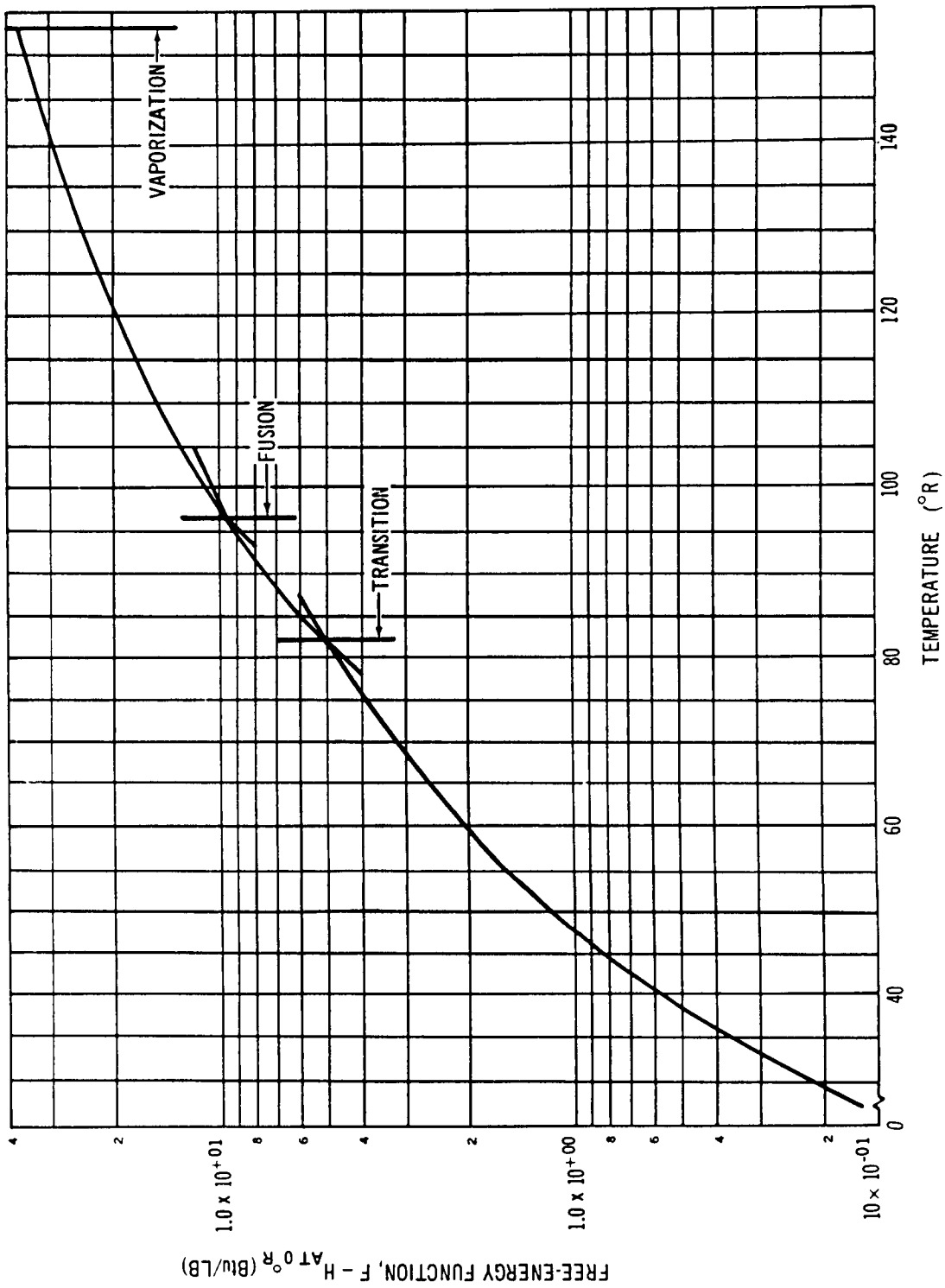

Figure II-1.1j. Free-Energy Function of Solid and Liquid Fluorine (Reference 54)

Table II-1.1j (page 1 of 3)
FREE-ENERGY FUNCTION OF GASEOUS FLUORINE

Temperature °R	Free-energy Function, $-(F - H_O)$[a] Btu/(lb)	Reference
153.04	131.37	287
144.00	140.75	287
180.00	159.85	287
216.00	199.02	287
252.00	239.30	287
288.00	280.53	287
324.00	322.58	287
360.00	365.38	287
450.00	475.20	287
536.69	584.25	287
540.00	588.50	287
720.00	823.64	287
900.00	1068.19	287
1080.00	1320.56	287
1260.00	1579.59	287
1440.00	1844.44	287
1620.00	2114.46	287
1800.00	2389.11	287
1980.00	2667.97	287
2160.00	2950.67	287
2340.00	3236.92	287
2520.00	3526.47	287
2700.00	3819.09	287
2880.00	4114.58	287
3060.00	4412.78	287
3240.00	4713.53	287
3420.00	5016.71	287
3600.00	5322.18	287
3780.00	5629.85	287
3960.00	5939.61	287

[a] H_O = 0°K for gaseous phase.

Table II-1. 1j (page 2 of 3)

FREE-ENERGY FUNCTION OF GASEOUS FLUORINE

Temperature °R	Free-energy Function, $-(F - H_O)$[a] Btu/(lb)	Reference
4140.00	6251.38	287
4320.00	6565.07	287
4500.00	6880.60	287
4680.00	7197.91	287
4860.00	7516.93	287
5040.00	7837.60	287
5220.00	8159.87	287
5400.00	8483.68	287
5580.00	8808.99	287
5760.00	9135.75	287
5940.00	9463.93	287
6120.00	9793.47	287
6300.00	10124.35	287
6480.00	10456.52	287
6660.00	10789.95	287
6840.00	11124.62	287
7020.00	11460.49	287
7200.00	11797.53	287
7380.00	12135.72	287
7560.00	12475.04	287
7740.00	12854.45	287
7920.00	13156.93	287
8100.00	13499.46	287
8280.00	13843.02	287
8460.00	14187.60	287
8640.00	14533.16	287
8820.00	14879.69	287
9000.00	15227.18	287
9180.00	15575.60	287
9360.00	15924.94	287

[a] H_O = 0°K for gaseous phase.

Table II-1.1j (page 3 of 3)
FREE-ENERGY FUNCTION OF GASEOUS FLUORINE

Temperature °R	Free-energy Function, $-(F - H_O)$[a] Btu/(lb)	Reference
9540.00	16275.19	287
9720.00	16626.32	287
9900.00	16978.33	287
10080.00	17331.20	287
10260.00	17684.91	287
10440.00	18039.45	287
10620.00	18394.82	287
10800.00	18750.99	287

[a] H_O = 0°K for gaseous phase.

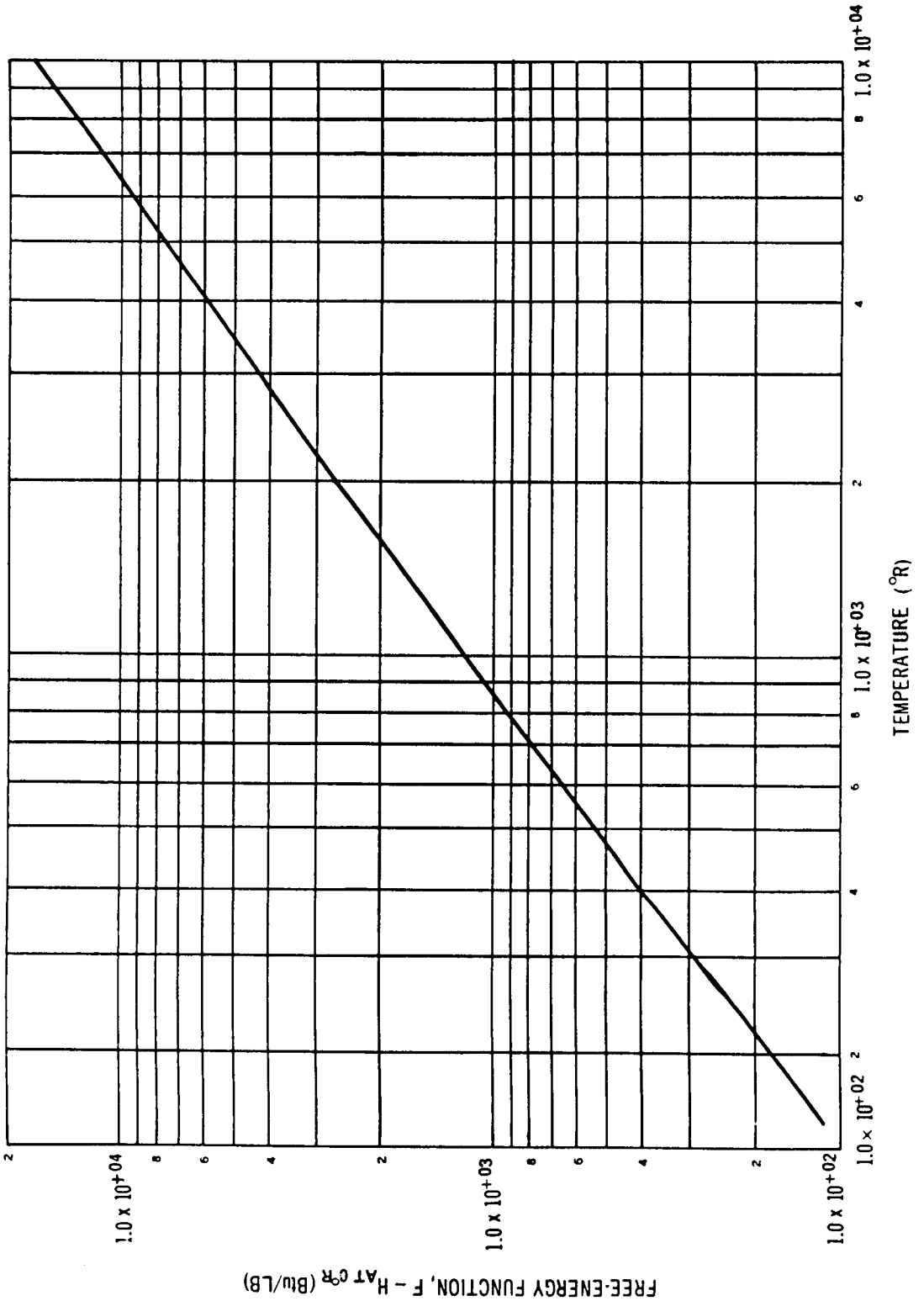

Figure II-1.1k. Free-Energy of Gaseous Fluorine (Reference 287)

Table II-1.1k

VISCOSITY OF LIQUID FLUORINE

Temperature °R	Viscosity lb force sec/sq ft	Reference
124.6	8.6526×10^{-6}	212
131.9	7.289	212
135.5	6.851	212
140.8	6.245	212
145.5	5.743	212
149.9	5.368	212

Conversion Factors

$$\frac{lb_f sec}{ft^2} \text{ times } 32.2 \rightarrow \frac{lb_m}{ft\text{-}sec}$$

$$\frac{lb_f sec}{ft^2} \text{ times } 47850 \rightarrow \text{Centipoises}$$

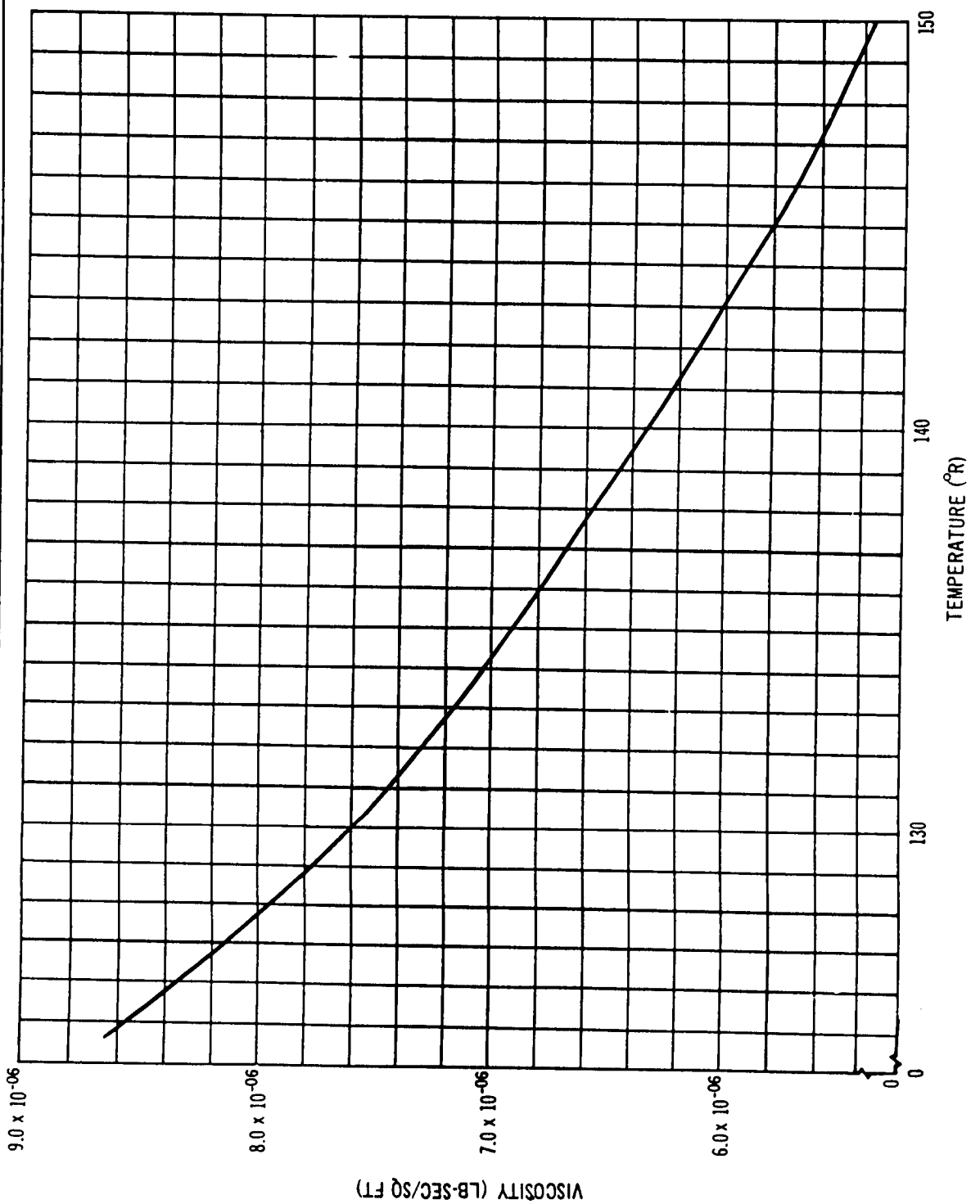

Figure II-1.1ℓ. Viscosity of Liquid Fluorine (Reference 229)

Table II-1.1ℓ
VISCOSITY OF GASEOUS FLUORINE

Pressure, psia	Temperature °R	Viscosity $\frac{\text{lb force (sec)}}{\text{(sq ft)}}$	Reference
14.657	156.2	1.1592×10^{-9}	269
14.657	162.0	1.6020	292
14.657	214.0	1.8275	269
14.773	267.8	2.2551	269
14.773	302.2	2.5084	269
14.773	304.7	2.9742	292
14.754	346.1	2.8802	269
14.754	360.0	3.5089	292
14.754	383.6	3.1162	269
(a)	413.3	3.3647	269
(a)	448.0	3.6070	269
(a)	491.8	4.3714	269
(a)	520.4	4.8978	292
(a)	588.8	5.3197	292
(a)	768.1	6.4329	292
(a)	847.8	6.8715	292

[a] Approximately atmospheric pressure.

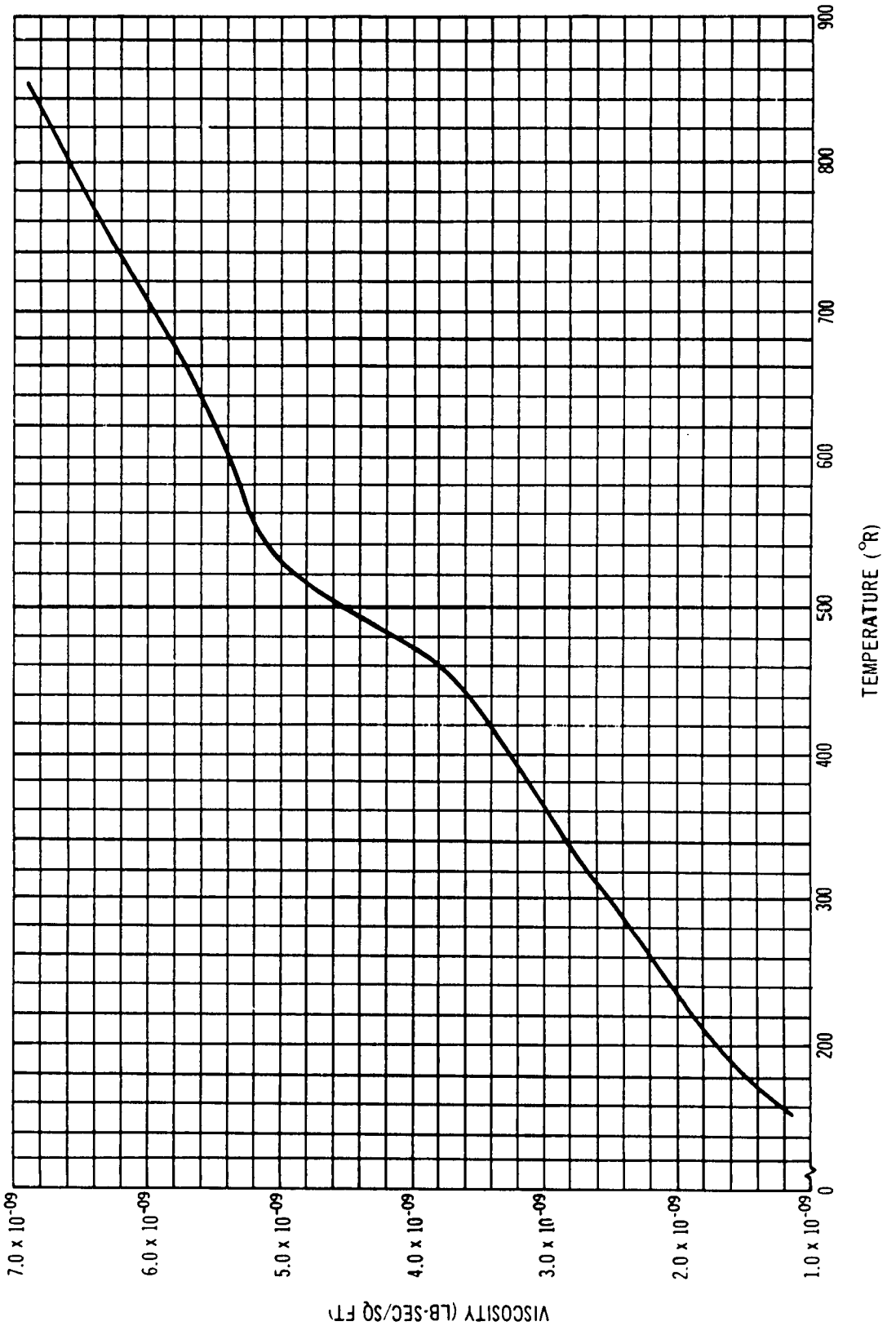

Figure II-1.1m. Viscosity of Gaseous Fluorine at One Atmosphere (References, 269 and 292)

Table II-1.1m
SURFACE TENSION OF LIQUID FLUORINE

Temperature °R	Surface Tension lb/ft	Reference
119.18	129.16×10^{-5}	78
124.56	122.65	212
126.47	121.28	78
127.13	119.23	78
128.16	119.23	212
129.69	116.62×10^{-5}	78
131.76	114.43	212
132.03	115.33	78
135.16	112.99	78
135.34	111.55	78
135.54	111.01×10^{-5}	212
137.52	108.95	212
138.87	107.79	78
140.76	105.52	212
143.82	101.48	74
145.80	100.04	212

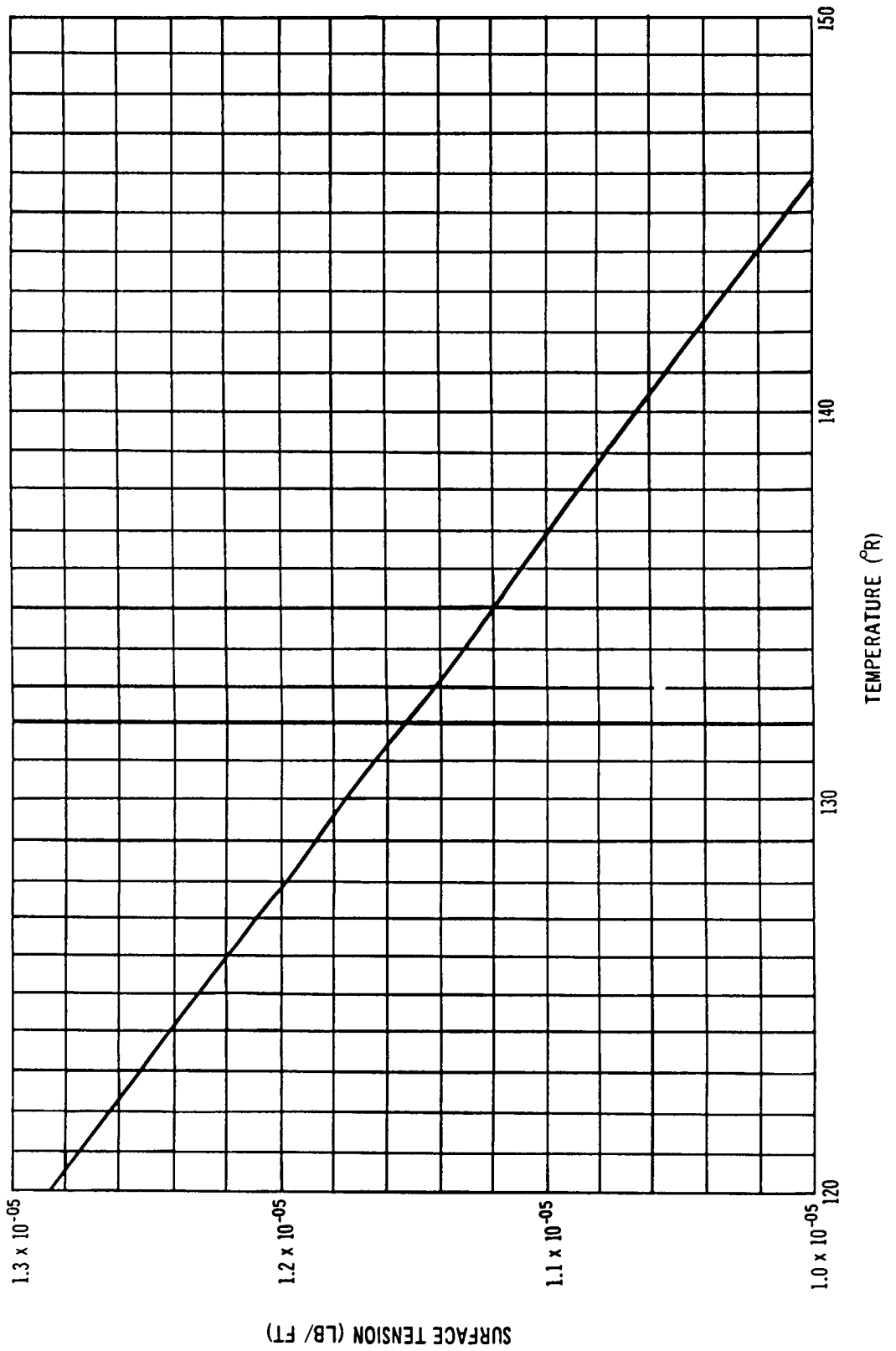

Figure II-1.1n. Surface Tension of Liquid Fluorine (References 74, 78, and 212)

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Table II-1.1n

THERMAL CONDUCTIVITY OF LIQUID FLUORINE

Temperature °R	Pressure psia	Pressure atm	Thermal Conductivity Btu/(ft)(hr)(°R)	Reference
146.7	37	3.52	8.83×10^{-2}	90
147.1	87	6.92	8.95	90
147.2	5	1.34	8.83	90
147.2	187	13.72	9.00	90
147.2	390	27.53	9.05	90
153.0	37	3.52	8.56×10^{-2}	90
153.0	187	13.72	8.64	90
166.0	20	2.36	7.89	90
166.0	390	27.53	7.98	90
169.7	187	13.72	7.62	90
170.1	37	3.52	7.55×10^{-2}	90
188.1	87	6.92	6.85	90
188.1	187	13.72	6.89	90
188.1	328	23.31	6.99	90
192.8	87	6.92	6.58	90
206.1	187	13.72	5.95×10^{-2}	90
206.5	380	26.85	6.02	90
208.6	306	21.82	5.95	90
209.0	168	12.43	5.85	90
221.4	250	18.01	5.32	90
226.8	285	20.39	4.84×10^{-2}	90
230.4	340	24.13	4.69	90

Table II-1.1o

THERMAL CONDUCTIVITY OF GASEOUS FLUORINE AT ONE ATMOSPHERE

Temperature °R	Thermal Conductivity Btu/(ft)(hr)(°R)	Reference
Gaseous Fluorine at 1 Atmosphere		
180	4.98×10^{-3}	282
270	7.76	282
360	10.55	282
450	13.16	282
493.2	14.32	282
540	15.55×10^{-3}	282
630	17.80	282
720	19.91	282
810	21.99	282
900	24.02	282
990	26.08×10^{-3}	282
1080	28.21	282
1170	30.26	282
1260	32.32	282
1350	34.30	282
1440	36.36	282

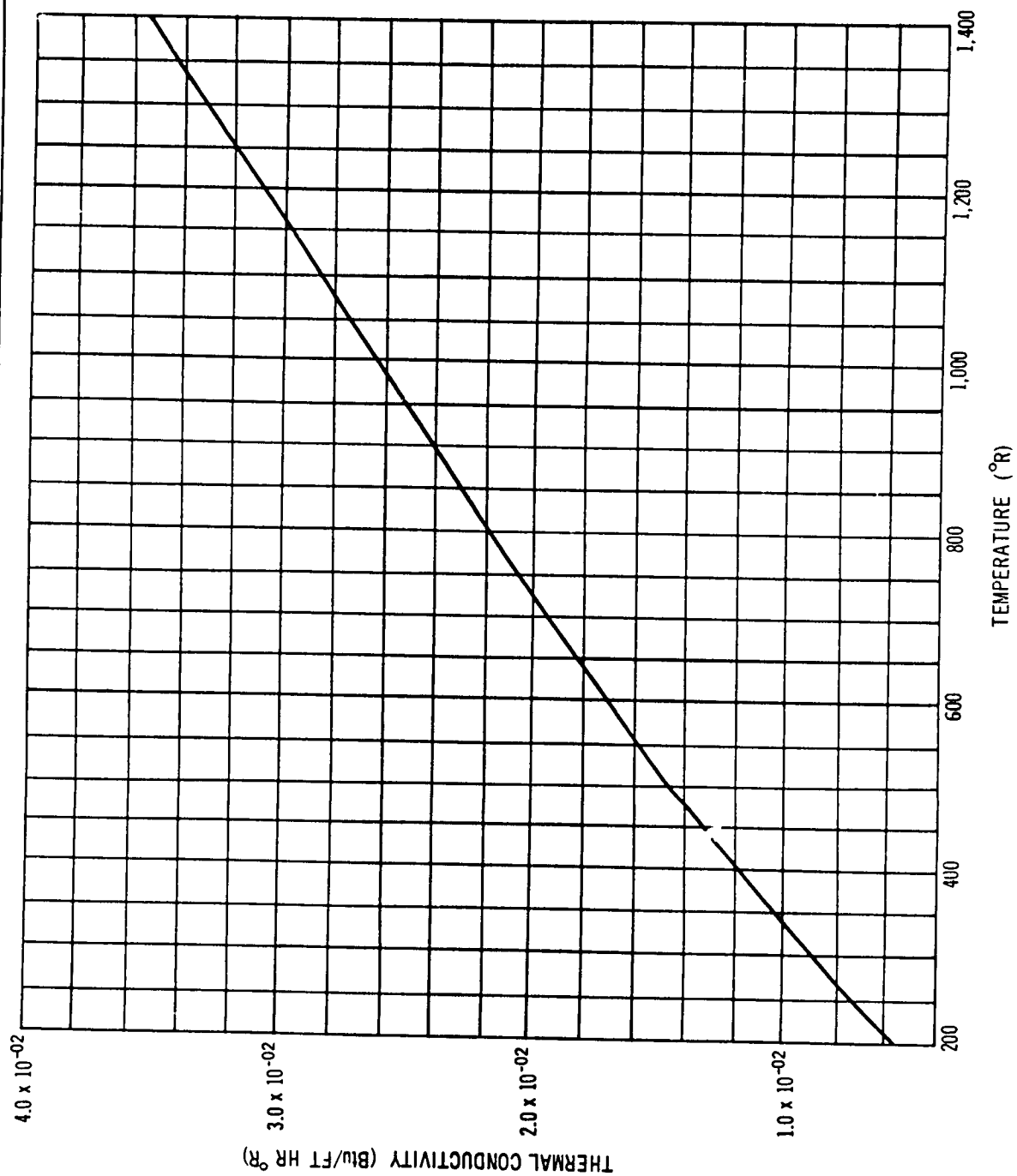

Figure II-1.1o. Thermal Conductivity of Gaseous Fluorine at One Atmosphere (Reference 282)

Table II-1.1p
DIELECTRIC CONSTANT OF LIQUID FLUORINE

Temperature °R	Dielectric Constant	Reference
103.32	1.567	267
108.92	1.561	267
115.94	1.553	267
123.07	1.546	267
131.40	1.536	267
135.02	1.533	267
142.92	1.524	267
149.78	1.517	267

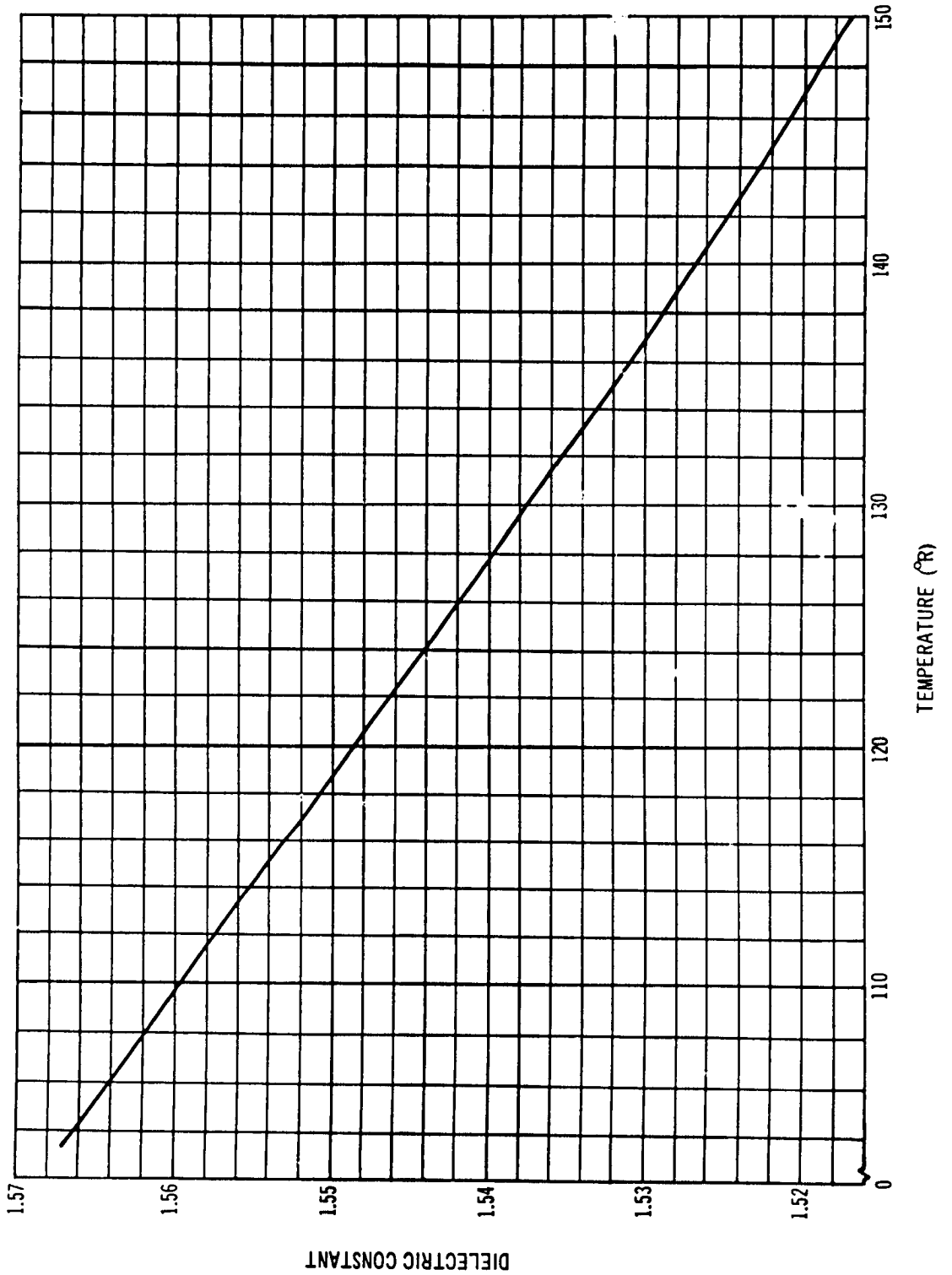

Figure II-1.1p. Dielectric Constant of Liquid Fluorine (Reference 267)

Table II-1.1q

EQUILIBRIUM CONSTANT OF DISSOCIATION AS FUNCTION OF TEMPERATURE, $F_2 \rightleftharpoons 2F$

Temperature °R	Equilibrium Constant, K_p, atm	Reference
536.6	2.74×10^{-48}	32
540.0	5.97×10^{-48}	32
720.0	1.26×10^{-34}	32
900.0	1.334×10^{-26}	32
1080.0	3.11×10^{-21}	32
1260.0	2.18×10^{-17}	32
1440.0	1.69×10^{-14}	32
1620.0	3.04×10^{-12}	32
1800.0	1.95×10^{-10}	32
2700.0	5.41×10^{-5}	32
3600.0	2.99×10^{-2}	32
4500.0	2.36	32
5400.0	17.40	32
6300.0	109.00	32
7200.0	432.00	32
9000.0	3019.00	32

Table II-1.1r (page 1 of 2)

SUMMARY OF FLUORINE PHYSICAL AND THERMODYNAMIC PROPERTIES

Molecular weight	38.00
Normal boiling point: °R °K	153.036 85.02
Density of liquid at normal boiling point, lb/cu ft	93.96
Density of vapor at normal boiling point, lb/cu ft	0.3519
Heat of vaporization at normal boiling point, Btu/lb	71.514
Entropy of vaporization, Btu/(lb)(°R)	0.48363
Critical temperature: °R °K	259.128 143.96
Critical pressure, atm	55.00
Critical density, lb/cu ft	29.437
Critical compressibility factor	0.375
Specific heat of liquid (constant pressure and normal boiling point), Btu/(lb)(°R)	0.36697
Specific heat of gas (constant pressure and normal boiling point), Btu/(lb)(°R)	0.18305
Specific heat of gas (constant pressure), Btu/(lb)(°R) at 70°F	0.19784
Specific heat of gas (constant volume), Btu/(lb)(°R) at 70°F	0.14565
Ratio of heat capacities, C_p/C_v	1.3583
Thermal conductivity of liquid at B.P., Btu/(hr)(ft)(°R)	0.0915
Thermal conductivity of vapor at normal boiling point, Btu/(hr)(ft)(°R)	0.00415

Table II-1.1r (page 2 of 2)

SUMMARY OF FLUORINE PHYSICAL AND THERMODYNAMIC PROPERTIES

Critical thermal conductivity, Btu/(hr)(ft)(°R)	0.0231
Absolute viscosity of liquid at normal boiling point, lb mass/(sec)(ft)	1.65×10^{-4}
Absolute viscosity of gas at normal boiling point, lb mass/(sec)(ft)	3.725×10^{-8}
Critical absolute viscosity, lb mass/(sec)(ft)	1.2337×10^{-5}
Index of refraction of liquid at normal boiling point (probably 5890 Å)	1.200
Index of refraction of gas at 32°F and 1.0 atm at 5890 Å	1.000214
Dielectric constant of liquid at normal boiling point	1.51
Dielectric constant of gas (at B.P.)	1.43
Normal melting or freezing point (liquid to solid I): °R	96.372
°K	53.540
Triple point temperature, °K	53.54
Triple point pressure, atm	2.184×10^{-3}
Triple point density, lb/cu ft: Solid	81.20
Liquid	107.064
Heat of fusion (liquid to solid I), Btu/lb	5.778
Entropy of fusion, Btu/(lb)(°F)	5.9913×10^{-2}
Transition temperature, °R: Solid I to solid II	81.99
Heat of transition, Btu/(lb): Solid I to solid II	8.237
Entropy of transition, Btu/(lb)(°R): Solid I to solid II	0.1005

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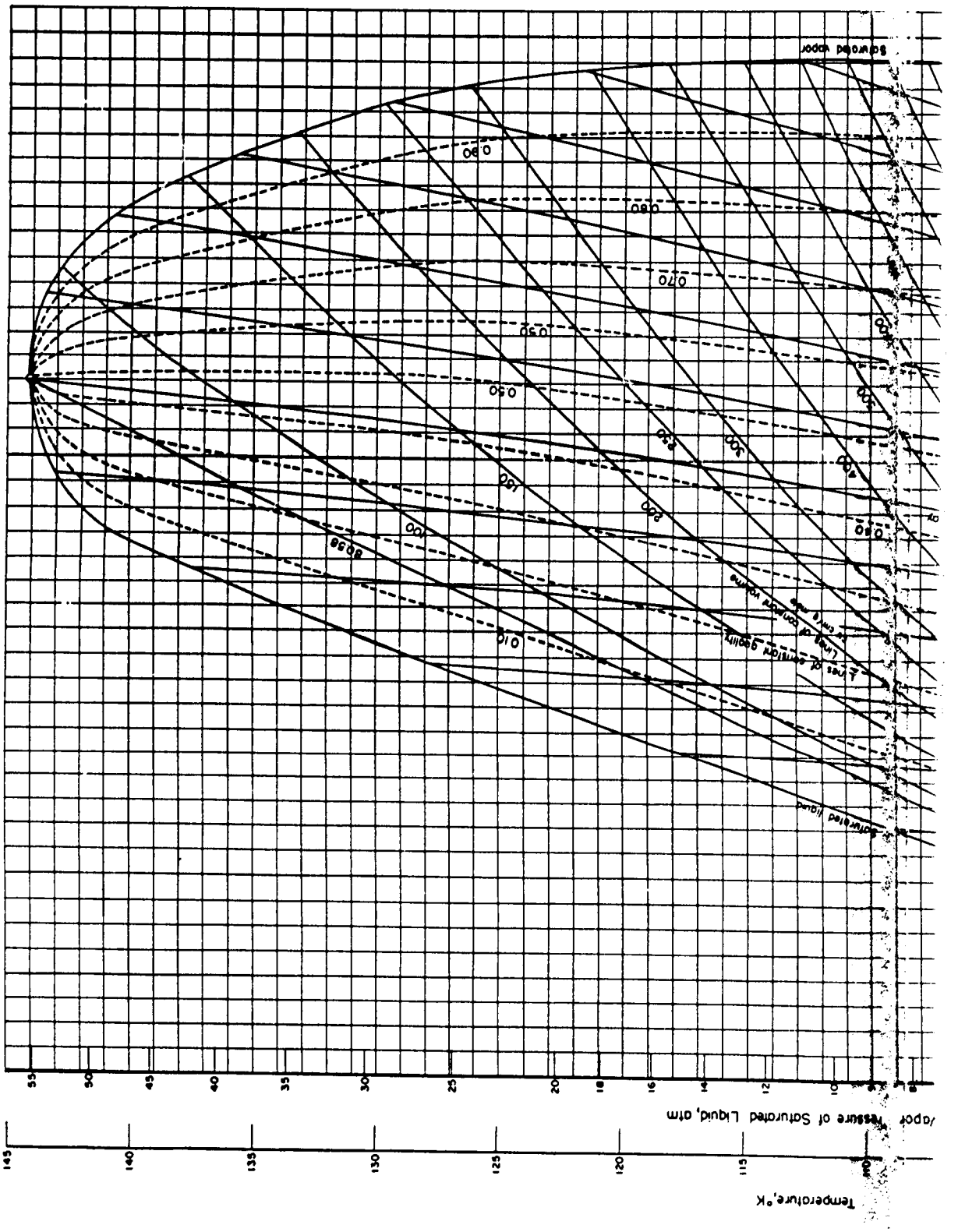
Temperature-Enthalpy Diagram for Fluorine, Fricke(1).



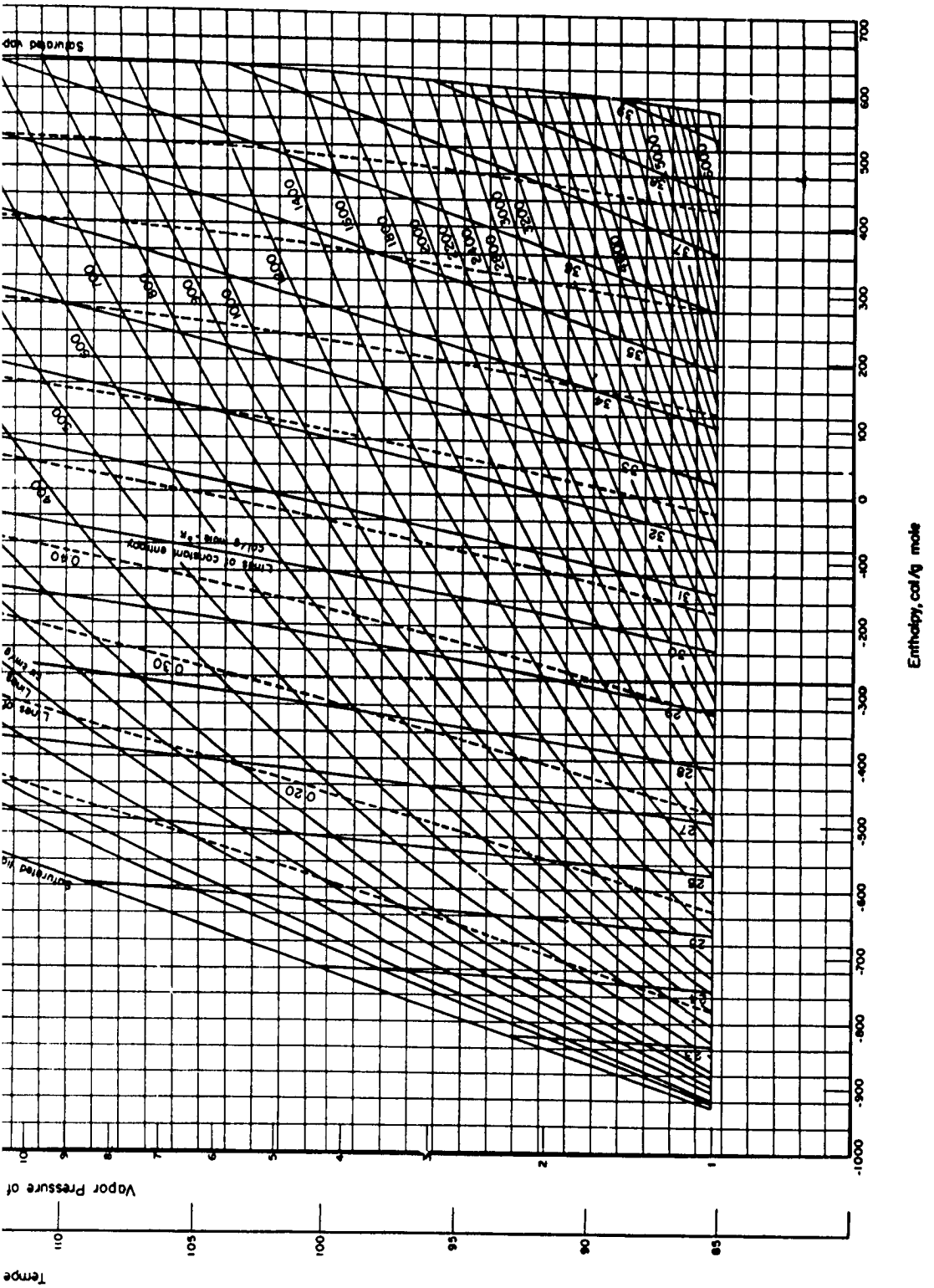


Figure II-1.1q. Temperature--Enthalpy Diagram for Fluorine

1.2 Contaminants

A contaminant is defined as any matter which, when in intimate contact with another material, results in that material being in an impure state for its end use. The contaminant can be present as foreign material lodged on or below the material surface. Normally the major contaminants present on a material surface are organic in nature. This type of contamination is a result of the environment to which the material is subjected during its manufacture, cleaning, testing, or installation in a system. Although organic contaminants are usual, inorganics may also exist on the surface, or within the material. Usually the inorganic contamination is the result of the addition of foreign matter during the production of the raw material or in the fabrication of sub-components from the raw material.

Surface contaminants, predominantly organic, react very rapidly with fluorine with a substantial release of heat. Contamination from organic material is practically impossible to prevent, since the cutting and forming coolants, preservatives, cleaning fluids, and deposits from handling during manufacturing are usually organic compounds. The amount of contamination that can be tolerated is dependent upon many factors, such as the heat released per unit of time from the contaminant-fluorine reaction, the heat source volume, and thermodynamic properties of the material and fluid. At present, there is no practical means of predicting the quantity or degree of contamination which can be tolerated, and if there were, there are no reasonable inspection methods available to measure the quantity of contamination that is present. Application of the recommended manufacturing procedures presented in Section III should limit the organic contamination sufficiently, so that the subsequent functional life, in the fluorine environment, will not be impaired. As procedures are developed, and experience is gained in their use, the procedures may be re-evaluated and reduced in complexity.

Contaminants which are present below the material surface, lodged within the body of the material, can be either organic or inorganic. This type of contamination normally results from impurities, during either production of the raw material, or from the operations performed on the raw material, e.g., casting, molding, welding, or forging. The allowable tolerance of this

type of contamination is not as easily evaluated as that of the surface contaminants. If during the functional life of a component, a subsurface contaminant is exposed to fluorine, a reaction could occur. The release of heat may be sufficient to raise the local base material to its kindling temperature. This condition could result in total consumption of the base material, since these types of reactions may be self propagating. The means by which this exposure could occur would depend primarily upon the type of base material in which the contaminant is lodged. If the base material was a metal, the exposure would occur only by fluid erosion, or by a structural failure, (i. e., crack) of the metal surface. To evaluate the amount of surface failure allowable, entails a determination of the depth to which the erosion and/or cracking could be tolerated before failure of the component would occur. In addition, it is necessary to determine the extent to which the system as a whole would be compromised if such a failure occurred. These evaluations would provide a basis for the evaluation of subsurface contaminants as a function of depth, size, and distribution.

Exposure of subsurface contaminants within polytetrafluoroethylene and ceramic materials (including cermets) can occur by the same methods as in metals. However, this exposure would more often occur first by permeation of the material by gaseous or liquid fluorine. These materials contain molecular-voids, as well as macro-voids, by virtue of the state of the raw material from which the component is fabricated, i. e., particle packing of ceramic powder and polymer chain packing of polymeric materials. These voids, although randomly oriented, provide a path through the material, which allows permeation of fluorine. Unfortunately, the literature which is presently available and which defines this fluorine permeation rate, contains no test data. Until such time as this data is available, determination of the allowable depth and degree of subsurface contamination, especially for long term mission applications, remains an art rather than an engineering science. The designer of hardware, utilizing these materials must consider this in evaluating a design. In lieu of specific allowable subsurface tolerance levels, it is recommended that contamination be kept to an absolute minimum. This requires the exercise of stringent, but also reasonable controls during the

phases of manufacturing to minimize the possible contamination. A recommended polytetrafluoroethylene specification is presented in Appendix III-1. Adherence to this specification will provide suitable material for fluorine service. Refer to paragraph II-2.0 for specific discussion of this material.

1.2.1 Passivation of Metals

Fluorine passivation of a system, or the components therein, is defined as the formation of a fluoride film on the material's fluid contacting surface. This film is formed by exposing the system components to a gaseous fluorine environment under controlled static conditions at a higher temperature and pressure than contemplated for service.

As noted in Reference 91, passivation of metal surfaces before exposure to liquid fluorine is unnecessary unless the surface is suspected of having traces of contaminants. A passivation procedural outline is presented in Appendix III-5 which can be used advantageously to inert by reaction and complete fluorination, these contaminants. During this passivation procedure, energy, as heat, is released and absorbed by the surrounding material/gas; hence, these controlled reactions lower the potential energy plateau before dynamic conditions are imposed.

In any production cleaning and handling procedure it is sometimes impossible to remove all contaminants from any component. Only small quantities of contaminants should remain after cleaning, per the procedure in Appendix III-4, and therefore, the heat energy addition from reacting these with fluorine will be minor. Too often, this "cleaning" feature of the passivation process, is the prime purpose of passivation. This is an unreliable practice since the predictability of the various material-fluorine reaction products and the reacting energy levels is, at best, very poor. Therefore, the use of "passivation cleaning" could result in damage and/or failure of a system, component or subcomponent. Often these failures happen without a full

understanding of the failure phenomena, and in some cases, even the realization that a failure has occurred. In short, this increases the number of variables in the system and therefore makes it extremely difficult to evaluate failures. It is recommended that passivation be employed only after the system has been cleaned per Appendix III-4 and certified "for fluorine service."

Extreme care must be exercised in the handling and storage of components which have been exposed to fluorine prior to installation into a system to prevent moisture from contacting the fluoride film. Most metal fluorides are hygroscopic and contact with atmospheric moisture is sufficient to cause them to be hydrolyzed. This absorption of water transforms the film from a ductile, tenacious compound to one which is very brittle and contains poor adhesive characteristics. This hydrolyzed film is analogous to rust and is readily removed (flaked off) from the substrate metal. This hydrolysis, therefore not only leaves the material unprotected, but also can cause surface damage. This is particularly undesirable on finely finished surfaces such as sealing surfaces. Since this material may be quite mobile, if it is introduced into a system, it could cause either partial or complete malfunction of one or more system components. In addition, subsequent exposure of the hydrolyzed film to fluorine results in the formation of hydrogen fluoride (HF) which readily ionizes and subjects the local area to a high concentration of HF. To prevent these detrimental effects it is imperative that contact with atmospheric moisture be minimized after the formation of a fluoride film.

1.2.2 Contaminant Removal from Nonmetals

Although the state-of-the-art in the use of polymerics cautions their usage, cleaning will be required if they are incorporated into fluorine systems. Polytetrafluoroethylene represents the most likely material and it exhibits

porosity to fluorine. This porosity necessitates the cleaning of the subsurface material as well as the surface proper. Two procedures have been proposed by various investigators to accomplish this. Both procedures have their advocates and desirable properties. Their use is recommended, but the results can not be guaranteed without further evaluation.

1.2.2.1 Nitric Acid Cleaning

One method of contamination removal involves the boiling of finished polytetrafluoroethylene parts in concentrated nitric acid. The acid boiling is followed by suitable water rinses, followed by vacuum baking. No specific recommendation can be made as to the boiling time since this is dependent upon the configuration/thickness of the material.

1.2.2.2 Fluorine Cleaning

An alternate cleaning procedure exposes the polytetrafluoroethylene to fluorine to remove and/or neutralize surface as well as subsurface contamination. The exposure may be to either gaseous, liquid or both phases dependent upon the end usage and/or contamination. This procedure should not be depended upon to remove the organic oils in total since an impact residue will remain after exposure to fluorine (paragraph II-2.7.1.1).

1.2.2.3 Proof Test

The above procedure, exposing polytetrafluoroethylene to fluorine as a subcomponent part is recommended as a test to increase the confidence of compatibility of the finished part with fluorine. It must be noted that polytetrafluoroethylene is a porous material, containing molecular and macro-voids (paragraph II-1.2) and therefore, is easily recontaminated if not packaged and handled properly. Refer to Appendix III-4 for recommended packaging methods.

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2.0 Material Selection

2.1 Introduction

When liquid fluorine is used as an airborne oxidizer, the selection of materials requires a more complete understanding of the mechanisms of reaction to fluorine than has been necessary with less energetic oxidizers. Equally important is an understanding of how those parameters influence the design of hardware and the selection of construction materials.

Factors which influence material selection, for a particular application, and which should be taken into consideration are the following:

1. Environmental factors.
   - A. Fluorine fluid-state, and/or purity.
   - B. System flow conditions--pressure and/or velocity.
   - C. Duty cycle, including storage.
2. Material properties.
   - A. Thermal--conductivity, capacity and expansion.
   - B. Mechanical--friction and wear characteristics.
   - C. Physical.
   - D. Shock sensitivity in fluorine.
3. Material compatibility with fluorine.
4. Inter-material compatibility, electrolytic.
5. Ease of cleaning and inspection.
6. Cost versus reliability.

2.2 Metals

Metals, in general, exhibit good corrosion resistance to uncontaminated liquid fluorine with the exception of those which form fluorides which are volatile at low temperature, see Table II-2.0a. The resistance of materials to gaseous fluorine attack is generally lower than that for the liquid and the rate of corrosion increases significantly with increased temperature. If the heat released during the fluorine-material reaction is not adequately dissipated, the material temperature will increase sharply which, in turn, increases the corrosion rate. This process is self-propagating and the material may reach its ignition

point. The rate of thermal dissipation, and ultimately the equilibrium temperature, is a function of the thermal conductivity and heat sink capability of both the material and the fluid. Additional factors which arise from flow conditions such as: friction, scouring, cavitation, and boundary layer destruction, can also contribute to the increase in surface temperature, but to a lesser degree.

2.3 Nonmetals

Although nonmetals are not as compatible as metals they have been used extensively in present systems and represent a potentially simpler solution to the design problem than the use of metals. Attractive uses for these materials are in static and dynamic seals as well as thermal and electrical insulations. Among the organic materials, the highly fluorinated resins, i.e., polytetrafluoroethylene offers the greatest resistance to chemical reaction with fluorine. If the heat released during the fluorine-material reaction is not adequately dissipated (most of these materials possess good insulation characteristics) the local temperature increase can cause material ignition which may become self-propagating. At present the understanding of what is acceptable polytetrafluoroethylene is inadequate due to the limited documentation of successful and unsuccessful uses. For this reason, its use cannot be encouraged. Should designers desire to accept a calculated risk or implement a parallel test evaluation program, its use could be considered. Appendix III-1, "Polytetrafluoroethylene, Molded, Energetic Propellant Serivce," and III-2 "Polytetrafluoroethylene, Molded, Cryogenic, Ultra Pure for Fluorine Service," are recommended specifications for procurement of polytetrafluoroethylene, which should meet the requirements for fluorine service. Appendix III-1 incorporates all of the properties, and spells out necessary tests to verify those properties which are believed to be critical to its use in fluorine. Although the appendixes have been prepared from the best available information, their applicability has not been verified by actual test and therefore they must be used with caution. Appendix III-2 is included to provide a specification for laboratory grade material to assist in the fundamental investigation of polytetrafluoroethylene and its compatibility with fluorine.

It should be noted that an apparent inconsistency exists in the compatibility data for resilient nonmetals in liquid, and gaseous mixtures of fluorine and oxygen. For concentrations between fifty and one hundred percent fluorine, ignition has been shown to occur in the liquid phase, while no ignition occurred at a higher temperature in the gaseous phase under static conditions, Reference 43. This would indicate that the total energy level of the compound, rather than the absolute temperature, may be the controlling parameter in FLOX and fluorine systems. It should be noted that polytetrafluoroethylene samples may exhibit tolerance to gaseous fluorine even though the same sample may not be compatible with liquid fluorine. This, however, should not be construed to mean that polytetrafluoroethylene can not be used in liquid fluorine. Extreme care should be exercised in interpreting results of tests which resulted in failure of this material. Before interpreting data, the physical and chemical properties should be determined as well as the cleanliness evaluated. Appendix III-1 should be referred to for a list of the properties which are considered significant. It also indicates maximum and minimum values for these parameters.

Ceramic materials, containing metals, although they lack good physical properties are, in general, resistant to attack by fluorine, even at high temperatures. These materials should be considered for bearings and dynamic seal applications only, due to their physical limitations. They find specific application as rotating seals in pumps.

In summary, the degree of reactivity between fluorine and any material is primarily a function of temperature, with a secondary dependence upon fluorine ion concentration (applicable to FLOX systems) and the fluid velocity. Any means that can be used to reduce the surface temperature will, in turn, reduce the reactivity of the material.

2.4 Moisture Contamination

Although materials may indicate compatibility (low corrosion rates) with anhydrous liquid or gaseous fluorine, contamination by moisture may form sufficient hydrofluoric acid to increase the corrosion rates to a prohibitive level. Under these conditions, compatibility with hydrogen fluoride rather

than fluorine becomes the primary consideration. If moisture may be present, even in small amounts, material selection must be based upon hydrogen fluoride compatibility as well as compatibility with fluorine.

2.5 Summary Conclusions

1. In general, the compatibility of material, or rather the tolerance of materials to fluorine, can be correlated to the ignition temperature. If a material can be kept below its ignition temperature, no catastrophic failure will occur. System design should be approached with this in mind. Parameters which should be considered are heat transfer rates and thermal capacity, i.e., remove sufficient heat of reaction to prevent the material from reaching its fluorine ignition temperature.

2. The common metals of construction used to produce airborne feed system components are compatible with fluorine. The recommended order of preference within individual metal grouping is presented in Table II-2.0-b. The temperature limit of each metal grouping shown is based on static tests. If energy additions result from fluid and/or component dynamics, it may be necessary to modify the order of preference. The variables necessitating these modifications are too numerous to allow inclusion here and must therefore, be reserved for the judgment of the individual designer.

   Table II-2.0c presents the chemical composition of various metals. Many of these metals are currently being used for fluorine service; however, their inclusion, in this table, should not be construed to give carte blanche sanction to their use.

3. Intergranular corrosion must be considered for any long term storage exceeding thirty days. This is particularly important if the metal contains alloying elements in amounts exceeding their solubility limit. Metallurgical phase diagrams may be consulted to determine these limits. If these elements, e.g., silicon in aluminum, form low temperature volatile fluorides, intergranular corrosion with an attendant decrease in component strength will occur. In general, this phenomena is only applicable to cast alloys since the wrought alloys normally do not contain elements which form low temperature volatiles.

4. Stress corrosion of metals stressed up to their respective yield strengths in liquid fluorine is not a necessary design consideration. Although there are no definitive data available, stress corrosion in gaseous fluorine is not considered to be significant and may therefore be disregarded.

5. No degradation of metal mechanical properties, such as tensile strength, results from exposure to fluorine unless intergranular corrosion or embrittlement occurs.

6. The only polymeric material which may be considered for fluorine service is polytetrafluoroethylene (Teflon TFE or Halon TFE) which meets or exceeds the requirements specified in Appendix III-1. Paragraph II-2.3 should be consulted for precautionary information on its use.

7. Thin metal film, plating, and solid boundary lubricants are the only lubricants recommended for fluorine service. Teflon TFE tape may be used if it meets or exceeds the requirements specified in Appendix III-1. Refer to paragraph II-2.3 for limitation in the use of Teflon tape.

2.6 Metals

2.6.1 Static Environment

A measure of metal resistance to corrosion by gaseous and liquid fluorine is in part a function of the density and tenacity of the fluoride film formed on the surface of the metal. Some metals form a gaseous or liquid film even at room temperature, others form brittle, porous, and powdery films, yet others form a very ductile, tenacious film. The common materials of construction, such as, stainless steel, Monel, nickel, aluminum, copper and alloys thereof, form a ductile, tenacious film. The existence of this protective film inhibits metal corrosion at high temperature, for example above cryogenic temperatures. Its capacity for limiting corrosion at low temperatures, particularly liquid fluorine temperature, has not been demonstrated (Ref. 47) and is felt to be unnecessary.

Table II-2.0a lists some metals and elements which form gaseous or low melting fluorides (Ref. 61, 192, and 145). Metal alloys which contain appreciable amounts of these elements which form gaseous or low melting fluorides, are not recommended as structural materials for handling fluorine.

Experimental work (Ref. 47) was performed to determine the compatibility and resistance to corrosion of various metals, and carbon with liquid fluorine. Specimens of aluminum, stainless steel, titanium, magnesium, nickel, and copper alloys were statically exposed to liquid fluorine at ambient pressure for various periods from a few hours up to two weeks. The average corrosion rates of these metals are shown in Table II-2.6a.

Tests were performed to determine the effect of liquid fluorine upon the stress corrosion characteristics of the metals listed above (Ref. 47). These tests were performed, primarily, upon curved bars which were stressed to various levels up to the yield strength of the material, and then submerged in liquid fluorine for seven to fifteen days. Visual examination (dye penetrant and sixty power-optical inspection) indicated no stress cracking or corrosion. The results of these tests are shown in Table II-2.6b.

Tensile rupture tests of titanium, brass, copper, Monel, and aluminum specimens were performed in liquid fluorine with no apparent reaction when the specimens were ruptured, except titanium (Ref. 47). Of the six tests performed with titanium, one specimen was observed to have ignited.

It should be noted that the testing described in Reference 47 used fluorine which was liquified from standard fluorine cylinder gas. The current assay of this grade of fluorine is defined in Table II-2.6c.

In order to evaluate the tensile properties of some metals, specimens of ten materials were immersed in liquid nitrogen and liquid fluorine for one year and then tested in a standard tensile testing machine, Reference 144. The results of these tests are presented in Table II-2.6d and indicate no tensile and ultimate strength degradation of the materials subjected to long term liquid fluorine exposure.

An extensive program was conducted to determine the rate of fluoride film formation as well as the film thickness (Ref. 51). This program exposed powdered metals to commercial grade fluorine gas at various temperature levels. The results are shown in Figures II-2.6a through II-2.6g. These data show that the formation of a fluoride film on the metal surfaces protects or inhibits the metal from further fluorine attack. These data indicated further, that after five to ten minutes exposure to gaseous fluorine at temperatures of -297°F to 186°F approximately eighty percent of the total fluoride film had been formed. This substantiates, in part, the passivation time requirement described in Appendix III-5. There appeared to be little reaction between the metal powders and gaseous fluorine at -297°F. Further, the film thickness was less when exposed to -113°F fluorine than when

exposed to 86°F fluorine. The freezing point of hydrogen fluorine (HF), is approximately -117°F and because of the high reaction rate of HF with any material, it is concluded that the metal corrosion rate is a function of the quantity of HF in the gaseous fluorine as well as the temperature. Additional tests (Ref. 51) confirmed the hygroscopic nature of metal fluorides. It was concluded that the metal fluoride film is hydrolyzed and destroyed by subsequent exposure to atmospheric humidity and fluorine. The prevention of moisture leakage into a fluorine system is imperative to the successful operation of the system.

Flexing tests (Ref. 47) were performed on copper, yellow brass, aluminum, and Monel specimens in liquid fluorine to determine the tenacity of the metal fluoride film. The tests were performed by fixing one end of the specimen while the other end was fastened to a reciprocating rod which applied a load, with resulting specimen deformation, at the rate of one cycle per second. The results indicated no increase in corrosion due to flexing when compared to the data from unstressed sample tests, after five hours of testing. Although neither the rod stroke nor the specimen stress levels were reported, it is concluded that the metal fluoride film was sufficiently flexible to prevent its cracking under these loading conditions.

It should be noted, due to the very small thickness of these films, that any bending moments applied to these specimens will result in the application of corresponding maximum tension and/or compression forces in the film. Consideration of the beam theory shows that the resulting traverse shear loads would be transmitted across the "metal to film" adhesion boundary. It can then be concluded that the tensile and compression strengths and the ductility of the film is sufficient to withstand bending moment application without degradation. Also, the mechanical bond of the film to the base material is of sufficient strength to transmit transverse shear loads due to bending without loss of bond.

A series of tests were conducted to determine the ignition temperature of several metals in uncontaminated fluorine (Ref. 50). The results of these tests are shown in Table II-2.6e. It is interesting to note that the ignition

temperature of Monel is much lower than that of aluminum, iron, copper, and 302 stainless steel, whereas in actuality, Monel is considered much better for handling fluorine than any of the above mentioned metals.

Contaminants in the fluorine, i.e., hydrogen fluoride, oxygen difluoride, etc., are the cause of the major portion of the metal corrosion. Reference 51 reports contaminants that can be present in commercially available fluorine, (Table II-2.6c), as: CF_4, SF_6, SiF_4, HF, OF_2, COF_2, SO_2F_2, C_2F_6, and CO_2. Of these, oxygen difluoride, OF_2, is one of the more reactive contaminants in liquid fluorine, and is miscible to the extent that ten percent OF_2 in liquid fluorine forms a single phase at -320°F, Reference 47.

Short term immersion tests were performed, (Ref. 51), wherein specimens of aluminum alloys, stainless steel, copper, and cartridge brass were exposed to purified liquid fluorine which was contaminated with one or ten percent OF_2 for periods of fifteen and seventy-five minutes. Comparing these data with the liquified commercial fluorine gas corrosion data indicated a slightly greater corrosion rate in the OF_2 contaminated fluorine. This corrosion increase was so small that the consideration of corrosion effects from OF_2, of the quantity present in commercially available fluorine (Table II-2.6c) may be discounted.

The most active contaminant that may be present in gaseous fluorine is hydrogen fluoride (HF). Although HF may be present in liquid fluorine, the solubility limit is approximately 0.3 percent by weight. The corrosion data presented in Table II-2.6b is based upon this amount of HF in solution. Also, as discussed above, the melting point of HF is approximately -117°F, therefore, any accelerated corrosion which might occur below this temperature should not be conclusively attributed to the presence of HF; however, the presence of solid hydrogen flouride may contribute to corrosion.

Moisture which is contained within or allowed to leak into a fluorine system will unite with the fluorine to form hydrogen fluoride, hydrofluoric acid, hydrogen peroxide, oxygen difluoride, ozone, and oxygen (Ref. 192). Of these, hydrogen fluoride and hydrofluoric acid are the most reactive and are generally referred to summarily as hydrogen fluoride (HF).

The complete removal of contaminants from the metal surfaces which will be contacted by fluorine is as important as the proper material selection. These contaminants are defined as any foreign matter, organic or inorganic, which is not completely fluorinated. This requires thorough and meticulous cleaning of the material prior to its use with fluorine. Appendix III-4, provides a cleaning procedural outline which, if followed, should adequately remove all surface contaminants which might react with fluorine except for chemisorbed water.

In addition to the use of proper cleaning procedures, it is recommended that all components and systems be passivated using the passivation procedural outline, Appendix III-5, prior to operation of the system. This operation does not only permit formation of the fluorine film prior to system operation, but may also act as a cleaning process. In the event that not all contaminants were removed from the material during cleaning, or that the material was recontaminated during packaging, installation, etc., exposure to fluorine gas and the removal of the resultant products by this passivation process will assist in their removal.

Present industrial practices result in the most common contaminants, of metals, being hydrocarbonous. These materials are used during the manufacturing phase as coolants, preservatives, etc., and during assembly operations as lubricants to facilitate subcomponent assembly.

Metal surfaces which had been coated with a hydrocarbon (hexadecane) were exposed to stoichiometric ratios of gaseous fluorine to determine the extent of hydrocarbon removal (Ref. 51). After exposure, oily deposits were observed on the metal surfaces. After analysis of these deposits, it was concluded that the fluorine reacted with the hydrogen to replace it with fluorine, leaving the carbon bonds intact. In some cases, a more complex reaction occurred which resulted in degradation of the hydrocarbon to the point that the carbon bonds were broken with the solid product of reaction being free carbon. Either of these reactions results in the formation of hydrogen fluoride and a fluorine energy sensitive product (energy sensitivity is discussed in Paragraph II-2.6.2).

The use of hydrocarbons on metal surfaces which will eventually contact fluorine should be minimized or eliminated. Passivation will not completely remove hydrocarbon contamination, therefore, it is essential that the cleaning process completely removes all traces of hydrocarbons. It should be noted that the reaction products of fluorine and hydrocarbonous material are impact sensitive.

2.6.1.1 Metals Summary

Although the resistance of metals to pure fluorine is an important factor in the evaluation and selection of materials it must be recognized that most fluorine contains hydrogen fluoride. The presence, in either a solution or in solid form, of hydrogen fluoride increases the rate at attack. It can be anticipated that the rate at which fluorine will attack metals will be increased if the fluorine contains hydrogen fluoride. Commercial grade fluorine normally contains hydrogen fluoride equal to its solubility limit, 0.3% by weight, and systems which contain pure fluorine initially, will have hydrogen fluoride formed if moisture is allowed to contaminate the system or the storage facility.

2.6.1.1.1 Nickel and Nickel Alloys

Of the more common materials of construction, nickel ("A", "D", and "L") and the Monels (H, K, F, and S) offer the greatest resistance to fluorine attack. These metals may be used with fluorine up to 1200°F whereas the Inconels, Illium, Illium R, and Duranickel all of which offer less resistance than either the nickels or the Monels, are not recommended above 750°F. All of the nickels and fused nickel alloys react with fluorine to form a dense tenacious fluoride film which is characteristic of the more resistive metals. Corrosion rates of these metals at various temperature levels are shown in Table II-2.6f. Small amounts of sulfur in the fluorine will increase the attack upon these metals. Based on the current commercial specifications of fluorine (Table II-2.6c) the sulfur that may be present is sufficiently small so that it is of little concern unless sulfur is introduced into the gas during use.

Within this metal group, Monel, "K" Monel, and "S" Monel offer the greatest resistance to HF corrosion (Ref. 49, 66, 192, and 211). While it is not to be construed that whenever the presence of HF is to be suspected within a system that one of the three above mentioned metals should be used, consideration must be made as to the effects of HF upon metals and the attendent component's functionality in relationship to the system reliability.

Welding does not reduce the corrosion resistance of the above metals if fluxes are not used or are completely removed after welding.

2.6.1.1.2 Low Alloy Steel

Iron reacts with fluorine to produce a brittle, loosely adhering fluoride film composed of both ferrous and ferric fluorides (Ref. 49, 144, 192, 211, and 240). Due to the susceptibility of this film to "flaking" and the highly corrosive nature of HF which is always present to some degree in the solution, the low alloy steels are not recommended for fluorine service. Low carbon, low silicon steels have been used with fluorine up to 600°F (Ref. 192). Corrosion rates of iron and low alloy steels in fluorine at various temperature levels, are shown in Table II-2.6g.

2.6.1.1.3 Stainless Steel

The austenitic stainless steels offer little or no advantage over low alloy steels in fluorine service except for the improved physical properties at cryogenic temperatures. Several of the constituents within these metals, silicon, carbon, molybdenum, and niobium react with fluorine to form volatile fluorides (Table II-2.0a) which contributes to pitting attack of the stainless steels (Ref. 211). These alloys have better resistance in the annealed condition than in the cold worked condition, but are readily attacked by fluorine above 300°F (Ref. 194). Corrosion rates of these alloys at various temperature levels are shown in Table II-2.6g.

A correlation between the upper temperature limit of these alloys and the temperature at which the chromium fluoride volatilizes, both being 300°F, was made in Reference 184. Based on the limited corrosion-film-constituents

determination work as reported in Reference 111, little or no trace of chromium was found on the surfaces of 347 and 410 stainless steel specimens which were tested. Although these data are not sufficient to refute this temperature correlation, it does indicate that additional data are required to lend credence to it.

2.6.1.1.4 Aluminum and Aluminum Alloys

Fluorine reacts with aluminum to form a dense tenacious fluoride film similar to the nickel films. Although aluminum readily reacts with oxygen in air to form a tenacious oxide film, when exposed to fluorine the oxygen in the oxide film is replaced by fluorine, forming a fluoride and releasing oxygen. In addition, fluorine is absorbed into the fluoride film, and reacts with the virgin material, resulting in an additional film thickness. This process continues until the denseness of the film becomes such as to inhibit the fluorine absorption, refer to Figure II-2.6d. Corrosion rates of some aluminum alloys at various temperature levels are shown in Table II-2.6h. Based on this information, aluminum and alloys thereof are not recommended for use with fluorine above 900°F.

Hydrogen fluoride reacts with aluminum fluoride, completely destroying this protective film, thus allowing fluorine to attack the base metal at a rate approaching that of unpassivated aluminum. It is then apparent that the use of aluminum in a fluorine system should only be made after evaluation of the amount of HF which might be present in the system, in relationship to system and mission reliability.

In general, alloying elements in aluminum lowers the resistance to corrosion. For example silicon, one of the more common elements, reacts with fluorine to form a volatile fluoride, at or above -140°F, refer to Table II-2.0a. Depending upon the percentage and dispersion of silicon in the solid solution, possible surface pitting could occur upon exposure to fluorine. Further, the most common type of welding rod used to weld aluminum contains approximately five percent silicon. If an extremely fine finish were required for any application, aluminum alloys containing more than one percent silicon are not recommended.

In an attempt to evaluate the fluorine reaction with the silicon phase, in cast aluminum A356, specimens were statically exposed to "scrubbed" gaseous fluorine, a fluorine which has been passed through a sodium fluoride filter to reduce the hydrogen fluoride level, (0.01 percent by volume of HF) at ambient temperature and sixty-seven psig pressure for twenty-one days, Reference 97. The specimens were of two porosity levels, Grades II-F and III-F as defined by NASA specification MFSC-STD-100. Figure II-2.6h shows the precipitated silicon dispersion of unexposed specimens. Microscopic examination of the exposed specimens revealed that the precipitated silicon, which was exposed at the material surface, was "leached out". The depth of silicon removal extended to the depth of continuous penetration of the silicon precipitate from the material surface, Figures II-2.6i and j. The chill rate of a Grade II-F casting is greater than that of a Grade III-F; consequently, the uncombined silicon has less time during cooling to migrate to the grain boundaries. This results in more silicon being trapped within the grains and shorter continuous lengths of silicon at the boundaries. The average depth of the resulting surface pits (78 and 32 pits per linear inch of cross sectioned area viewed for Grades II-F and III-F respectively), were 0.0002 inch for Grade II-F and 0.00079 inch for Grade III-F. It is apparent that these pits act as stress risers at the material surface although the effect upon the material strength is unknown.

2.6.1.1.5 Copper and Copper Alloys

Copper reacts with fluorine to form a relatively dense tenacious fluoride film. The film thickness is twice that of a corresponding nickel fluoride film (Ref. 211). Copper offers good corrosion resistance to fluorine up to 930°F, (Ref. 192). The use of copper is not recommended when the fluoride film is exposed to moisture and then reexposed to fluorine. This results in a mobile film which may be removed in the form of solid particles.

Copper alloys such as red brass, yellow brass, and bronze are usable up to 500°F (Ref. 63 and 66). Fluorine reacts with the tin and zinc in the brasses, causing a type of intergranular corrosion. Lead-copper alloys are readily attacked by fluorine, due to the poor solubility of lead within the copper solution, and the non-adhesion of the lead fluoride to the parent material (Ref. 211). The use of alloys containing lead, phosphorus, and silicon in an amount exceeding their solubility limit should be avoided if a high resistance to fluorine attack is desired. Corrosion rates at various temperature levels are shown in Table II-2.6i.

2.6.1.1.6 Magnesium

Magnesium, like aluminum, is always coated with an oxide film, which is converted to a fluoride film with subsequent reaction with virgin material under this film, in the same manner as discussed in paragraph II-2.6.1.1.4. Hydrogen fluoride in the fluorine prevents the formation of a fluoride film, thus resulting in a continuous reaction until the metal is completely destroyed. Magnesium and the alloys thereof are not recommended for fluorine service above 900°F (Ref. 211). Corrosion rates at various temperature levels are shown in Table II-2.6j. At temperatures below 900°F, magnesium is not recommended if exposed to hydrogen fluoride or to moist environment.

2.6.1.1.7 Titanium

Titanium does not form a very protective fluoride film when exposed to fluorine and is readily attacked above 300°F (Ref. 51). Various investigators have reported impact sensitivity in fluorine as well as excessive corrosion in contaminated fluorine. It is felt that this corrosion can be attributed to a high hydrogen fluoride content since good corrosion resistance has been obtained in commercially pure fluorine. Until these observations are more thoroughly investigated, titanium cannot be recommended for fluorine service.

2.6.1.1.8 Miscellaneous Metal Alloys

Chromium forms a relatively dense tenacious fluoride film, a divalent fluoride, below 300°F. If chromium is passivated below 30°F, a very resistive film, similar to the nickel fluoride film, is formed. Above 300°F

the divalent fluoride is converted to a tetravalent fluoride which is volatile, with the attendent loss of protective ability (Ref. 211). The recommended use of chromium is limited to systems below 300°F and initial passivation should be carried on below 30°F for satisfactory service.

Tantalum ignites in fluorine at 150°F and therefore, is not recommended for fluorine service above approximately 100°F. Limited research data exists on tantalum in fluorine even at lower temperatures, therefore, recommendation for application below 100°F can not be made without additional laboratory investigations.

It has been reported (Ref. 69) that beryllium forms a protective fluoride film below 600°F, approximately equal in protection to nickel fluoride, and at 750°F, half as protective as the nickel fluoride film. Reference 146 recommends that beryllium not be used for fluorine service at temperatures above 150°F. Further investigations are necessary to determine capability of this metal to withstand fluorine attack.

Rhodium, palladium, and platinum can be used in fluorine up to approximately 72°F. However, volatile fluorides of these metals are formed at relatively low temperatures so that extreme caution should be exercised in their use with fluorine above 100°F (Ref. 211).

Lead forms a brittle fluoride which does not protect the parent material from rapid attack by hydrogen fluoride (Ref. 211) and therefore is not recommended for fluorine service.

Niobium, columbium, molybdenum, tungsten, uranium, lithium, sodium, potassium, rubidium, cadmium, bismuth, silver and gold, show little tendency to be passivated (Ref. 69) thus the applicability of these metals to fluorine service is questionable. With the exception of gold and silver, these metals are not recommended for fluorine service. Indium and silver have been tested as seal plating material in liquid fluorine with no apparent failure (Ref. 246).

Tin reacts in a similar manner as lead and is rapidly attacked by hydrogen fluorine at all temperatures (Ref. 177). Tin has found some use as a dynamic seal in liquid fluorine pumps (Ref. 246).

Silver solders may be used to join two or more members. Silver is not very resistive to fluorine attack, but the addition of copper greatly improves its resistance, whereas cadmium lowers the resistance to attack, although the workability of the solder is increased (Ref. 192). Soft solders should not be used because of their high tin and lead content. When the use of solders is indicated, full consideration should be given to the potential galvanic corrosion effects.

Table II-2.6k lists the composition of various silver solders. The (*) indicates recommended alloys although other compositions may be considered, however, they should be evaluated for the particular application prior to use.

2.6.2 Dynamic Environment

Most system components or materials will be subjected to both static and dynamic fluid conditions throughout the functional life of the system. The static limitations, as discussed in paragraph II-2.6.1, must be supplemented and/or modified to account for energy additions resulting from the fluid or component dynamics. Component dynamics, or energy sensitivity, is discussed in paragraph II-5.0.

The material local temperature can be increased by two means other than external heating or chemical reaction: (1) energy resulting from impacting one member upon another, for example, a valve poppet striking the seat during closing of the valve; (2) energy resulting from fluid impact upon system members, (3) scouring of the metals by the fluid, (4) fluid friction, and (5) cavitation at the metal interface. In general, all of this energy is converted into heat which, if not rapidly dissipated, could result in a significant increase in material temperature. The extent of the temperature increase is not only dependent upon the amount of energy available for heating, but also upon the thermal properties of the material and fluid. The rate of heat dissipation, and ultimately the equilibrium temperature, is a function of the thermal conductivity and the heat capacity of the metal and the fluid. Although the fluid in the dynamic state imparts some energy into the system through friction, scouring and turbulence, the predominating factor is the large equivalent heat sink of the flowing fluid.

2.6.2.1. Metals

Numerous systems have been used and are being used currently to contain and transport fluorine in a dynamic state. Generally, little or no information has been reported describing these systems unless a failure occurred. Further, any failure documentation presented is too limited to correlate with other data or to project and form additional conclusions other than those reported. It should be noted that the majority of the systems used to date were of a facility type, such as, heavy wall tubing with American Standard Association standard pipe flanges, or flared connections for the small sizes, and also heavy valves and other components. It is virtually impossible to correlate this type of system data with a flight weight system due to the massiveness and rigidity of the facility type system. In short, flight systems will require the use of a different set of parameters, than are currently utilized in ground systems.

Several types of fluid dynamic tests have been performed in liquid fluorine at -306°F (Reference 42). High velocity flow tests were performed by subjecting stainless steel, nickel, brass, and aluminum orifices to liquid fluorine with velocities, pressures, and exposure times up to 300 feet per second, 1500 psig, and 500 seconds respectively. No measurable corrosion or chemical attack was observed. To determine the effects of turbulence upon the material-fluorine chemical reaction, wedge shaped specimens of aluminum, brass, and stainless steel were subjected to liquid fluorine with a velocity, flow rate, and exposure time of 120 feet per second, 20 pounds per second, and two seconds respectively. No corrosion effects due to turbulence were observed. In addition, a series of fluid impact tests were performed by impacting specimens of aluminum nickel, and stainless steel with liquid fluorine whose velocity and flow rate, and the specimen exposure time were 300 feet per second, 2.5 pounds per second, and five seconds respectively. No measurable corrosion or chemical attack occurred.

Additional dynamic tests were performed in "scrubbed" (0.02 percent, by volume, of HF) liquid fluorine at -235°F and 400 psig with specimens of cast aluminum alloy A356-T6 (Reference 97). Individual orifice specimens of

A356-T6 cast aluminum were subjected to 50 and 150 feet per second fluorine velocities through 0.039 and 0.065 inch diameter orifices respectively for durations of thirty minutes. No change in orifice diameter resulted and no evidence of physical erosion was observed. During the same tests, impingement specimens, oriented normal to the fluid flow, were placed two inches downstream of the orifice specimen to permit direct impingement of the high velocity liquid fluorine upon the specimens. Post-test inspection revealed superficial damage to the impacted surfaces at both velocities. The observed damage was attributed to physical erosion from high velocity condensed contaminants suspended within the liquid fluorine. Pretest and post-test surface roughness measurements of the damaged surfaces revealed no roughness change after thirty minutes of test.

2.7 Nonmetals

2.7.1 Static Environment

Many nonmetallic materials are commonly used as bearings, static and dynamic seals, sealants, and lubricants in oxidizer feed system components. In order to evaluate the fluorine compatibility, of these materials, extensive testing was performed in liquid and gaseous fluorine at ambient and 1500 psig pressures (Reference 109 and 210). The liquid and gaseous fluorine temperatures were -320°F and room temperature respectively. The test results are shown in Table II-2.7a. It should be noted that, in general, the reactivity of those materials tested increased when the pressure and temperature of the fluorine was increased.

2.7.1.1 Lubricants

The above test has shown that there is insufficient data to establish a reaction threshold for any of the materials tested. Some materials did not react in either liquid or gaseous fluorine at ambient pressure whereas they did react at 1500 psig. Many of the materials, especially those used as boundary lubricants, are very important in the assembly and disassembly of components. As discussed in paragraph II-6.0, when two clean metal surfaces

are in intimate contact under load, for example, a threaded fastener, some degree of "cold welding" is likely to occur. To prevent this it is necessary that a lubricating film be provided between clean contacting metal surfaces subjected to load and/or thermal cycling.

The oils and greases which have shown any degree of compatibility with fluorine under static conditions, Table II-2.7a, are the fluoropolymers; Kel-F and Fluorolube. The primary constituent of these solutions is polychlorotrifluoroethylene to which is added various proprietary compounds to impart specific performance characteristics. In the case of greases, a base material is necessary to act as the container and carrier of the primary lubricant. Fluorine will react with these compounds and base materials, the rate will depend upon the specific materials, their thermodynamic properties, and the thermodynamic capability of the surrounding materials to transfer heat away from the reaction zone. These reactions are considered secondary since the polychlorotrifluoroethylene, the major solution consituent, will also react with the fluorine. The replacement of the chlorine by fluorine is exothermic as follows:

$$(-CF_2 - CF\,Cl-)_n + \frac{n}{2}(F_2) \rightarrow (-CF_2 - CF_2-)_n + \frac{n}{2}(Cl_2) + \text{energy}$$

Note, the perfluoroethylene, $(-CF_2 - CF_2-)_n$, one of the products of reaction, is energy sensitive. If sufficient energy (80.5 K cal/mole) is available to break the carbon to carbon bond the perfluoroethylene reaction continues as follows:

$$(-CF_2 - CF_2-)_n + \text{energy} \rightarrow n\,(CF_4) + n\,(C)$$

The carbon tetrafluoride is a completely fluorinated nonreactive product whereas the free carbon will generally be amorphous in structure (soot) and is hypergolic with fluorine under all conditions. This mechanism of reaction was substantiated, in part, by exposure of a hydrocarbon (hexadecane) to stoichiometric fluorine as described in Reference 51 and discussed briefly in paragraph II-2.6.1. Analysis of the reaction products indicated that, in some

cases, the fluorine had replaced the hydrogen leaving the carbon to carbon bonds intact. In other cases, a more complete reaction had occurred with the carbon to carbon bonds being broken resulting in an end product of impact sensitive free carbon (soot). Note: With an excess of fluorine the reaction could also be as follows:

$$(-CF_2-CF_2-)_n + 4nF_2 \rightarrow 2n\,(CF_4) + \text{energy}$$

In the absence of any fluorine compatible "standard" boundary lubricants a very thin coating of a "soft" metal, such as, copper, gold, etc. on the contacting surfaces will reduce galling and/or fretting since the soft metal acts as a lubricant. It should be noted that the cold welding of the parent materials will be replaced only by a cold welding of the metal coatings, usually to a lesser degree; see Table II-6.2a. The required force to shear these welded areas is much less than that required for similar welded parent materials due to the lower shear strength of the soft materials. These soft metals, used for coatings, possess a low life cycle, and upon repeated contacting these metals work harden to some extent. This results in successively higher forces to shear the welded areas. Paragraph II-4.4, discusses this compressive work hardening. In addition, excessive galling results from the repeated shearing of the metal coatings, with the result that large areas of the base material may be exposed and therefore become susceptible to cold welding. Galling phenomena are discussed in detail in paragraph II-6.0.

Solid boundary lubricants offer advantages over the soft metal coatings in that they are not as life cycle limited and because they offer fretting protection due to their low elasticity properties. These lubricants are laminar solids with low shear strength and the ability to "firmly" bond to the rubbing surface. Of those materials, which have been tested or used, calcium fluoride is a known solid lubricant which is completely compatible with fluorine. This material lends itself to flame spraying techniques since it melts at 2500°F without sublimation. Flame spraying permits the direct application of the lubricant without the use of noncompatible binders or carrier materials. The coefficient of sliding friction of calcium fluoride on Inconel is approximately 0.25, at room temperature, as compared to 0.4 for steel on steel. Another

compatible solid lubricant is a eutectic mixture of barium fluoride and calcium fluoride. Refer to paragraph II-6.0 for a discussion of this material. As long as the solid lubricating film remains intact complete fretting protection is provided to the base material. This fretting protection is provided by the yielding of the solid lubricant between the moving surfaces.

2.7.1.2 Polymerics

Selected solid nonmetallic materials, which are currently used as seals and gaskets in oxidizer systems, have been tested (Reference 43). These tests exposed the samples to mixtures of either gaseous fluorine and oxygen or liquid fluorine and oxygen. The amount of fluorine was incrementally increased until a reaction occurred or until the material was exposed to one hundred percent fluorine. The results of these tests are shown in Figure II-2.7a, "Solid Nonmetallic Materials Statically Exposed to FLOX". The gaps between the reaction and nonreaction symbols are the result of the incremental increase in the fluorine content of the mixture. It was noted that reactions occurred more readily in the liquid mixtures than in the gaseous ones. It was concluded that the reactivity of these materials is more sensitive to the fluorine concentration of the mixture than to an increase in temperature since temperature was the only parameter varied. This reaction sensitivity is also noted in References 193 and 210. It was also observed that when a reaction occurred in liquid fluorine it could be classified as either explosive or of the slow burning, surface type and appeared to be related to the porosity of the material. The porous material reacting explosively, the less porous material exhibiting a slow burning, surface reaction.

Analysis of the test results and materials tested (Reference 43) indicated that the degree of crystallinity of the material significantly affects its reactivity threshold. The greater the crystallinity the greater the compatibility. This property can be most easily controlled by proper cooling rates during the molding operations--the faster the cooling rate the more amorphous the material will be. Further, an amorphous material can be properly heat treated resulting in an increase of crystallinity to an equivalent level attainable through proper cooling during molding. One heat treatment method, which has been successfully used with Kel-F 81, was to heat the material to

a temperature just below its melting point and then allow it to cool slowly (33°F per hour) to room temperature. This procedure is recommended for polytetrafluoroethylene TFE. It must be recognized that crystallinity is difficult to measure; therefore, other measurable parameters must be used to evaluate this parameter. Refer to Appendix III-1 and III-2 for recommended material specifications and a discussion of these other parameters.

Although a large portion of the materials tested resulted in no reaction after static exposure to liquid fluorine for a minimum of five minutes, dynamic testing resulted in reactions of some of these materials at relatively low fluid energy levels.

It should be recongized that gaseous fluorine diffuses through polytetrafluoroethylene due to the porous nature of the material. The rate of diffusion is not sufficient to cause a material loss of system pressure, but may be sufficient to cause a reaction with adjacent material. It is this diffusion of fluorine which can allow reaction with subsurface contaminants in polytetrafluorothylene.

2.7.2 Dynamic Environment

2.7.2.1 Polymerics

The recommended use of polymeric materials in a fluorine system would be as gaskets and seals only. In this type of application at least a portion of the material is subjected to fluorine in a dynamic state. In order to evaluate the fluid velocity and pressure reactive effects upon some of the materials which did not react in fluorine at static conditions, Figure II-2.7a, dynamic fluid tests were performed and described in Reference 43. Figure II-2.7b, presents the results of the dynamic tests. One series of tests was performed by subjecting nine materials to short duration, high velocity gaseous fluorine (ambient temperature) flow. Orifice specimens, 1/4 inch diameter were fabricated from Halon, TFE, and TVS; Teflon, FEP; Kel-F 81, 81 amorphous, and 82; Rulon A; and Kynar all withstood average fluorine velocities of 700 to 880 feet per second for thirty seconds without reacting. All of the specimens

were subjected to sonic velocity (900 feet per second) for some portion of this thirty second period which ranged from 2 to 16 seconds. An orifice specimen of Viton A, 0.2 inch diameter orifice, successfully withstood a gaseous fluorine velocity of approximately 280 feet per second without reacting, but did react at a velocity of 535 feet per second. Further gaseous tests were performed by flowing fluorine at ambient temperature, through 1/8 inch diameter orifice specimens of Teflon TFE, Kel-F 81 amorphous, and Kel-F 82 at sonic velocity (900 feet per second). The Teflon TFE successfully withstood this flow condition for thirty minutes with no reaction. The Kel-F 81 amorphous and Kel-F 82 reacted after five and fifteen minutes exposure, respectively. The Kel-F 81 amorphous and Kel-F 82 specimens had previously been exposed to gaseous fluorine at 372 and 279 feet per second respectively for thirty minutes with no reaction.

Additional testing (Reference 43) of sixteen polymerics were performed in a mixture of liquid fluorine and oxygen, (FLOX), maintained at a temperature of -320°F and pressures ranging from 200 to 1250 psig. Again, the fluorine content of the fluid mixture was incrementally increased until one hundred percent fluorine was reached, or a reaction occurred at some velocity level. At each incremental mixture the fluid velocity was increased until the material reacted or sonic velocity was reached. The reactive profiles, or limits, of ten to the most promising materials tested in this series of tests are shown in Figure II-2.7b, "Liquid FLOX Reactivity Profile". The remaining material tests, Lucite, CPE401, CPE402, CPE403-XCL and nickel-filled Teflon, all reacted at fluid velocities of less than 45 feet per second in less than eighty percent FLOX with the exception of nickel-filled Teflon. This material reacted in one hundred percent fluorine at a fluid velocity of 120 feet per second, which is much less than the nonreactive limit of both Teflon TFE and Halon TFE as shown in Figure II-2.7b.

Of those materials tested, (Reference 43), only Halon TFE and Teflon TFE may be considered for airborne fluorine service. Refer to paragraph II-2.3 for precautionary information on its usage. Suppliers and investigators of fluorine and fluorine handling systems have indicated random failures of

Teflon gaskets, O-rings, etc. Generally, insufficient data are available to reasonably project the cause of such failures although the concensus is that contamination was the greatest single influencing factor. Based on the best available information, the proposed polytetrafluoroethylene material specification is presented in Appendix III-1, "Polytetrafluoroethylene, Molded, Energetic Propellant service". Material which does not meet the requirements of this specification should not be considered for fluorine service. Appendix III-2, "Polytetrafluoroethylene, Molded, Cryogenic, Ultra-pure for Fluorine Service"; has been prepared as a proposed specification to be used as a base from which to evaluate the various parameters to obtain a fundamental understanding of its compatibility with fluorine. If future testing discloses that material produced within the confines of Appendix III-1 does not meet the compatibility requirements of a specific application, material should be obtained meeting Appendix III-2. If compatibility is then obtained, the various parameters may then be varied to establish the minimum grade acceptable. Should material under Appendix III-2 fail to be compatible, it must be concluded that a different material and/or design must be utilized.

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Table II-2.0a
(References 61, 192, and 145)
LOW MELTING ELEMENTAL FLUORIDES

Element	Fluoride	Melting Point °F	Boiling Point °F
Nitrogen	NF_3	-358	-164
Carbon	CF_4	-299	-198
Oxygen	OF_2	----	-269
Boron	BF_3	-197	-150
Silicon	SiF_4	-141	-140
Hydrogen	HF	-117	67
Phosphorus	PF_3	-256	-150
	PF_5	-137	-121
Sulfur	SF_6	-83	Sublimes
Arsenic	AsF_3	15	145
	AsF_5	-112	-63
Molybdenum	MoF_6	63	95
Tungsten	WF_6	36	68
Vanadium	VF_5	----	232
Niobium	NbF_5	162	428
Germanium	G_eF_4	5	Sublimes

Table II-2.0b (page 1 of 3)

RECOMMENDED METALS FOR FLUORINE SERVICE

(Materials within each material group are listed in order of preference)

Material	Temperature Limit	Remarks
I. Stainless Steel		
A. Austenitic		
316L 304L A-286 321, 347 316 317 308 ARMCo 21-6-9 309S 310S 304 17-7PH 17-4PH	300°F	Minimum C and Si with a maximum Ni, relative to the Cr, reduces the corrosion rate. Care must be exercised with the high Cr content steel so as not to result in stress corrosion susceptibility.
B. Martensitic		
440C	300°F	High carbon content, consider only for bearing surfaces.
II. Nickel Fused Alloys		
K Monel wrought S Monel cast Monel R Monel H Monel	1200°F	K&S Model are the only materials recommended for HF containment.
Inconel X Inconel 625 Inconel 718	750°F	

Table II-2.0b (page 2 of 3)
RECOMMENDED METALS FOR FLUORINE SERVICE

Material	Temperature Limit	Remarks
III. Nickel		
A Nickel D Nickel E Nickel Z Nickel	1200°F	
IV. Copper & Copper Alloys		
A. Copper		
Electrolytic TP Free Cutting, High Conductivity High Strength, High Conductivity Oxygen Free	700°F	High rate of attack if the fluorine contains oxygen
B. Brass		
Commercial Bronze Red Low Cartridge Yellow Admiralty (inhibited) Aluminum (inhibited)	500°F	Pb is not soluble in Cu, therefore, any alloy containing Pb should not be used in fluorine systems. Alloys containing P and/or Si in an amount exceeding their solubility limit should not be used in fluorine.
C. Bronze		
Phosphor, Grade A Phosphor, Grade C Phosphor, Grade D Phosphor, Grade E	500°F	
Aluminum 5% Aluminum 7% Aluminum 10% Cupro Nickel 10% Cupro Nickel 30%	500°F	

Table II-2.0b (page 3 of 3)
RECOMMENDED METALS FOR FLUORINE SERVICE

Material	Temperature Limit	Remarks
V. Aluminum Alloys 1100 (2S) 6061 A356 2017 2024	900°F	
VI. Titanium Alloys 6AL-4V	300°F	Limited use is recommended due to the shock sensitive characteristic of Ti in oxygen and the possible corrosion in fluorine plus HF reported by some investigators.
VII. Plating Metals Tin Silver Indium Rhodium Gold		Sn, in bronzes, reacts with fluorine at approximately 500°F. Au shows little tendency to be passivated. Ag is not very resistant to fluorine attack, but the addition of Cu improves this resistance. Indium is impact sensitive in LF_2.

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Table II-2.0c. Materials Chemical Composition

ALLOY	Al	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Sn	Pb	P	S	C	N	Mo	Cb + TA	V	O	Ag	Te	Be	Co	OTHER
ALUMINUM ALLOYS																									
1100	99.0 MIN.	1.0	Tr	0.20	0.05	–	–	–	0.10	–	–		–		–	–	–	–	–	–	–	–	–	–	0.15
2017	Rdr	0.8	1.0	3.5 – 4.5	0.40 – 1.0	0.20 –0.8	0.10	–	0.25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.15
2024	Rdr	0.5	0.5	3.8 – 4.9	0.3 – 0.9	1.2 – 1.8	0.10	–	0.25	–	–		–		–		–	–	–		–	–	–	–	0.15
6061	Rdr	0.4 – 0.8	0.7	0.15 – 0.4	0.15	0.8 – 1.2	0.15 – 0.35	–	0.25	0.15	–	–	–	–		–	–	–	–	–	–	–	–	–	0.15
A356	Rdr	6.5 – 7.5	0.12	0.10	0.05	0.25 0.40	–	–	0.05	0.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.15
STAINLESS STEEL																									
304	–	1.0	Rdr	–	2.0	–	18.0 – 20.0	8.0 – 12.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–		–	–	–	–	–
304L	–	1.0	Rdr	–	2.0	–	18.0 – 20.0	8.0 – 12.0	–	–	–	–	0.045	0.03	0.03	–	–	–	–	–		–	–	–	–
308	–	1.0	Rdr	–	2.0	–	19.0 – 21.0	10.0 – 12.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
309S	–	1.0	Rdr	–	2.0	–	22.0 – 24.0	12.0 – 15.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
310S	–	1.0	Rdr	–	2.0	–	24.0 – 26.0	19.0 – 22.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
316	–	1.0	Rdr	–	2.0	–	16.0 – 18.0	10.0 – 14.0	–	–	–	–	0.045	0.03	0.08	–	2.0 – 3.0	–	–		–	–	–	–	–
316L	–	1.0	Rdr	–	2.0	–	16.0 – 18.0	10.0 – 14.0	–	–	–	–	0.045	0.03	0.03	–	2.0 – 3.0	–	–	–	–	–	–	–	–
317	–	1.0	Rdr	–	2.0	–	18.0 – 20.0	11.0 – 15.0	–	–	–	–	0.045	0.03	0.08	–	3.0 – 4.0	–	–	–	–	–	–	–	–
321	–	1.0	Rdr	–	2.0		17.0 – 19.0	9.0 – 12.0	–	5 × C MIN.	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
347		1.0	Rdr	–	2.0	–	17.0 – 19.0	9.0 – 13.0	–	–	–	–	0.045	0.03	0.08	–	–	10 × C (MIN.)	–	–	–	–	–	–	–
A286	0.35	0.4 – 1.0	Rdr	–	1.0 – 2.0	–	13.5 – 16.0	24.0 – 28.0	–	1.75 – 2.25	–	–	–	–	0.08	–	1.0 – 1.5	–	0.1 – 0.5	–	–	–	–	–	–
ARMCO 21-6-9	–	1.0	Rdr	–	–	8.0 – 10.0	19.0 – 21.5	5.5 – 7.5	–	–	–	–	0.06	0.03	0.08	0.15 – 0.25	–	–	–	–	–	–	–	–	–
17-4PH	–	1.0	Rdr	3.0 – 5.0	1.0	–	15.5 – 17.5	3.0 – 5.0	–	–	–	–	0.04	0.03	0.07	–	–	0.25 – 0.45	–	–	–	–	–	–	–
17-7PH	0.75 – 1.5	1.0	Rdr	–	1.0	–	16.0 – 18.0	6.5 – 7.75	–	–	–	–	0.04	0.03	0.09	–	–	–	–	–	–	–	–	–	–
440 C	–	1.0	Rdr	–	1.0	–	16.0 – 18.0	–	–	–	–	–	0.04	0.03	0.95 – 1.2	–	0.75	–	–	–	–	–	–	–	–
NICKEL & ALLOYS																									
A NICKEL	–	0.35	0.4	0.25	0.35	–	–	99.0* MIN.	–	–	–	–	–	0.015	0.15	–	–	–	–		–	–	–	–	–
D NICKEL	–	0.05	0.15	0.05	4.5	–	–	Rdr	–	–	–	–	–	0.005	0.1	–	–	–	–	–	–	–	–	–	–
E NICKEL	–	0.05	0.15	0.05	2.0	–	–	Rdr	–	–	–	–	–	0.005	0.1	–	–	–	–	–	–	–	–	–	–
Z NICKEL	4.0 – 4.75	1.0	0.60	0.25	0.5	–	–	93.0*	–	0.25 – 1.0	–	–	–	0.01	0.3	–	–	–	–	–	–	–	–	–	–

ALUMINUM ALLOYS																									
1100	99.0 MIN.	1.0	Tr	0.20	0.05	–	–	–	0.10	–	–		–		–	–	–	–	–		–	–	–	–	0.15
2017	Rdr	0.8	1.0	3.5 – 4.5	0.40 – 1.0	0.20 –0.8	0.10	–	0.25	–	–	–	–	–	–	–	–	–	–		–	–	–	–	0.15
2024	Rdr	0.5	0.5	3.8 – 4.9	0.3 – 0.9	1.2 – 1.8	0.10	–	0.25	–	–		–		–		–	–	–		–	–	–	–	0.15
6061	Rdr	0.4 – 0.8	0.7	0.15 – 0.4	0.15	0.8 – 1.2	0.15 – 0.35	–	0.25	0.15	–	–	–	–		–	–	–	–		–	–	–	–	0.15
A356	Rdr	6.5 – 7.5	0.12	0.10	0.05	0.25 0.40	–	–	0.05	0.2	–	–	–	–	–	–	–	–	–			–	–	–	0.15
STAINLESS STEEL																									
304	–	1.0	Rdr	–	2.0	–	18.0 – 20.0	8.0 – 12.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–		–	–	–	–	–
304L	–	1.0	Rdr	–	2.0	–	18.0 – 20.0	8.0 – 12.0	–	–	–	–	0.045	0.03	0.03	–	–	–	–	–		–	–	–	–
308	–	1.0	Rdr	–	2.0	–	19.0 – 21.0	10.0 – 12.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
309S	–	1.0	Rdr	–	2.0	–	22.0 – 24.0	12.0 – 15.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
310S	–	1.0	Rdr	–	2.0	–	24.0 – 26.0	19.0 – 22.0	–	–	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
316	–	1.0	Rdr	–	2.0	–	16.0 – 18.0	10.0 – 14.0	–	–	–	–	0.045	0.03	0.08	–	2.0 – 3.0	–	–		–	–	–	–	–
316L	–	1.0	Rdr	–	2.0	–	16.0 – 18.0	10.0 – 14.0	–	–	–	–	0.045	0.03	0.03	–	2.0 – 3.0	–	–	–	–	–	–	–	–
317	–	1.0	Rdr	–	2.0	–	18.0 – 20.0	11.0 – 15.0	–	–	–	–	0.045	0.03	0.08	–	3.0 – 4.0	–	–	–	–	–	–	–	–
321	–	1.0	Rdr	–	2.0		17.0 – 19.0	9.0 – 12.0	–	5 × C MIN.	–	–	0.045	0.03	0.08	–	–	–	–	–	–	–	–	–	–
347		1.0	Rdr	–	2.0	–	17.0 – 19.0	9.0 – 13.0	–	–	–	–	0.045	0.03	0.08	–	–	10 × C (MIN.)	–	–	–	–	–	–	–
A286	0.35	0.4 – 1.0	Rdr	–	1.0 – 2.0	–	13.5 – 16.0	24.0 – 28.0	–	1.75 – 2.25	–	–	–	–	0.08	–	1.0 – 1.5	–	0.1 – 0.5	–	–	–	–	–	–
ARMCO 21-6-9	–	1.0	Rdr	–	–	8.0 – 10.0	19.0 – 21.5	5.5 – 7.5	–	–	–	–	0.06	0.03	0.08	0.15 – 0.25	–	–	–	–	–	–	–	–	–
17-4PH	–	1.0	Rdr	3.0 – 5.0	1.0	–	15.5 – 17.5	3.0 – 5.0	–	–	–	–	0.04	0.03	0.07	–	–	0.25 – 0.45	–	–	–	–	–	–	–
17-7PH	0.75 – 1.5	1.0	Rdr	–	1.0	–	16.0 – 18.0	6.5 – 7.75	–	–	–	–	0.04	0.03	0.09	–	–	–	–	–	–	–	–	–	–
440 C	–	1.0	Rdr	–	1.0	–	16.0 – 18.0	–	–	–	–	–	0.04	0.03	0.95 – 1.2	–	0.75	–	–	–	–	–	–	–	–
NICKEL & ALLOYS																									
A NICKEL	–	0.35	0.4	0.25	0.35	–	–	99.0° MIN.	–	–	–	–	–	0.015	0.15	–	–	–	–		–	–	–	–	–
D NICKEL	–	0.05	0.15	0.05	4.5	–	–	Rdr	–	–	–	–	–	0.005	0.1	–	–	–	–	–	–	–	–	–	–
E NICKEL	–	0.05	0.15	0.05	2.0	–	–	Rdr	–	–	–	–	–	0.005	0.1	–	–	–	–	–	–	–	–	–	–
Z NICKEL	4.0 – 4.75	1.0	0.60	0.25	0.5	–	–	93.0°	–	0.25 1.0	–	–	–	0.01	0.3	–	–	–	–	–	–	–	–	–	–
MONEL	–	0.5	2.5	Rdr	2.0	–	–	63.0 – 70.0	–	–	–	–	–	0.024	0.3	–	–	–	–	–	–	–	–	–	–
K MONEL	2.0 – 4.0	1.0	2.0	Rdr	1.5	–	–	63.0 – 70.0	–	–	–	–	–	–	0.25	–	–	–	–	–	–	–	–	–	–
S MONEL	0.5	3.5 – 4.5	2.5	27.0 – 31.0	1.5	–	–	60.0 MIN.	–	–	–	–	–	–	0.25	–	–	–	–	–	–	–	–	–	–
R MONEL	–	0.5	2.5	Rdr	2.0	–	–	63 – 70°	–	–	–	–	–	0.025 0.06	0.3	–	–	–	–	–	–	–	–	–	–
H MONEL	0.5	2.7 – 3.7	2.5	27.0 – 33.0	1.5	–	–	61.0 – 68.0	–	–	–	–	–	–	0.3	–	–	–	–	–	–		–	–	–
MONEL 400		0.15	1.35	31.5	0.9	–	–	66.0°	–	–	–	–	–	0.005	0.12	–	–	–	–	–	–	–	–	–	–
INCONEL X	0.4 1.0	0.5	5.0 – 9.0	0.2	0.3 – 1.0	–	14.0 – 16.0	70.0 MIN.	–	2.25 2.75	–	–	–	0.10	0.08	–	–	0.7 – 1.2	–	–	–	–	–	–	–
INCONEL 625	0.40	0.50	5.0	–	0.50	–	20.0 23.0	Rdr	–	0.40	–	–	–	0.015	0.10	–	0.80 1.0	3.15 – 4.15	–	–	–	–	–	1.0	–
INCONEL 718	0.2 1.0	0.75	Rdr	0.75	0.50	–	17.0 21.0	50.0 55.0	–	0.3 1.3	–	–	–	–	0.10	–	2.8 3.3	4.5 – 5.75	–	–	–	–	–	–	–
COPPER & ALLOYS																									
TOUGH PITCH	–	–	–	–	MIN.	–	–	–	–	–	–	–	–	0.005	–	0.02	–	–	–	–	–	–	0.07	0.102	–
FREE CUTTING	–	–	–	99.4 – 99.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.4 –	–

S MONEL	0.5	4.5	2.5	31.0	1.5	–	–	MIN.	–	–	–	–	–	–	0.25	–	–	–	–	–	–	–	–	–	–	–
R MONEL	–	0.5	2.5	Rdr	2.0	–	–	63 – 70*	–	–	–	–	–	0.025 0.06	0.3	–	–	–	–	–	–	–	–	–	–	–
H MONEL	0.5	2.7 – 3.7	2.5	27.0 – 33.0	1.5	–	–	61.0 – 68.0	–	–	–	–	–	–	0.3	–	–	–	–	–	–		–	–	–
MONEL 400		0.15	1.35	31.5	0.9	–	–	66.0*	–	–	–	–	–	0.005	0.12	–	–	–	–	–	–	–	–	–	–
INCONEL X	0.4 1.0	0.5	5.0 – 9.0	0.2	0.3 – 1.0	–	14.0 – 16.0	70.0 MIN.	–	2.25 2.75	–	–	–	0.10	0.08	–	–	0.7 – 1.2	–	–	–	–	–	–	–
INCONEL 625	0.40	0.50	5.0	–	0.50	–	20.0 23.0	Rdr	–	0.40	–	–	–	0.015	0.10	–	0.80 1.0	3.15 – 4.15	–	–	–	–	–	1.0	–
INCONEL 718	0.2 1.0	0.75	Rdr	0.75	0.50	–	17.0 21.0	50.0 55.0	–	0.3 1.3	–	–	–	–	0.10	–	2.8 3.3	4.5 – 5.75	–	–	–	–	–	–	–
COPPER & ALLOYS																										
ELECTROLYTIC TOUGH PITCH	–	–	Tr	99.9 MIN.	–	–	–	–	–	–	–	0.005	–	0.003	–	–	–	–	–	0.01 – 0.07	0.102	–	–	–	–
FREE CUTTING HI-CONDUCT	–	–	–	99.4 – 99.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.4 – 0.6	–	–	–
HI-STRENGTH, HI-CONDUCT	–	–	–	Rdr	–	–	–	1.5 – 2.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.35 – 0.5	–	–
OXYGEN FREE	–	–	–	99.95 MIN.	–	–	–	–	–	–	–	–	–		–	–	–	–	–	–	–	–	–	–	–
COMMERCIAL BRONZE	–	–	0.05	89.0 – 91.0	–	–	–	–	Rdr	–	–	0.05	–	–	–	–	–	–	–	–	–	–	–	–	0.13
RED BRASS	–	–	0.05	84.0 – 86.0	–	–	–	–	Rdr	–	–	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–
LOW BRASS	–	–	0.05	78.5 – 81.5	–	–	–	–	Rdr	–	–	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–
CARTRIDGE BRASS	–	–	0.05	68.5 – 71.5	–	–	–	–	Rdr	–	–	0.07	–	–	–	–	–	–	–	–	–	–	–	–	–
YELLOW BRASS	–	–	0.05	64.0 68.5	–	–	–	–	Rdr	–	–	0.15	–	–	–	–	–	–	–	–	–	–	–	–	–
ADMIRALTY BRASS	–	–	0.06	70.0 – 73.0	–	–	–	–	Rdr	–	0.9 – 1.2	0.07	0.02 – 0.1	–	–	–	–	–	–	–	–	–	–	–	–
ALUMINIUM BRASS	1.8 – 2.5	–	0.06	76.0 – 79.0	–	–	–	–	Rdr	–	–	0.07	0.02 – 0.1	–	–	–	–	–	–	–	–	–	–	–	–
PHOSPHOR BRONZE, (5%) Gr A	–	–	0.10	Rdr	–	–	–	–	0.3	–	3.5 – 5.8	0.05	0.03 – 0.35	–	–	–	–	–	–	–	–	–	–	–	–
PHOSPHOR BRONZE, (8%) Gr C	–	–	0.10	Rdr	–	–	–	–	0.2	–	7.0 – 9.0	0.05	0.03 – 0.35	–	–	–	–	–	–	–	–	–		–	–
PHOSPHOR BRONZE, (10%) Gr D	–	–	0.10	Rdr	–	–	–	–	0.2	–	9.0 – 11.0	0.05	0.03 – 0.25	–	–	–	–	–	–	–	–	–	–	–	–
PHOSPHOR BRONZE, Gr E	–	–	–	Rdr	–	–	–	–	–	–	1.0 – 1.5	–	Tr	–	–	–	–	–	–	–	–	–	–	–	–
ALUM BRONZE, 5%	4.0 – 7.0	–	0.5	92.0 – 96.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
ALUM BRONZE, 7%	6.0 – 8.0	–	1.5 – 3.5	88.0 – 92.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
ALUM BRONZE, 10%	9.0 – 11.0	0.25	2.0 – 4.0	78.0 – 85.0	1.5	–	–	4.0 – 5.5	–	–	0.2	–	–	–	–	–	–	–	–	–	–	–		–	–
CUPRO NICKEL 10%	–	–	0.5 – 2.0	86.5 MIN	1.0	–	–	9.0 – 11.0	1.0	–	–	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–
CUPRO NICKEL, 30%	–	–	0.4 – 0.7	65 MIN	1.0	–	–	29.0 – 33.0	1.0	–	–	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–
PHOSNIC BRONZE	–	–	–	98.15 MIN.				0.85 – 1.35	–	–	–	–	0.18 – 0.3	–	–	–	–	–	–	–	–	–	–	–	–
TITANIUM																										
6AL-4V)	5.5 – 6.5	–	–	–	–	–	–	–	–	Rdr	–	–	–	–	0.1	0.03	–	–	3.5 – 4.5	–	–	–	–	–	0.6

Rdr – REMAINDER
* – PLUS COBALT
Tr – TRACE

NOTE: ALL SINGLE VALUES ARE MAXIMUM UNLESS OTHERWISE NOTED.

Table II-2.6a (page 1 of 2)
(Reference 47)

AVERAGE CORROSION RATES OF UNSTRESSED METALS IN LIQUID FLUORINE**

Material	Alloy	Average Corrosion Rate (mils/yr)
Aluminum	A356*	0.4
Aluminum	1100	0.6
Aluminum	2017	1.3
Aluminum	5052	1.7
Aluminum	6061	0.6
Aluminum	7079	0.7
Stainless Steel	304	0.2
Stainless Steel	316	0.3
Stainless Steel	347	0.4
Stainless Steel	420	0.3
Hi Strength Steel	PH 15-7 Mo	0.2
Hi Strength Steel	AM-350-C	0.4
Hi Strength Steel	AM-350-CX	0.3
Hi Strength Steel	AM-350-D	0.5
Hi Strength Steel	AM-350-DX	0.7
Nickel		0.2
Monel		0..5
Cupro-Nickel	10% Ni	0.2
Cupro-Nickel	30% Ni	0.6
Titanium	C120AV	1.2
Titanium	A110AT	1.1
Magnesium	HK-31	0.8
Magnesium	AZ-31	0.9

*Reference 97
**Hydrogen fluoride concentration not recorded.

Table II-2.6a (page 2 of 2)

AVERAGE CORROSION RATES OF UNSTRESSED METALS IN LIQUID FLUORINE**

Material	Alloy	Average Corrosion Rate (mils/yr)
Magnesium	HK-31 (coated with Dow-17)	0.1
Magnesium	AZ-31 (coated with Dow-17)	0.6
Everdur	1010	0.8
Copper		0.4
Brass	Yellow	0.5
Brass	Cartridge	0.2
Brass	Casting	1.5

**Hydrogen fluoride concentration not recorded.

Table II-2.6b (page 1 of 4)
(Reference 47)

STRESS CORROSION SAMPLES OF SELECTED METALS IN LIQUID FLUORINE

Material	Alloy	Yield Stress (psi)	Max Stress Applied (psi)	Exposure Time (Hrs)	Remarks
Copper	Soft	10,000	3,440	356	*No evidence of stress corrosion or cracking.
Copper	Hard	48,000	48,000	336	No evidence of stress corrosion or cracking.
Brass	Yellow	60,000	3,440	356	*Some localized dezincification or copper plating.
Brass	Yellow	60,000	60,000	336	No evidence of stress corrosion or cracking.
Everdur	1010	60,000	60,000	336	No evidence of stress corrosion or cracking.
Cupro-Nickel	30%-702	60,000	60,000	338	No evidence of stress corrosion or cracking.
Aluminum	1100	17,000	17,000	335	*No evidence of stress corrosion or cracking.
Aluminum	2017	40,000	40,000	335	No evidence of stress corrosion or cracking.
Aluminum	5052	31,000	31,000	335	No evidence of stress corrosion or cracking.
Aluminum	5052	31,000	8,540	334	*No evidence of stress corrosion or cracking.
Aluminum	6061	40,000	40,000	335	No evidence of stress corrosion or cracking.

Table II-2.6b (page 2 of 4)
(Reference 47)

STRESS CORROSION SAMPLES OF SELECTED METALS IN LIQUID FLUORINE

Material	Alloy	Yield Stress (psi)	Max Stress Applied (psi)	Exposure Time (Hrs)	Remarks
Aluminum	7079	68,000	8,540	334	*No evidence of stress corrosion or cracking.
Aluminum	7079	68,000	68,000	164	No evidence of stress corrosion or cracking.
Stainless Steel	304	30,000	100,000	265	No evidence of stress corrosion or cracking.
Stainless Steel	304	30,000	13,760	325	*No evidence of stress corrosion or cracking.
Stainless Steel	316	30,000	100,000	265	No evidence of stress corrosion or cracking.
Stainless Steel	347	30,000	100,000	265	Some signs of localized corrosion; however, no cracks were discovered.
Stainless Steel	420	60,000	100,000	265	No evidence of stress corrosion or cracking.
Hi-Strength Steel	AM-350-C	56,300	56,300	336	No evidence of stress corrosion or cracking.
Hi-Strength Steel	AM-350-CX	172,000	172,000	336	No evidence of stress corrosion or cracking.
Hi-Strength Steel	AM-350-D	60,000	60,000	336	No evidence of stress corrosion or cracking.

Table II-2.6b (page 3 of 4)
(Reference 47)

STRESS CORROSION SAMPLES OF SELECTED METALS IN LIQUID FLUORINE

Material	Alloy	Yield Stress (psi)	Max Stress Applied (psi)	Exposure Time (Hrs)	Remarks
Hi-Strength Steel	AM-350-DX	179,400	179,400	336	No evidence of stress corrosion or cracking.
Hi-Strength Steel	PH 15-7 Mo	55,000	13,760	325	*Test not completed due to punctured rupture disc.
Hi-Strength Steel	PH 15-7 Mo	55,000	13,760	325	*Copper, apparently from brass washer, plated out on 1/4 in. section. No evidence of stress corrosion or cracking.
Hi-Strength Steel	PH 15-7 Mo	55,000	55,000	338	No evidence of stress corrosion or cracking.
Titanium	C 120 AV	130,000	120,000	164	No stress corrosion or cracking.
Titanium	A 110 AT	112,200	120,000	164	No stress corrosion or cracking.
Magnesium	AZ-31	30,000	30,000	338	Slight stress relaxation. No stress corrosion.
Magnesium	HK-31	30,000	30,000	338	Sample broke at end where fastened down. Apparently caused by insufficient width of metal at end of sample. No sign of corrosion.

Table II-2.6b (page 4 of 4)
(Reference 47)

STRESS CORROSION SAMPLES OF SELECTED METALS IN LIQUID FLUORINE

Material	Alloy	Yield Stress (psi)	Max Stress Applied (psi)	Exposure Time (Hrs)	Remarks
Magnesium	HK-31	30,000	30,000	338	Marked stress relaxation. No stress corrosion.
Magnesium	HK-31	30,000	30,000	338	No stress corrosion or cracking.
Nickel		95,000	95,000	164	No stress corrosion or cracking.
Monel		100,000	75,000	336	No stress corrosion or cracking.

*Denotes 1/4 in. rod stressed sample.
All others are horseshoe type specimens.

Table II-2.6c
MANUFACTURERS' SPECIFICATIONS
GASEOUS AND LIQUID FLOURINE

Gaseous Fluorine (GF_2)--Allied Chemical

F_2	98.5% Minimum
O_2, N_2 and other inerts	1.0% Maximum
CO_2, HF and other gases	0.5% Maximum

Gaseous Fluorine (GF_2)--Air Products

F_2	98.3% Minimum by difference
O_2	0.4% Maximum
N_2	0.9% Maximum
CF_4	0.08% Maximum
HF	0.2% Maximum

Liquid Fluorine (LF_2)--Allied Chemical

F_2	99.0% Minimum by difference
O_2 and N_2	1.0% Maximum by weight
HF and CF_4	0.3% Maximum by weight

The above results (LF_2) to be on a Helium-free basis

Table II-2.6d

AVERAGE TENSILE PROPERTIES OF 1-YEAR SPECIMENS (REF. 66)

Metal	Treatment (liquid at -320°F)	Average Yield Stress, psi	Average Ultimate Stress, psi
Stainless steel 304	Nitrogen	60,620	93,960
	Fluorine	63,440	94,100
Stainless steel 410	Nitrogen	74,680	88,920
	Fluorine	73,700	89,380
Armco steel 15-7 Ph-Mo	Nitrogen	71,660	143,420
	Fluorine	70,700	141,900
Copper	Nitrogen	53,580	57,640
	Fluorine	54,080	58,660
Aluminum 1100	Nitrogen	21,480	23,120
	Fluorine	21,700	22,940
Aluminum 6061	Nitrogen	41,840	45,820
	Fluorine	41,480	46,360
Nickel	Nitrogen	89,960	96,900
	Fluorine	89,680	96,420
Monel	Nitrogen	58,020	93,740
	Fluorine	58,120	93,040
Titanium A110 AT	Nitrogen	125,400	151,600
	Fluorine	126,200	152,000
Titanium C120 AV	Nitrogen	124,000	153,200
	Fluorine	121,400	152,200
Magnesium AZ31	Nitrogen	35,500	41,600
	Fluorine	34,160	41,720
Magnesium HK-31	Nitrogen	49,000	49,960
	Fluorine	46,000	48,240

Editor's Note: Results indicate no degradation of tensile properties in fluorine as compared with nitrogen.

Table II-2.6e
(Reference 150)
IGNITION TEMPERATURES OF SELECTED METALS IN FLUORINE

Metal	Number of Tests	Ignition Temp. °F	Average Ignition Temp. °F	% Maximum Variation from Average
Aluminum	4	*	1382	---
Copper	5	1337 1193 1238 1238 1377	1277	8.0
Iron	4	1251 1233 1233 1249	1242	0.8
Molybdenum	5	394 381 354 408 354	378	8.3
Monel	4	818 793 698 710	755	12
Nickel	6	2134 2005 2226 2183 2208 1983	2091	6
302 Stainless Steel	4	1380 1465 1132 1058	1259	13
Tungsten	4	446 565 473 500	496	18

*An average of 4 tests gave an ignition temperature greater than the melting point of aluminum (1220°F).

Table II-2.6f

CORROSION OF NICKEL AND NICKEL ALLOYS IN FLUORINE

Nickel Alloy	Reference	Corrosion Rates (Inches/Year) According to Temperature (°F)											
		-320 to -310	50 to 250	250 to 400	400 to 550	550 to 700	700 to 800	800 to 900	900 to 1000	1000 to 1100	1100 to 1200	1200 to 1300	1300 to 1400
A	66*	241×10^{-4}	0.001	0.0033	---	---	0.0017	---	---	0.0246	---	---	---
A	66**	---	0.0009	Nil	0.0010	---	0.0012	---	0.0156	---	---	---	---
A	66/	---	Nil	0.0001	---	0.0004	---	--	---	0.0138	---	---	---
A	63	25×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
L	66*	359×10^{-4}	0.0024	---	0.0032	---	0.0014	---	---	0.0201	---	---	---
L	63	25×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
D	59	---	---	---	---	---	---	---	---	---	0.002	---	---
99.4%	133	---	---	---	---	---	0.0084	0.0228	0.0612	---	0.348	0.192	0.408
99.4%	47	0.2×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
99.4%	49	7.3×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
99.4%	69	---	---	---	---	---	---	---	---	0.0002	---	0.314	0.816
Low Carbon	61	---	---	---	---	---	---	---	---	---	0.0003	---	---
Duranickel	61	---	---	---	---	---	---	---	---	---	0.0008	---	---
Illium	66*	900×10^{-4}	0.0020	0.0062	---	0.0127	---	---	4.04	---	---	---	---
Illium R	63	100×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
Monel	66*	1603×10^{-4}	0.0025	0.0010	---	0.0019	---	---	---	0.0298	---	---	---
Monel	66**	146×10^{-4}	0.0005	---	0.0010	---	0.0018	---	---	0.0113	---	---	---
Monel	66/	52×10^{-4}	0.0002	0.0002	---	0.0012	---	---	---	---	0.0072	---	---
Monel	133	---	---	---	---	---	0.006	0.018	0.024	000	0.72	0.96	1.8
Monel	66	20×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
Monel	70	0.5×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
Monel	49	84×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
Monel	69	---	---	---	---	---	---	---	---	---	---	---	---
Monel Cast	66*	1180×10^{-4}	0.0020	0.0010	---	---	0.0039	---	0.0429	---	---	Nil	3.5
Monel Cast	63	125×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
Inconel	66	267×10^{-4}	0.0017	0.0012	---	0.0775	---	---	3.451	---	---	---	---
Inconel	133	---	---	---	---	---	0.456	1.152	0.744	---	2.04	1.52	6.12
Inconel	63	250×10^{-4}	---	---	---	---	---	---	---	---	---	---	---
Inconel	69	---	---	---	---	---	---	---	---	4.8	---	6.0	33.5

*Five hour test
**Twenty-four hour test
/Five day test
(Other tests duration not specified)

T II-2.6g

Table II-2.6g
CORROSION OF IRON AND STEEL IN FLUORINE

Metal Steel	Reference	Corrosion Rates (Inches/Year) According to Temperature (°F)									
		-320 to -310	50 to 100	100 to 200	250 to 400	400 to 500	500 to 600	600 to 700	700 to 800	800 to 900	900 to 100
Low Carbon Steel	66*	267×10^{-4}	0.0047	---	0.0047	---	---	0.3986	---	---	Consumed
Low Silicon Iron	192	---	---	---	0.0037	---	---	---	---	---	---
High Silicon Iron	192	---	---	---	0.0067	---	---	---	---	---	---
Sheet Iron 0.007% Si	133	---	---	---	---	0.192	0.048	0.0024	0.144	---	88.8
SAE 1010	192	---	---	0.0001	---	---	---	---	---	---	---
SAE 1015	133	---	---	---	---	---	9.96	---	---	---	---
SAE 1020	232	---	---	---	0.4524	5.76	11.04	1.74	3.16	18.24	178.8
SAE 1030	133	---	---	---	0.456	0.576	7.82	1.764	6.48	18.24	---
SAE 1030	133	---	0.024	0.108	0.180	238	---	---	---	---	---
Music Wire	133	---	---	---	---	---	4.5	---	---	---	---
Armco Iron	192	---	---	0.0007	---	---	---	---	---	---	132.0
Armco Iron	133	---	---	---	---	0.024	0.108	0.096	0.288	3.6	139.2
Armco Iron	232	---	---	---	0.0024	0.0024	---	0.0984	2.832	3.6	139.2
Mild Steel	63	2.40×10^{-4}	---	---	---	---	---	---	---	---	---
Mild Steel	232	---	---	---	---	0.1932	0.0528	---	0.1368	3.6	88.8
27% Carbon Steel	232	---	---	---	0.0072	0.0942	---	---	1.836	6.48	237.6
15-7(MO) PH	47	2×10^{-4}	---	---	---	---	---	---	---	---	---
15-7(MO) PH	49	0.1×10^{-4}	---	---	---	---	---	---	---	---	---
AM 350	48	4×10^{-4}	---	---	---	---	---	---	---	---	---
304 Stainless	66*	1376×10^{-4}	0.0017	---	---	0.0061	---	1.588	---	---	---
304 Stainless	63	200×10^{-4}	---	---	---	---	---	---	---	---	---
304 Stainless	47	0.2×10^{-4}	---	---	---	---	---	---	---	---	---
304 Stainless	49	0.25×10^{-4}	---	---	---	---	---	---	---	---	---
304 Stainless	66**	56×10^{-4}	---	---	---	---	---	---	---	---	---
309 (Cb) Stainless	133	---	---	---	---	---	0.9	5.544	7.98	---	---
310 Stainless	133	---	---	---	---	---	0.408	4.248	6.732	---	---
316 Stainless	47	4×10^{-4}	---	---	---	---	---	---	---	---	---
347 Stainless	66*	1577×10^{-4}	0.0027	---	---	0.0038	---	---	4.248	---	---
347 Stainless	63	1180×10^{-4}	---	---	---	---	---	---	---	---	---
347 Stainless	133	---	---	---	---	1.72	2.556	6.2	9.54	---	---
347 Stainless	48	0.4×10^{-4}	---	---	---	---	---	---	---	---	---
410 Stainless	49	0.6×10^{-4}	---	---	---	---	---	---	---	---	---
420 Stainless	47	3×10^{-4}	---	---	---	---	---	---	---	---	---
430 Stainless	47	---	---	---	0.0084	---	3.060	0.936	0.936	---	---

*Five hour test
**One hundred and twenty hour test
(Other items not specified)

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Table II-2.6h (page 1 of 2)

CORROSION OF ALUMINUM IN FLUORINE

Metal Aluminum	Reference	Test Duration (hrs)	Corrosion Rates (in/yr) According to Temperature (°F)				
			-320 to -310	50 to 250	250 to 450	450 to 750	750 to 1000
1100-H14	66	0.5	876×10^{-4}	0.0805	0.0020	0.0061	1.822
	66	24	---	0.0024	0.0031	0.0295	0.1965
	66	24	---	---	0.0004	---	---
	66	120	---	0.0002	0.0000	0.075	0.2875
	133	5	---	---	---	0.0000	0.156
	63	5	90×10^{-4}	---	---	---	---
	47	*	0.6×10^{-4}	---	---	---	---
	49	*	0.2×10^{-4}	---	---	---	---
2017	47	*	1.3×10^{-4}	---	---	---	---
2024-T3	66	5	1665×10^{-4}	0.0079	0.0010	0.0020	0.0294
	66	24	---	0.0005	0.0008	0.0013	0.0063
	66	24	---	---	0.0028	---	---
	66	120	---	0.0001	0.0001	0.0066	0.0014
	63	5	1500×10^{-4}	---	---	---	---
3003-H14	66	5	2103×10^{-4}	0.0009	0.0005	0.0010	0.0215
	66	120	31×10^{-4}	---	---	---	---
	63	5	30×10^{-4}	---	---	---	---
5052	47	*	2×10^{-4}	---	---	---	---

Table II-2.6h (page 2 of 2)

CORROSION OF ALUMINUM IN FLUORINE

Metal Aluminum	Reference	Test Duration (hrs)	Corrosion Rates (in/yr) According to Temperature (°F)				
			-320 to -310	50 to 250	250 to 450	450 to 750	750 to 1000
5154-H34	66	5	1878×10^{-4}	0.0081	0.0040	0.0050	0.0074
	66	24	---	0.0005	0.0016	0.0016	0.0060
	66	24	---	---	0.0021	---	---
	66	120	---	0.0002	0.0004	---	---
A 356	97	24	20×10^{-4}	0.0016			
5154-0	66	120	---	---	---	0.0004	0.0013
	63	5	900×10^{-4}	---	---	---	---
6061	47	*	1×10^{-4}	---	---	---	---
	49	*	2×10^{-4}	---	---	---	---
7079	47	*	1×10^{-4}	---	---	---	---
Sheet	192	5	---	---	---	---	0.48-0.72

*Test duration not specified.

Table II-2.6i

CORROSION OF COPPER AND COPPER ALLOYS IN FLUORINE

Metal Copper	Reference	Corrosion Rates (Inches/Year) According to Temperature (° F)						
		-320 to -310	50 to 250	250 to 450	650 to 850	850 to 1000	1000 to 1250	1250 to 1400
ETP	66*	1577×10^{-4}	.0033	.0072	.0308	.2322	--	--
Deoxidized	133	--	--	--	1.92	1.44	11.88	34.8
	63	1500×10^{-4}	--	--	--	--	--	--
Electrolytic Grade	47	4×10^{-4}	--	--	--	--	--	--
	49	$.03 \times 10^{-4}$	--	--	--	--	--	--
Sheet	61	--	--	--	--	2.4	--	36.0
	163	--	--	--	--	--	.54	1.10
Brass								
American #243	66*	556×10^{-4}	.0175	.0202	.3811	3.85	--	--
	63	600×10^{-4}	--	--	--	--	--	--
Red Brass	66	1577×10^{-4}	.0025	.0056	.0709	.3940	--	--
	03	1600×10^{-4}	--	--	--	--	--	--
Yellow Brass	47	5×10^{-4}	--	--	--	--	--	--
Cartridge Brass	47	2×10^{-4}	--	--	--	--	--	--
Casting Brass	47	15×10^{-4}	--	--	--	--	--	--
Everdur 1010	47	8×10^{-4}	--	--	--	--	--	--
90% Cupro-Metal	47	2×10^{-4}	--	--	--	--	--	--
70% Cupro-Nickel	47	6×10^{-4}	--	--	--	--	--	--

*5 hour test
(other tests duration not specified)

Table II-2.6j

CORROSION OF MAGNESIUM AND MAGNESIUM ALLOYS IN FLUORINE

Metal Magnesium	Reference	Test Duration Hrs	Corrosion Rates (in/yr) According to Temperature (° F)								
			-320 to -310	50 to 200	200 to 400	400 to 500	500 to 600	600 to 700	700 to 900	900 to 1000	1000 to 1100
M1A	66	5	1314×10^{-4}	Nil	---	.0019	---	---	.0079	.0394	---
M1A	66	24	----	.0041	.0017	.0017	---	.0024	---	---	.0158
M1A	66	120	----	.0003	.0002	---	---	.0008	---	---	.0106
M1A	63	*	220×10^{-4}	---	---	---	---	---	---	---	---
Dow Metal G	133	*	----	---	Nil	Nil	Nil	---	---	---	---
AZ81C-T6	66	5	2891×10^{-4}	Nil	---	.0013	---	---	.0131	---	.0394
AX81C-T6	66	5	8666×10^{-4}	---	---	---	---	---	---	---	---
AZ81C-T6	66	24	----	.0020	.0011	.0004	---	---	.0039	.0092	.0216
AZ81C-T6	66	120	----	.0002	.0002	---	---	.0003	---	---	.0033
AZ81C-T6	63	*	250×10^{-4}	---	---	---	---	---	---	---	---
HK31A-H24	66	5	429×10^{-4}	.0055	.0066	---	---	.0067	---	.0201	---
HK31A-H24	66	5	1226×10^{-4}	---	---	---	---	---	---	---	---
HK31A-H24	63	*	450×10^{-4}	---	---	---	---	---	---	---	---
AZ91C-T6	66	24	----	.0017	---	.0003	---	.0027	---	.0289	.2313
AZ91C-T6	66	120	----	.0002	---	.0002	---	.0011	---	---	.0015

*Time not specified.

Table II-2.6k

SILVER SOLDER COMPOSITION
(*Recommended for Fluorine Service)

Designation	Composition, %				Melting Range, °F	
	Ag	Cu	Zn	Cd	First Melt	Complete Liquid-fication
ASTM 1*	10	52	38	0.5	1510	1600
ASTM 2*	20	45	35	0.5	1430	1500
ASTM 3	20	45	30	5	1430	1500
ASTM 4*	45	30	25	-	1250	1370
ASTM 5*	50	34	16	-	1280	1425
ASTM 6	65	20	15	-	1280	1325
ASTM 7	70	20	10	-	1335	1390
ASTM 8	80	16	4	-	1360	1460

Table II-2.7a

NONMETALS EXPOSED TO GASEOUS AND LIQUID FLUORINE (Reference 210)

Table II-2.7a

Sample[a]	Sample exposed to liquid F at atmospheric pressure	Sample exposed to gaseous F at atmospheric pressure	Sample exposed to liquid F_2 at 1500 lb/sq in. gage pressure	Sample exposed to gaseous F_2 at 1500 lb/sq in. gage pressure	Sample injected into liquid F_2 at 1500 lb/sq in. gage pressure
LIQUIDS:					
Kel-F LO No. 10 (M. W. Kellogg Co.)	No reaction	No reaction	No reaction	Reaction[b]	Reaction
Fluorolube HO (Hooker Electrochemical Co.)	No reaction	No reaction	No reaction	Reaction[b]	(c)
N-43, $(C_4F_9)_3N$ (Minnesota Mining & Mfg. Co.)	No reaction	No reaction	No reaction	Reaction[d]	Reaction
Tap Water	No reaction	No reaction	No reaction	Reaction	No Reaction
Cenco Hyvac Oil (Central Scientific Co.)		No reaction			
Glyptal (General Electric Co.)		Burned			
Dow Corning 200 fluid (20 centi-stokes)		Burned			
Water glass		Burned			
Safety Solvent 178 (Fine Organics, Inc.)		Burned			
Leak-Tec (American Gas & Chemicals Inc.)		Burned			
Leak-Tec with glycerine		Burned			
Dry JP-4 fuel		Burned			
Carbon tetrachloride		Exploded			
GREASES:					
Kel-F Med. Wax (M. W. Kellogg Co.)	No reaction	No reaction	Reaction[e]	Reaction	
Kel-F No. 1 Grease (M. W. Kellogg Co.)	(c)	No reaction	(c)	(c)	
Fluorolube LG (Hooker Electrochemical Co.)	(c)	No reaction	(c)	(c)	
Fluorolube MG (Hooker Electrochemical Co.)	(c)	No reaction	(c)	(c)	
Permatex No. 3 (Permatex Co.)	No reaction	No reaction	Reaction	Reaction	
Q-Seal (Quigley Co.)	No reaction	No reaction	No reaction	Reaction	
Blue Goop (Crawford Fitting Co.)	Exploded	No reaction		Reaction	
Molylube (Bel-Ray Co., Inc.)	Exploded	No reaction		Reaction	
Plast-O-Seal (The Colonial Plastics Mfg. Co.)	Burned	No reaction		Reaction	
Permatex No. 1 (Permatex Co.)		Burned			
Permatex No. 2 (Permatex Co.)		Burned			
X-Pando seal coating (X-Pando Corp.)		Burned			
Tyte Unyte (J. C. Whitlam Mfg. Co.)		Burned			
White Lead		Burned			
SOLIDS:					
Ruby (Al_2O_3)	No reaction	No reaction	No reaction	No reaction	
Teflon (E. I. du Pont de Nemours & Co.)	No reaction	No reaction	No reaction	No reaction	
Kel-F Solid (M. W. Kellogg Co.)	No reaction	No reaction	Reaction[e]	Reaction	
Kel-F Elastomer 5500 (M. W. Kellogg	No reaction	No reaction	No reaction	Reaction	
Graphitar (United States Graphite Co.)	No reaction	No reaction	No reaction	Reaction	
Powdered Graphitar (United States Graphite Co.)		Burned			
Neoprene-covered Fiberglas	Exploded	No reaction		Reaction	
N-43 plus neoprene-covered Fiberglas		No reaction		Reaction	
Plexiglas (Rohm & Haas Co.)	No reaction	No reaction	Reaction	Reaction	
Tygon tubing (U. S. Stoneware Co.)	No reaction	No reaction	Reaction	Reaction	
Vinylite (Carbide and Carbon Chemicals Co.)	No reaction	No reaction	No reaction	Reaction	
Pennsalt PCC (Pennsylvania Salt Mfg. Co.)	No reaction	No reaction	No reaction	Reaction	
Pennsalt PCI (Pennsylvania Salt Mfg. Co.)	No reaction	No reaction	Reaction[e]	Reaction	
Flux on silver-soldered copper-to-base joint	No reaction	No reaction		Reaction	
Slag on stainless-steel weld joint	No reaction	No reaction	No reaction	Reaction	
Flux on silver-soldered stainless-steel joint	No reaction	Burned			
Dow Corning Elastomer		Burned			
Molykote Type Z Powder (Bel-Ray Co., Inc.)		Burned			
Litharge and glycerine		Burned			
Palmetto (Greene, Tweed & Co.)		Burned			

[a]Samples are listed by trade name in most cases; the compositions were not available.

[b]Reacted when exposed surface area was increased.

[c]Not tested; Kel-F and Fluorolube materials are all polymers of triflurochloroethylene; see preceding entry for representative results.

[d]Reacted in two out of four tests.

[e]Reacted in one out of two tests.

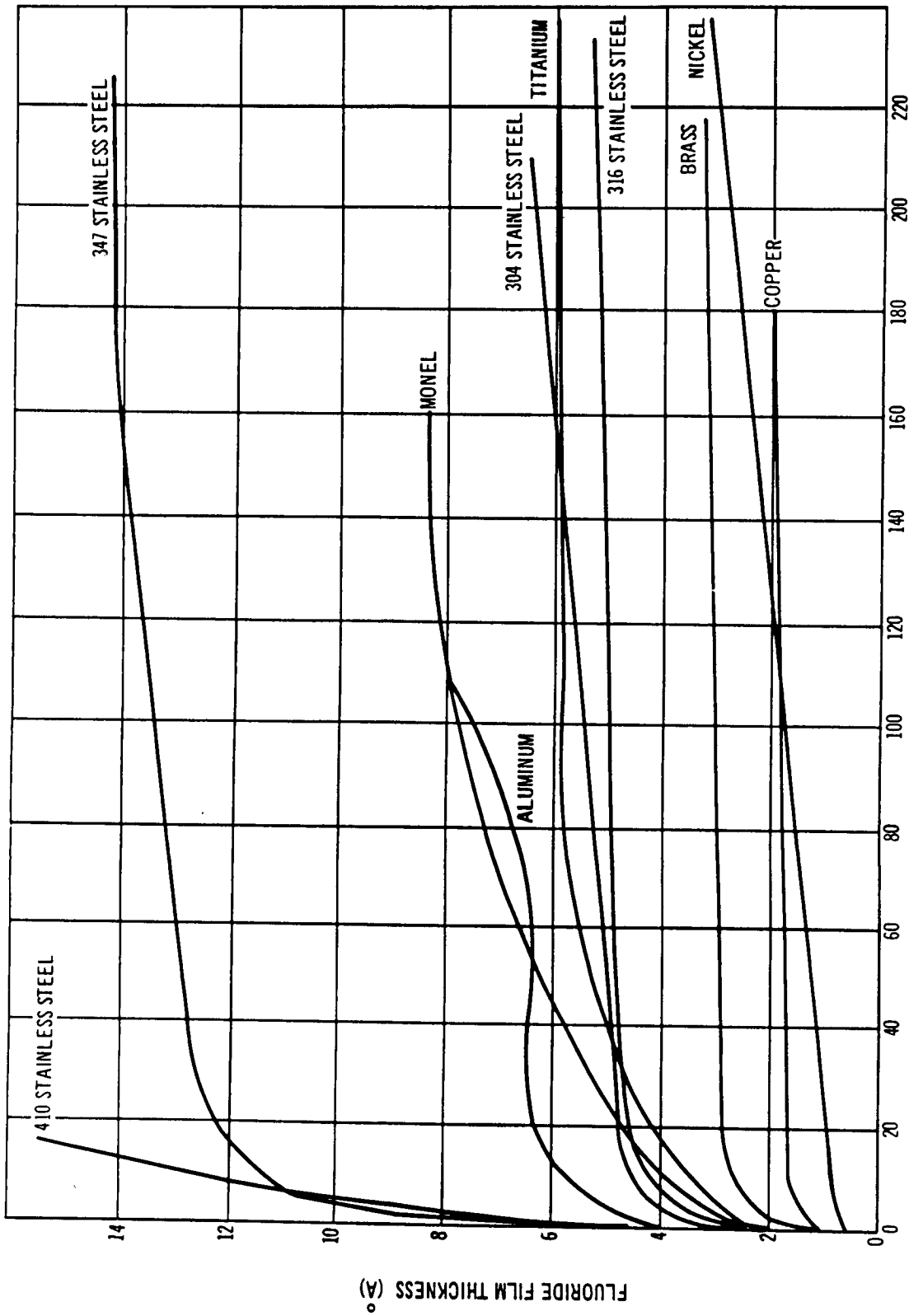

Figure II-2.6a. Variation of Fluorine Film Thickness on Metal Powders vs. Time of Exposure to Gaseous Fluorine at −113°F (Reference 51)

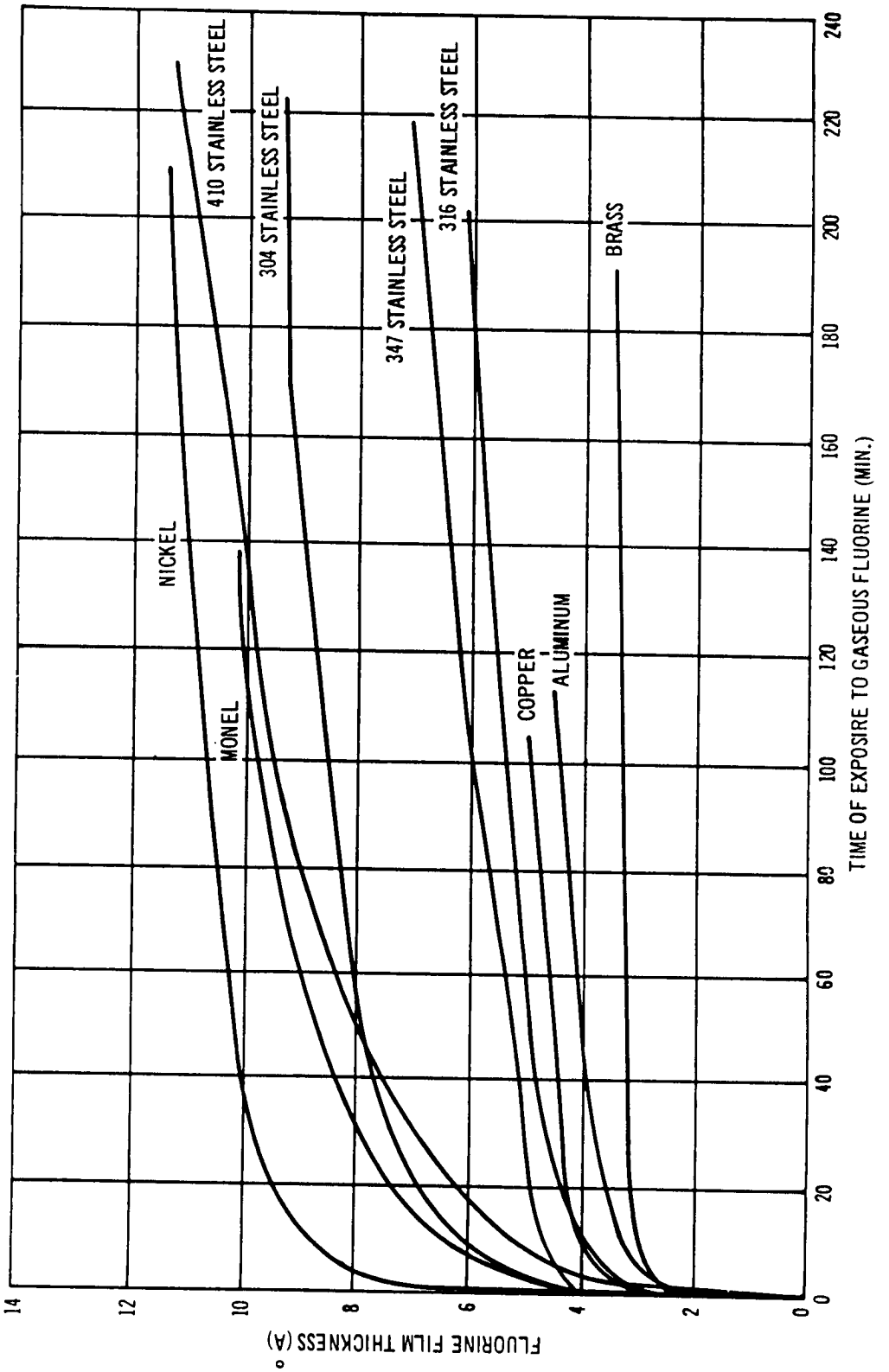

Figure II-2.6b. Variation of Fluoride Film Thickness on Metal Powders vs. Time of Exposure to Gaseous Fluorine at + 86°F (Reference 51)

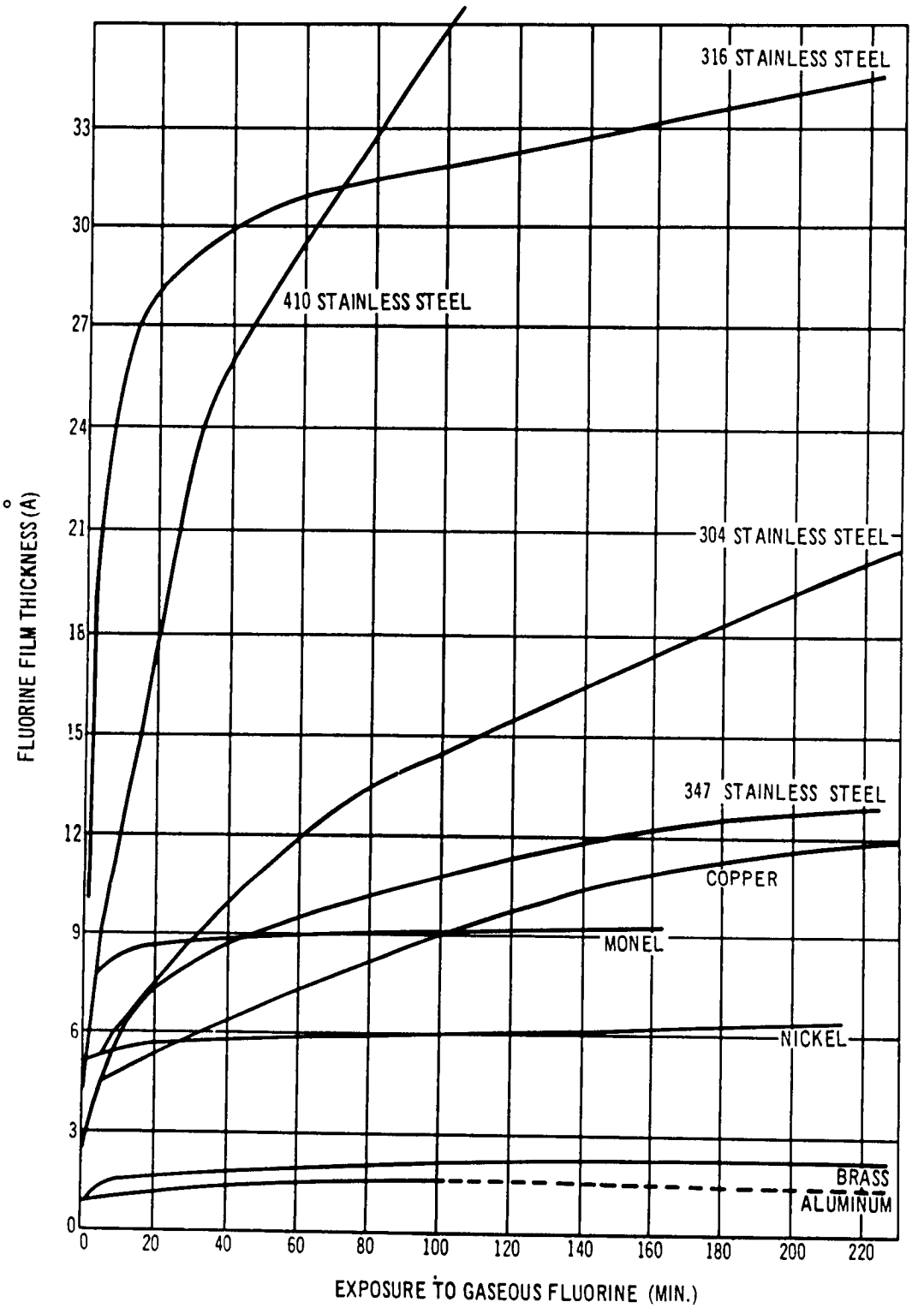

Figure II-2.6c. Variation of Fluorine Film Thickness on Metal Powders vs. Time of Exposure to Gaseous Fluorine at +183°F (Reference 51)

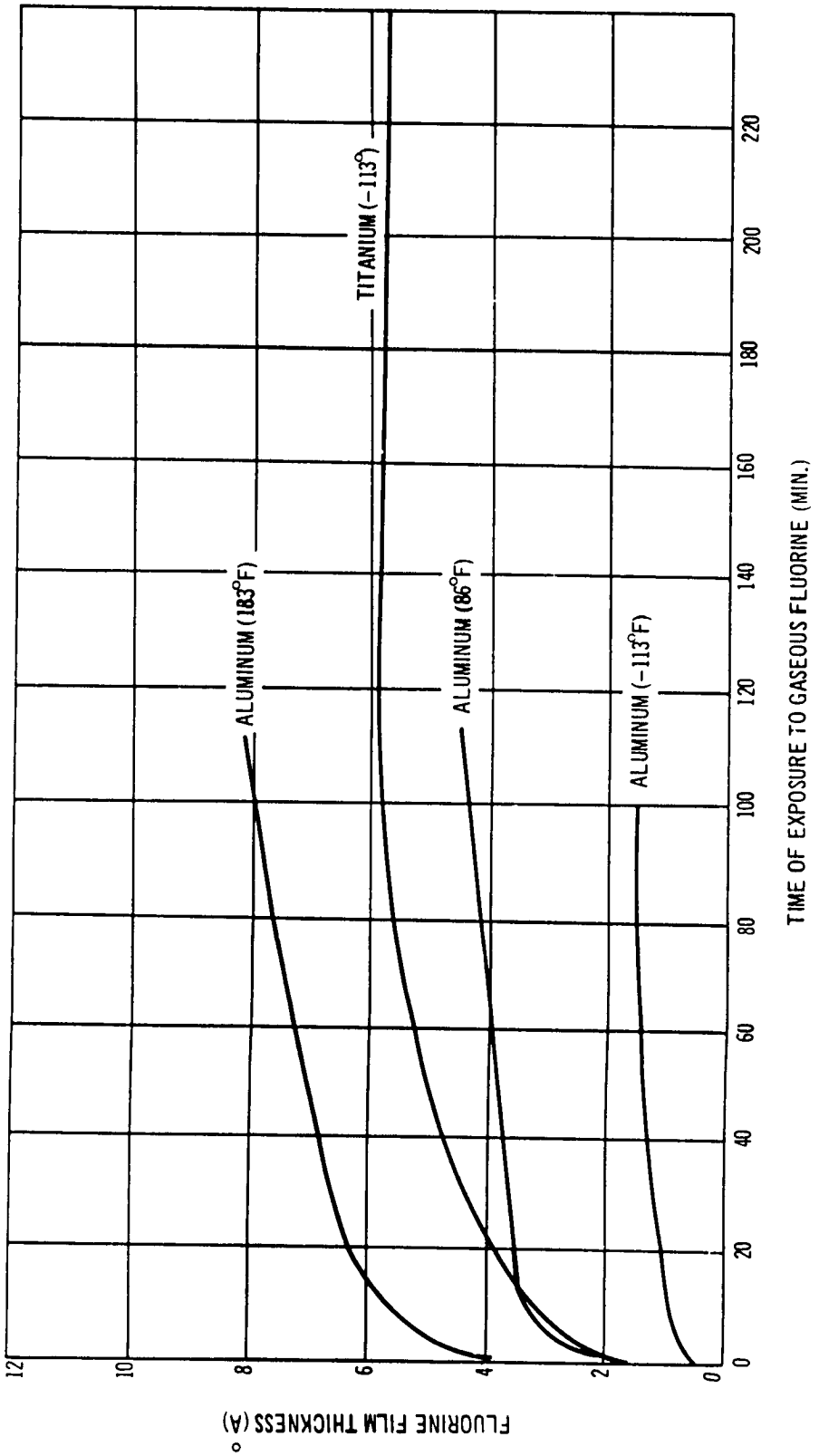

Figure II-2.6d. Variation of Fluorine Film Thickness on Aluminum and Titanium Powders vs. Time of Exposure to Gaseous Fluorine (Reference 51)

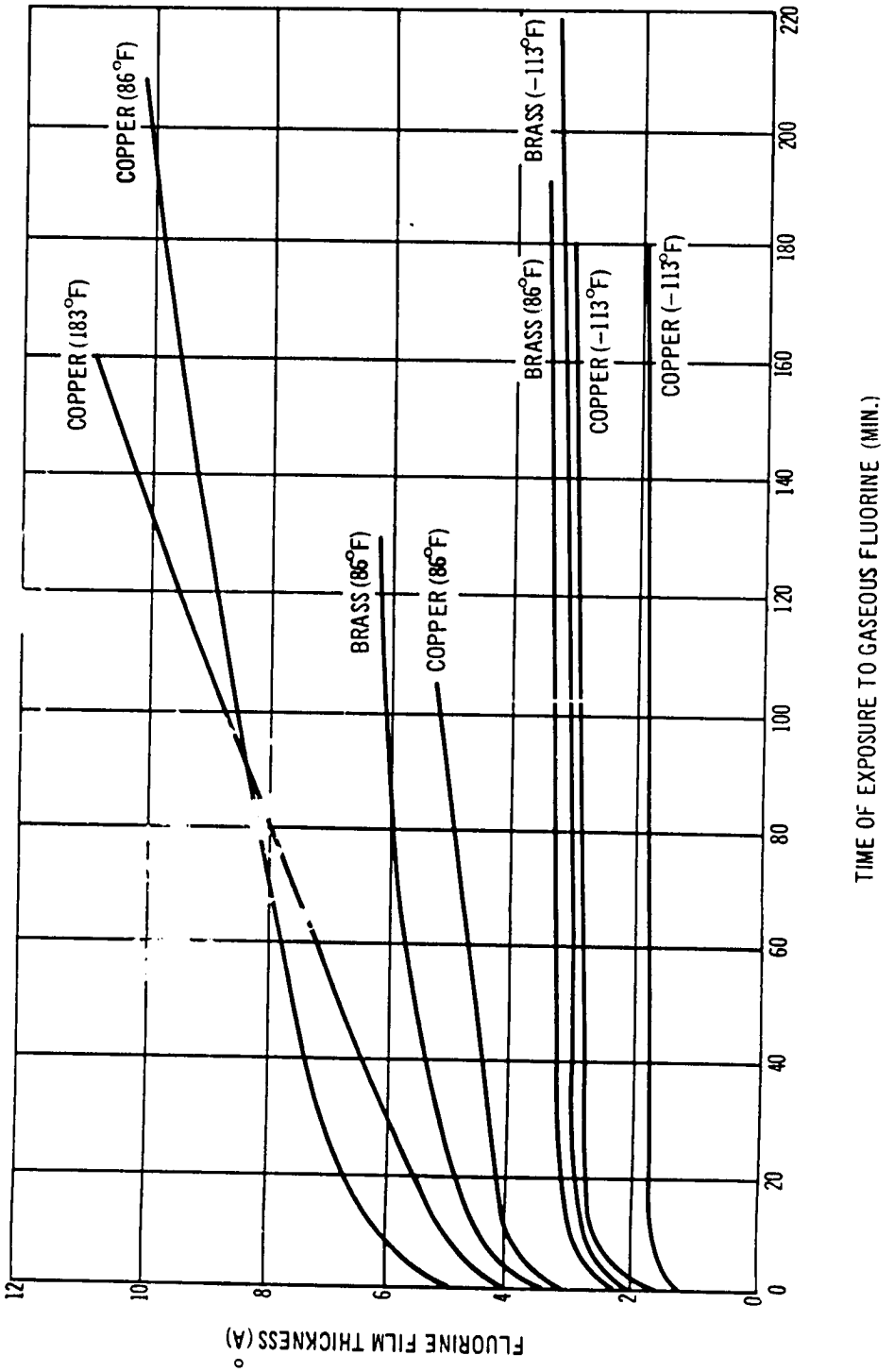

Figure II-2.6e. Variation of Fluoride Film Thickness on Copper and Brass Powders vs. Time of Exposure to Gaseous Fluorine at Different Temperatures (Reference 51)

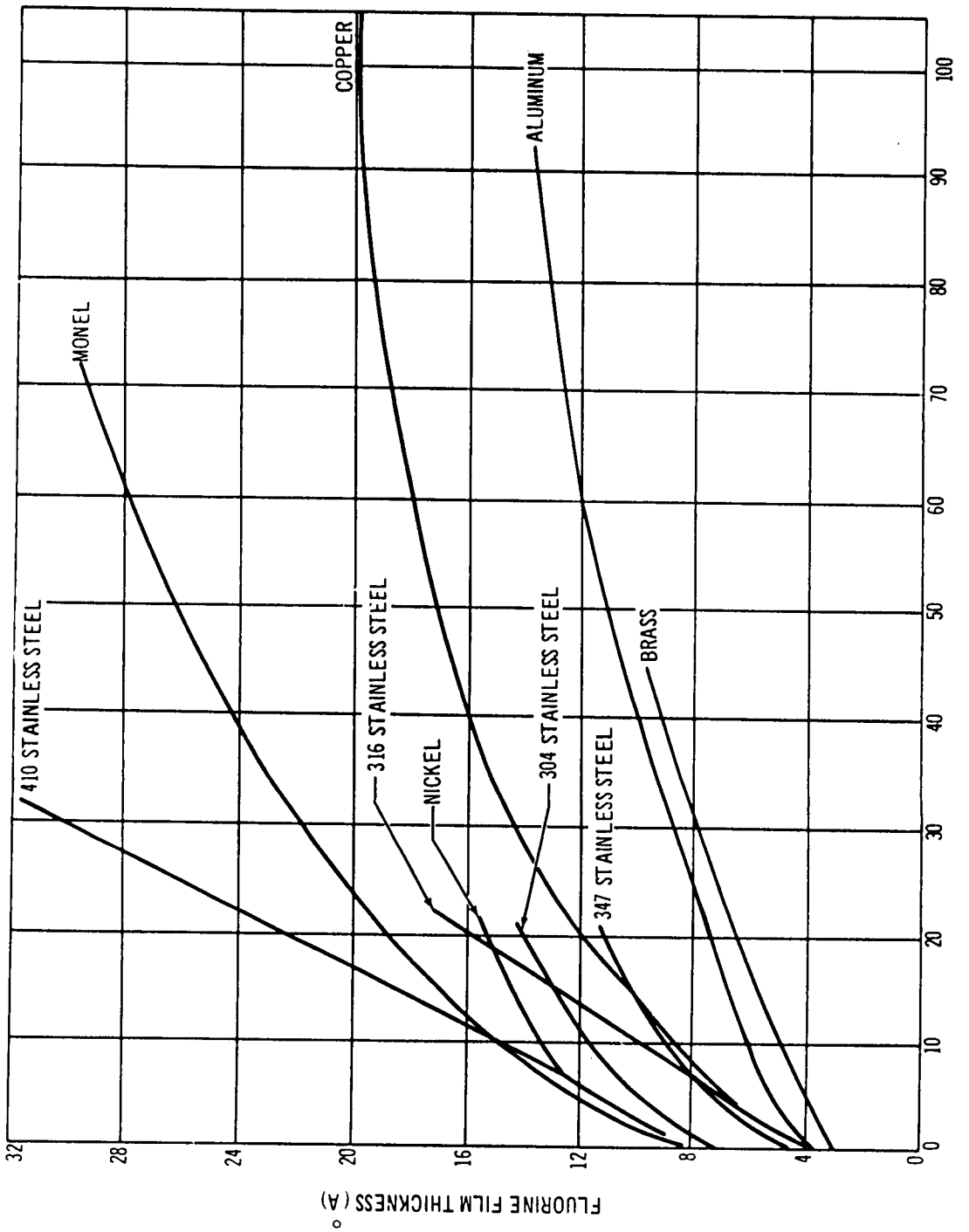

Figure II-2.6f. Variation of Fluorine Film Thickness on Metal Powders vs. Time of Exposure to Gaseous Fluorine at 86°F Total Run (Reference 51)

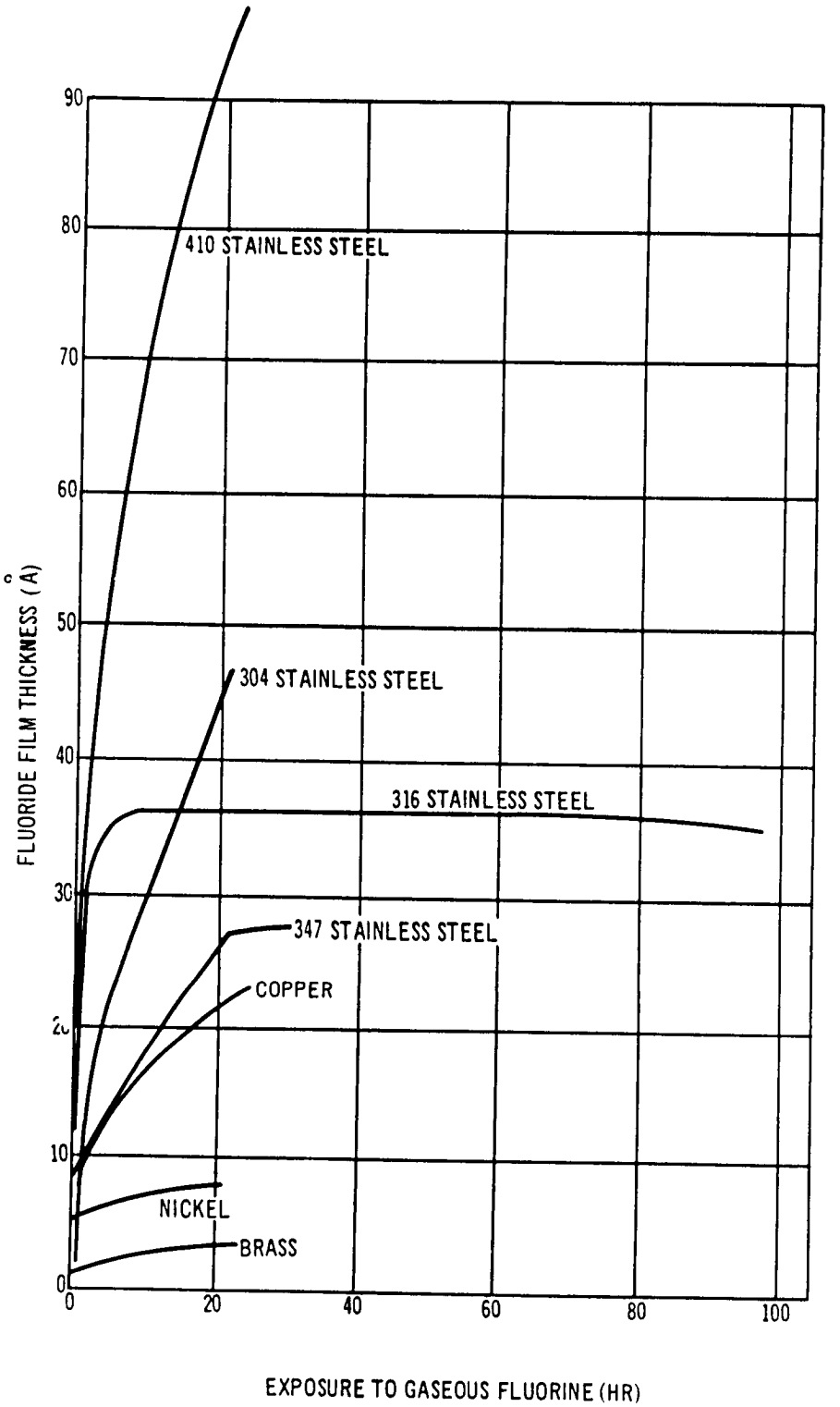

Figure II-2.6g. Variation of Fluorine Film Thickness on Metal Powders vs. Time of Exposure to Gaseous Fluorine at 103°F – Total Run (Reference 51)

UNETCHED CONDITION 1,000 X MAGNIFICATION

GRADE II-F

GRADE III-F

Figure II-2.6h. Silicon Dispersion in Cast Aluminum Alloy A356 (Reference 97)

UNETCHED CONDITION 1,000 X MAGNIFICATION

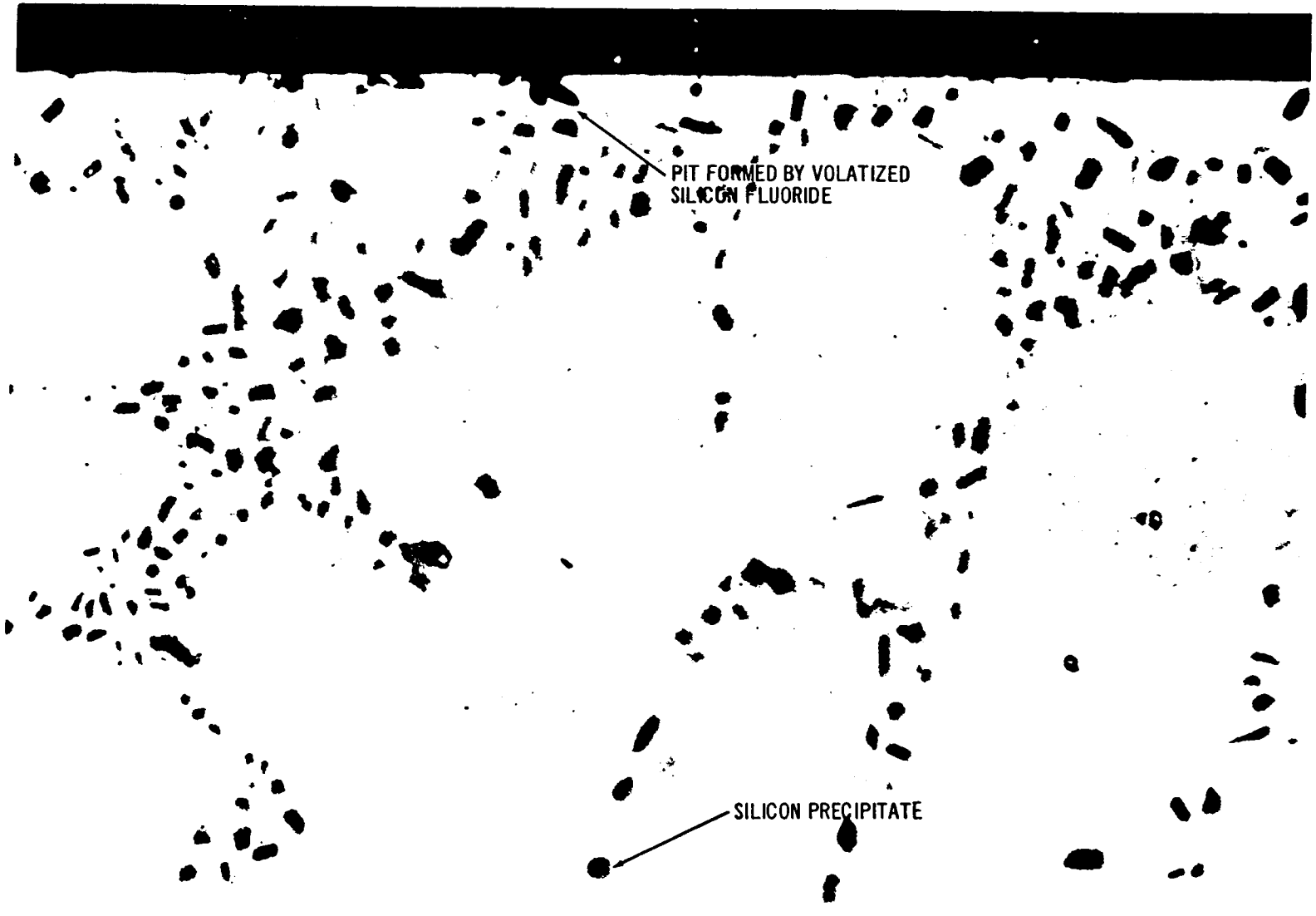

Figure II-2.6i. Grade II-F A356 Cast Aluminum Alloy Exposed to Gaseous Fluorine (Reference 97)

UNETCHED CONDITION 1.000X MAGNIFICATION

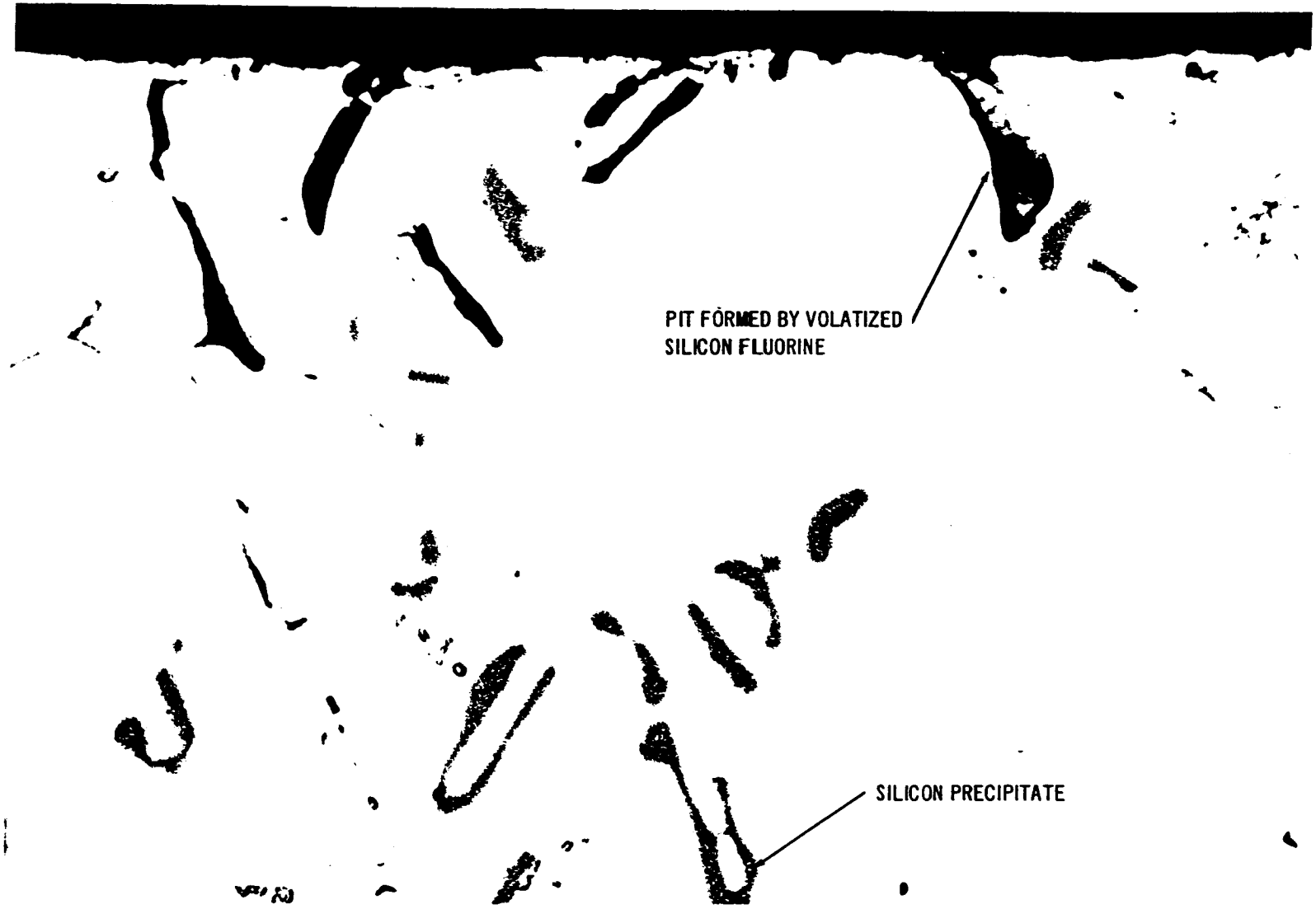

Figure II-2.6j. Grade III-F A356 Cast Aluminum Alloy Exposed to Gaseous Fluorine (Reference 97)

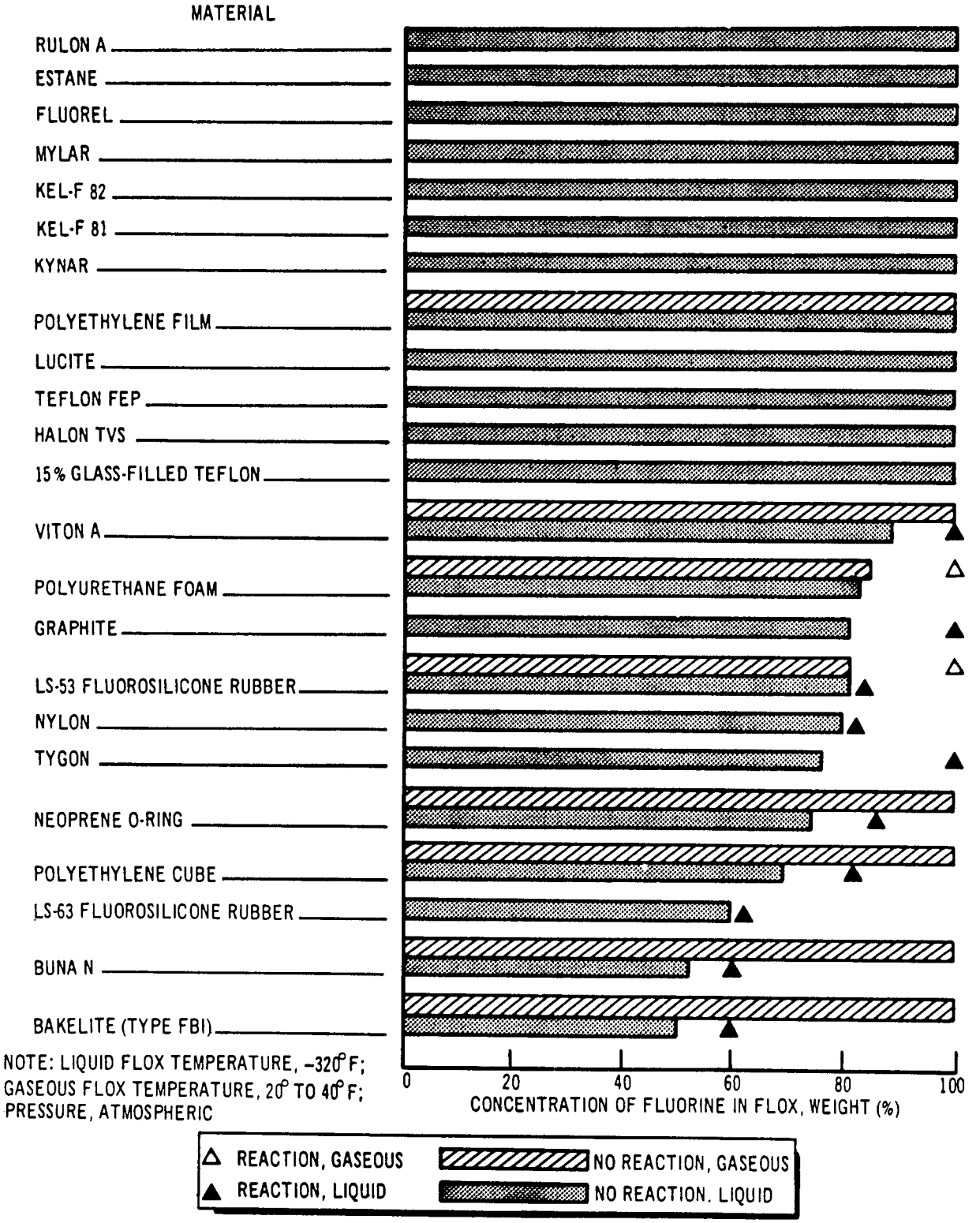

Figure II-2.7a. Solid Nonmetallic Materials Statistically Exposed to Flox (Reference 43)

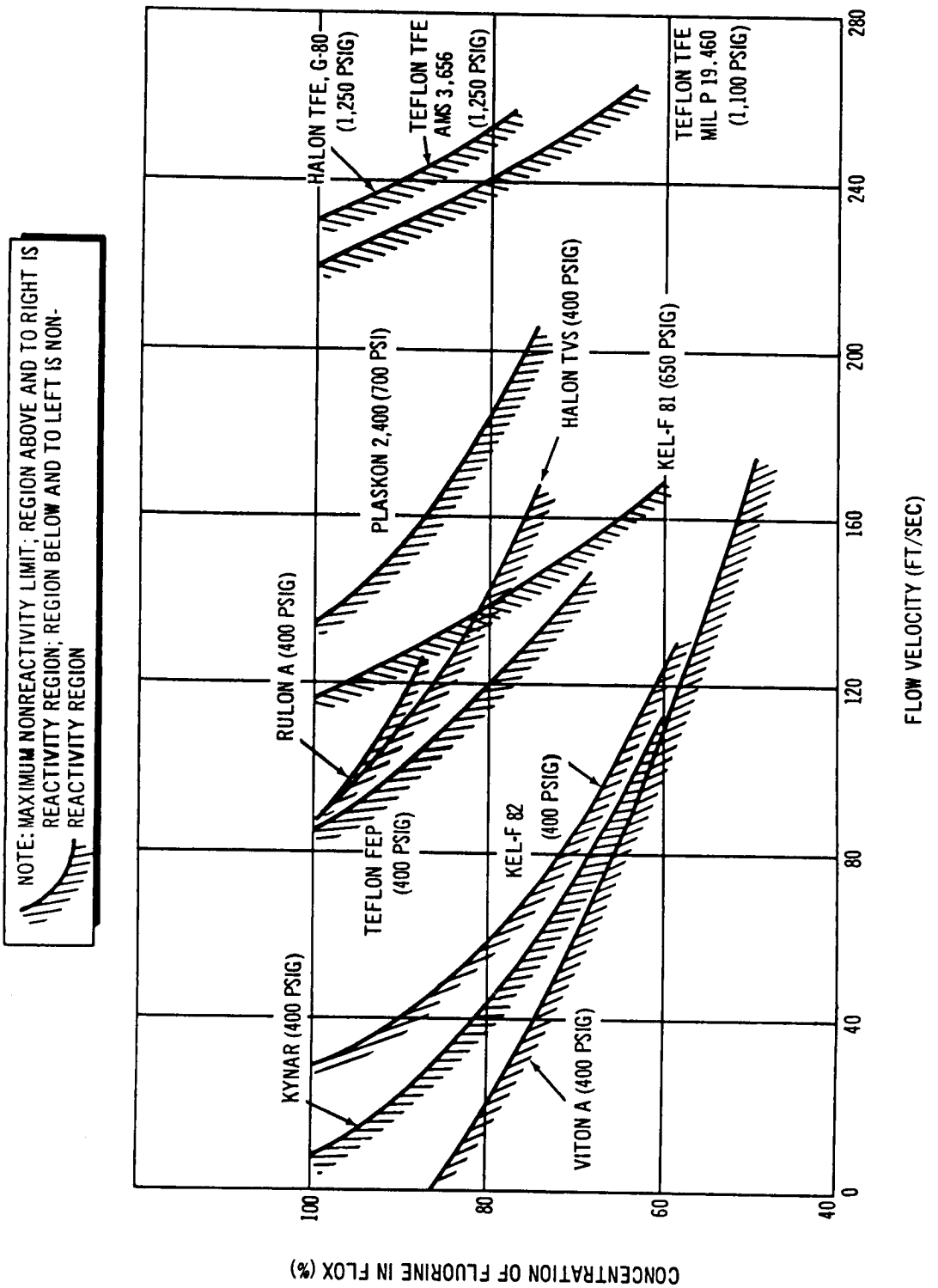

Figure II-2.7b. Liquid Flox Reactivity Profile (Reference 43)

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3.0 Component Considerations

3.1 Valves

Valves are required in airborne feed systems to control the movement of fluid. Their primary function is to provide a completely leak-free closure in the closed position and a completely unobstructed flow passage when opened. Applications may require valves to modulate flow, such as pressure regulating devices or to allow one way flow, such as, check valves. The airborne valve has developed to a high state of reliability while retaining many of the past design features. The majority of this technology remains unchanged for fluorine usage. Fundamentally, more care must be exercised in the selection of materials of construction, as well as in the physical design than presently is included in the LOX/hydrogen state-of-the-art. In general, less leakage can be tolerated with fluorine and provision must be made to assure a system capable of extreme cleanliness. Present LOX/hydrogen technology makes extensive use of the metals, particularly aluminum, which is also adaptable to fluorine service. In LOX/hydrogen systems polymeric materials are often employed to provide the required sealing. Although polymeric materials may be considered for fluorine secondary seals they can not, at present, be recommended as a primary seal, due to their potential shock sensitivity; since the method by which kinetic energy is converted into heat, and the degree of this conversion in an impact system is unknown. Paragraph II-2.3 should be referred to for information regarding the selection of polymeric materials. A general discussion will be found in paragraph II-5.0 on the impact sensitivity of these materials. Figure II-2.7b contains experimentally determined dynamic reactivity limits for various polymerics. The use of metals exclusively, including the sealing surface, presents the most desirable valve configuration. Figure II-3.1a lists a summary of the various valve selection criteria.

3.1.1 Poppet Valves

For those applications which require minimum leakage, poppet valves utilizing flat sealing surfaces, represent the most desirable configuration of any of the current airborne valve types. Minimum leakage is obtained by use of a flat

poppet and seat orientated perpendicular to the fluid flow path. This type construction allows the use of smooth flat sealing surfaces while retaining standard manufacturing methods. See paragraph II-4.0 for a detailed discussion of leakage phenomena. For fluorine service the poppet should be of "hard" metal; such as, a minimum Brinell hardness of 250 while the seat may be either a soft or hard metal. If a hard seat metal; such as, greater than 250 Brinell hardness is chosen, the apparent seat and/or poppet stress, should be maintained at a level below eighty percent of the appropriate material compressive yield strength, see Table II-3.2b, which will eliminate plastic deformation of the sealing surfaces. If a soft seat metal is chosen, such as, with less than 250 Brinell hardness, the apparent seat stress should be greater than the material compressive yield strength while maintaining the poppet stress at a level below eighty percent of its material compressive yield strength. This permits plastic deformation of the soft seat while the harder poppet remains elastic this results in lower leakage across the seal, refer to paragraph II-4.0, as compared to a hard seat. It should be recognized that the life cycle capability is reduced accordingly. It should be noted that the soft metals work harden to some extent under repeated plastic deformation and, therefore, their strength properties will change slightly as a function of the number of closing cycles. Since the functional life requirement of an airborne valve would probably not exceed one-hundred cycles, valves with soft seats are recommended for fluorine service. It should be noted that for a high response valve, high material stresses can occur due to the dynamics of closing members. The static load magnification factor for sudden loading can theoretically reach two, depending upon the dynamic parameters of the closing members. This effect could result in excessive plastic deformation of the seal materials with an attendant increase in leakage rate. Further, depending upon the elastic properties of the impacting materials and the magnitude of the constant closing force, "chattering" of the poppet on the seat can occur. This impacting effect may be minimized by reducing the response rate, or providing a "snubbing" of the poppet just prior to its seating.

The poppet valve inherently has a short stroke and therefore, lends itself to the use of a bellows as a shaft seal. The welding of one end of the bellows to the poppet shaft and the other end to the housing, through which the shaft moves, provides the most positive shaft seal available. While bellows seals afford the maximum leakage control, they are by no means the perfect solution for all applications. Present design limitations place the maximum live (convoluted) length between one and one-half and two times the bellows diameter to prevent squirm failure. Since the bellows stroke is directly related to its live length, the stroke is also restricted by the allowable diameter. Another factor which tends to restrict the stroke is cycle-life. The plastic deformation which occurs in over-extended bellows reduces the cycle-life significantly. Therefore, the use of bellows seals require that the valve stroke be minimized.

Only single ply, convoluted bellows are recommended for this shaft seal application. Both multiple ply convoluted and welded bellows possess several desirable mechanical features but the difficulty in obtaining and assuring the required degree of cleanliness in the interply void or the interior weld area currently renders them unsuitable for fluorine service.

In those designs where the use of a bellows seal would be impractible and/or undesirable, a polytetrafluorethylene seal, which meets or exceeds the requirements outlined in Appendix III-1 is recommended. Since polytetrafluoroethylene possesses a much higher coefficient of thermal expansions than metals, any such shaft seal will "shrink down" on the shaft upon being subjected to cryogenic temperatures. However, the actual temperature of the shaft and seal during valve functional operation is difficult to predict accurately. Further, the valve should function properly at both cryogenic and ambient temperatures, therefore, it is recommended that a garter spring, or similar loading member, be used to maintain a positive load of the seal lip upon the shaft. This method of obtaining a positive seal load upon the poppet shaft of a vent-relief valve was successfully tested and reported in Reference 97.

The valve body may be made of most common metals so long as the specific material limitations discussed in paragraph II-2.0 are considered. A reluctance to the use of cast materials, due to porosity, has been indicated by some manufacturers, but this reluctance is not felt to be directly related to fluorine. This is discussed in paragraph II-3.6.3.1, as it pertains to boost pump housing, and applies equally well to valve bodies. A poppet type vent-relief valve whose body was made of cast aluminum A356 was successfully fabricated and tested in gaseous fluorine and reported in Reference 97. No adverse effects which might occur due to casting porosity were observed.

The configuration of the valve body should minimize cracks and/or cavities in which contaminants could collect and be entrapped. This insures a higher attainable degree of cleanliness which, as discussed previously, is a prime prerequisite for fluorine service. The recommended materials for the major components of a poppet valve are presented in Table II-3.1a.

3.1.2 Butterfly Valves

Butterfly valves have good flow characteristics due to a minimum of members protruding into the flow stream when the valve is in the open position. This is particularly true in line sizes of two inches and greater. The attainable internal leakage control with this type of valve is relatively poor compared to a poppet valve. This is due, primarily, to the difficulty in maintaining the concentricity of the blade and the seal and the material wear of the closing members resulting from their wiping action. The butterfly valves currently used in airborne applications use a fluoropolymer elastomeric lip seal with a hard metal blade. Since this seal material possesses much higher elastic properties, it will readily align itself around the sealing surface of the blade even through an interference fit and/or eccentricity existed between the undeformed seal and blade. Further, little or no wear of these materials result from such frictional wiping action. The only fluoropolymeric material considered to be compatible with fluorine is polytetrafluoroethylene per Appendix III-1, however, due to its energy sensitivity limitation, refer to paragraph II-2.7.2, its use as a blade seal in fluorine is not recommended unless a successful qualification testing program is performed.

3.1.1 Cont'd

A conceptual design study has been completed for a typical type valve for LF_2 service using the criteria discussed above. The basic design of this valve is shown on Figure II-3.1c and is discussed in detail in Reference 326. A 90° offset design is used with all metal construction of those parts exposed to fluorine. The valve is pressure balanced, incorporating a bellows shaft seal and a compliant poppet seat. Special considerations given to several key design zones are:

3.1.1.1 Housing Design - Zone 1

The static seal flanges constitute the most critical areas of the valve housing. Special attention will be required to provide adequate sealing of the housing interfaces which are exposed to fluorine.

The housing should be designed so that the total circumferential length of static seals exposed to fluorine will be as small as possible. Welded construction should be used at all interfaces which do not require disassembly during the life of the valve.

The material selected for the housing should be compatible with fluorine and should be hard enough to remain in the elastic range when the all-metal static seals are plastically deformed. The material should also be capable of accepting the smooth surface finish (16 μ AA maximum) needed for all metal static seals and should be free from pits and pin holes in the sealing areas. This requirement can be met by making the entire housing of material which has the required characteristics or by making a casting with integral inserts of acceptable material cast in place. This second method would normally be given consideration when a large number of valves are to be produced. All valve housing welds should have 100% penetration with no potential contaminant entrapment areas. The welds should be X-ray inspected (100%) with no defects permitted.

3.1.1.2 Static Seals - Zone 2

A large number of proprietary all metal seal designs are capable of providing the required sealing stress under the expected range of temperature conditions. The selected seal designs must exhibit a built-in spring rate which is capable of producing plastic deformation of the sealing surface of the seal while leaving the sealing surface of the housing in the elastic range. Various metal plating surfaces can be applied to the seals to provide this condition. Gold and copper plated seals are both satisfactory for this purpose. However, the gold plating is somewhat better than the copper due to the stability of the gold plating which is less sensitive to HF attack.

3.1.1.3 Main Closure Element - Zone 3

The selection of the type of main closure element will normally depend on the internal leakage requirements, the desired cycle life of the valve and the amount of pressure drop which can be tolerated. The pressure drop criteria is not unique to fluorine service, and therefore, conventional considerations can be applied. Material selection is based on the same criteria as for other fluorine valve components. The leakage and cycle life considerations, are, however, unique for LF_2 service. The design requirements for low leakage rates and high cycle life are contradictory and therefore, no real valve designs can be completed without detailed information on the desired end usage. In general, the lowest leakage rates are obtainable with sealing surfaces loaded at a level which will result in plastic deformation of the sealing surface. However, continued plastic deformation of the sealing surface will cause wear particles to break off of the surface and result in a limited cycle life for the unit. The rate of wear will vary as a function of the degree of plasticity of the seat material and the cycle life is decreased as sealing capability is improved. Various combinations of leakage rate - cycle life values are possible by selecting different material characteristics for any of the conventionally actuated valves.

One combination of characteristics which is desirable for fluorine service uses an elastically loaded sealing surface for high cycle life with optimization of the mechanical characteristics of the sealing surface to provide acceptable leakage control. This method requires close control of the flatness, smoothness and mechanical alignment of the sealing element. The flat poppet type closure element provides a design which lends itself to fluorine applications and is the one selected for this typical design, Figure II-3.1.c. Two types of surface finishes are possible for the lapped sealing surfaces. These are:

A. Circular Lay - Circumferential lap marks.
B. Multi-directional Lay - All lapping patterns which are not circular.

In general, lower leakage rates are obtained with the circular lay than with the multi-directional lay for the same surface smoothness and flatness. A detailed discussion of the sealing potential of surfaces with elastic loading having multi-directionally lapped surfaces is presented in Section II 4.0. The circular lay finishes produce greater leakage control and are discussed in Reference 326.

Having determined the required surface finish and flatness needed to meet a given leakage requirement the designer must consider mechanical alignment and seat width requirements. The mechanical alignment of a poppet valve closure can be provided in a number of different ways. The valve design shown has a machined bellows incorporated into the closure seat element so that the seat becomes self-aligning. An added feature of this configuration is that the spring rate of the machined bellows controls the sealing forces and prevents accidental overloads which could cause plastic deformation of the sealing surface. The design pressure range of the valve will dictate the bellows spring rate and selection of the sealing land width. The width should be wide enough to keep the apparent stresses in the sealing surfaces in the elastic range. Seal widths of less than .010 inches should be avoided so that the seat retains some tolerance to possible physical damage from particulate contamination. The value of .010 inches is sufficient to prevent damage across 50% of the seal width from particles of 75 micron size or less.

The materials selected for the poppet and seat should be selected for fluorine compatibility and required physical properties. Good design practice is maintained when two different materials are used for these two parts. The use of dissimilar materials reduces surface adhesion and therefore, minimizes potential cold welding problems between unlubricated valve closure elements.

3.1.1.4 Shaft and Bearing Configuration - Zone 4

Several conventional shaft and bearing configurations are suitable for use in liquid fluorine valves when attention is given to the problems of marginal lubrication of the bearing. One simple method of handling a valve with a reciprocating shaft is to locate the bearing in the non-fluorine part of the valve and provide self-lubricating bearings. This arrangement is used on the typical valve shown in Figure II-3.1.c. The main shaft guide bushing is located on the actuator side of the shaft seal bellows and incorporates a low friction fluorocarbon film on the contact surface of the bushing. The lubricating film used on this type of application should be as compatible with fluorine as possible to minimize potential chemical reaction of the lubricant and the fluorine which could occur with a failure of the shaft seal bellows.

Conventional bearings may be operated in fluorine providing that sliding frictional loads are kept very low or eliminated entirely with the use of anti-frictional bearings. Either configuration must be limited to compatible materials with no incompatible lubrication or lubricant seals being specified. The bushing used for rotating shafts should be limited to the self-aligning types so that high unit loads will not occur due to valve distortion or shaft flexing. Ball bearings may be used if the type of bearing selected can be cleaned properly for fluorine service and has the clearances necessary for cryogenic service. The valve designer should pay particular attention to the bearing clearance selection due to the necessary limitations on valve closure alignment discussed in Paragraph 3.1.1.3.

3.1.1.5 Shaft Seals - Zone 5

A very limited number of types of shaft seals are recommended for fluorine service. The reciprocating shaft designs can be sealed with a welded bellows. The single ply hydroformed bellows is preferred for this application. Seamless or welded seam type of construction is acceptable if suitable provisions are made for welding and fabrication processes which are compatible with fluorine service. The bellows designer should make allowances for the decrease in bellows cycle life for fluorine use which has been indicated in preliminary testing (Reference 97). This allowance may be made by designing the bellows for the desired cycle life at ambient conditions and not allowing for the increase in material properties at cryogenic temperatures. A check should be made to insure that the material strength increase at cryogenic temperature is equal to or greater than the equivalent decrease in performance due to the presence of fluorine. Materials which do not exhibit the proper strength increase should be avoided or the design changed to lower the fiber stresses to an acceptable level.

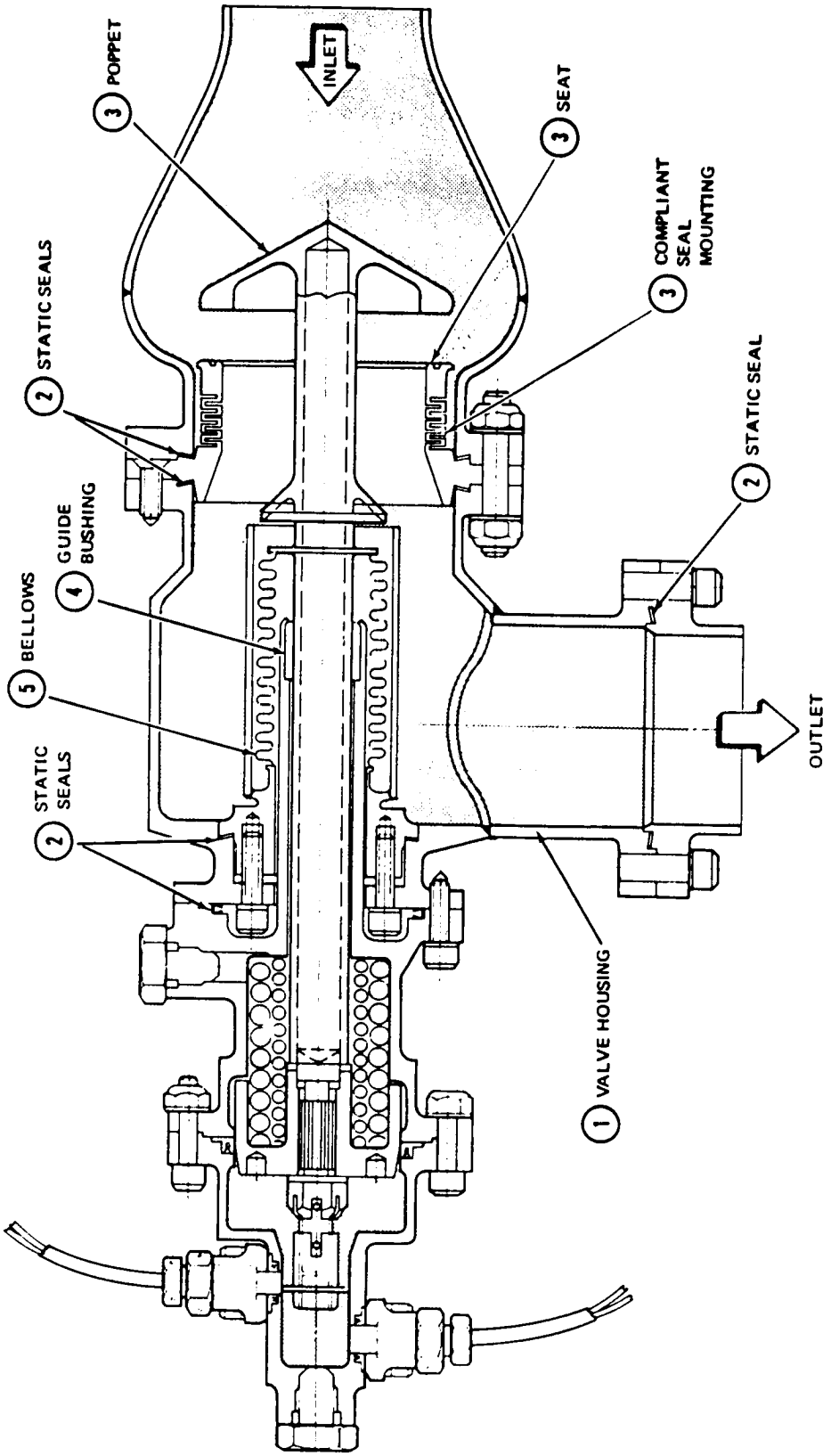


Figure 11-3.1C. Typical Valve Design

Currently, only a metal seal and metal blade is recommended for fluorine service. Due to the small blade and seal seat length (near line contact) and, therefore the high required seating load to obtain acceptable leakage rates, both the metal blade and metal seal are susceptible to high wear. In order to have proper compliance and longer life with the use of metal sealing surfaces it is essential that the seal be free to float; viz., have a bellows adaptor section such as shown in Figure II-3. 1b.

3. 1. 3 Check Valves

The primary function of a check valve is to prevent flow reversal. The successful performance of this function is particularly important in fluorine systems where upstream components or fluids must be isolated from fluorine exposure.

Check valves are entirely automatic in their operation, as their elements are activated by the flowing media. In spite of their simplicity, they are often one of the most troublesome components in a fluid system. Having no actuators, the seating force is often insufficient to accomplish a good seal. Most check valve designs are a compromise between good sealing and low pressure drop.

The sealing characteristics of a check valve are dependent upon the seal material, initial spring loading, type of closure, and the differential pressure across the closure element. When pressure reversal occurs, the check valve will leak until the back pressure becomes high enough to provide adequate seating force. The requirement for "zero" leakage at zero or very low reverse pressure necessitates the use of high initial spring load, with attendant increased pressure drop in the forward direction.

Several types of closures are available for check valves, the most common being; the ball, the poppet, and the swing configuration. Ball check valves create a relatively high pressure drop and have a tendency to chatter upon rapid closure. Rotation of the ball can create a leakage path if the ball surface is appreciably worn or grooved. Poppet type check valves may be

designed with either conical or spherical seating surfaces. The poppet element is typically a cylindrical cup which slides within another cylinder. The close tolerances and large sliding surface area make this arrangement undesirable for unlubricated fluorine service.

Most commercial all-metal check valves are suitable for either gaseous or liquid fluorine service; however, the poppet type is recommended. The preferred seat design being a flat sealing surface. Both the poppet and seal should be finished to a surface finish of five microinches rms or better and a perpendicularity of 0.0005 inch or less to assure "zero" leakage. The valve body should be machined or cast from a suitable grade of aluminum alloy (see paragraph II-2.6.1.1.4) for minimum weight. Static seals may be either 1100-0 aluminum alloy or Inconel-X if an elastic type seal is desired. The use of resilient material, polytetrafluoroethylene, may be considered for a seal provided the limitations noted in paragraph II-2.3 are observed.

3.2 Connections

3.2.1 Importance

The choices of line-to-line or line-to-component connections for any type of fluid system are numerous. Because of the large number of connecting joints required in any flight feed system, they present the greatest total fluid leakage potential. For this reason, they require careful and rigorous application of design techniques and considerations if the final system is to meet its mission requirements. Very minor modification of the connections currently used in cryogenic systems is required to adapt them to fluorine, viz., liquid oxygen and hydrogen.

Although connector leakage is a major concern in any type of system, it is of paramount importance in a fluorine system. Fluorine will react with atmospheric moisture to form an even more reactive compound hydrogen fluoride (HF). If a positive system pressure is maintained at a leaking connection, surrounding component materials will be subjected to these highly reactive fluids. Since almost all nonmetallic materials are incompatible

with fluorine and hydrogen fluoride, this type of leak could result in immediate failure of the surrounding electrical wiring due to the ignition of the insulating material. Subsequent failure of adjacent metal parts could result if sufficient heat were generated. Further, due to the high toxicity of this media, a safety hazard is generated, as discussed in Section IV. If a negative system pressure is maintained in an area where a leaking connection is located, the system itself is then subjected to contamination by intrusion of materials. The major portion of this contamination would be atmospheric moisture with a resulting increase of hydrogen fluoride. If the fluid temperature is below -117°F, the hydrogen fluoride will freeze and provide solid particle contaminants which could be detrimental to sealing surfaces, such as, valve seat sealing surfaces. If the fluid temperature is higher than -117°F, the hydrogen fluoride will be in a liquid, or gaseous state, resulting in higher corrosion rates of the containing materials.

3.2.2 Primary Considerations

Two general categories of connections are available; (1) separable, and (2) permanent. The separable connectors can be separated and reconnected numerous times and are typical of the threaded and bolted flange type. Permanent connections are made by welding, brazing, or swaging the mating ends of the components. The separable connection provides the component serviceability requirements of a feed system, but presents a more difficult sealing problem than does a permanent connection. Wherever possible, and practical, the use of permanent connections is highly recommended so as to provide a positive leak free seal. A connector seal may be designed to deform either elastically or plastically. When a connection is to be separable, the use of a soft gasket, which deforms plastically, usually results in the best seal. A connector which experiences severe temperature changes is an exception and will be discussed in paragraph II-3.2.3.

Experience (Reference 97) has demonstrated the effectiveness of soft aluminum, nickel or copper for soft seals, but other materials may be used. Often a flat, ring gasket between two flat surfaces is not sufficient to provide adequate sealing because of very high line pressure or inability to load the connection adequately. In these cases, knife-edged, saw-toothed or dimpled surfaces

may be considered to ensure local plastic deformation of the gasket. Refer to Reference 12 for examples of these designs. Table II-3.2b will aid the designer in selecting a suitable gasket material for a connector. It lists the yield strengths of seal materials.

Separable connection requirements are usually best met by using metal gaskets which deform elastically, or by eliminating the gasket and allowing the mating surfaces to seal directly. It is preferable to use the gasket, however, because it is more easily replaced in case of seal failure. By designing the contacting surfaces to stop leakage while remaining within their elastic limits, they may be separated many times without replacement or refinishing. The quality of the original finishes, subsequent surface damage and the strain-hardening of the seal materials determine the life of separable connections. The finest, flattest surfaces will provide the greatest repeatability because "zero" leakage is attained at lower stress levels, which reduces the adverse affects of strain-hardening. The harder materials, such as K-Monel and steel, should be used for these applications, but the gasket must be softer than the connectors to prevent damage to the connection. The importance of surface finish can be seen in Figures II-4.3u thru II-4.3z, which are discussed in paragraph II-4.3.4.1.

3.2.3 Thermal Cycling

When a connection is subjected to periodic temperature changes, which is likely in cryogenic systems, the mated parts will experience expansions and contractions. During the contractions, the connection will tend to open and the sealing forces will lessen. If the gasket had been deformed plastically, its surface asperities will not return to their original shapes and the leakage will increase. Such a condition requires continuous tightening of the connection to keep it from leaking, and is not tolerable in a flight vehicle. Even a flat elastic gasket is undesirable because the surfaces may become separated by a distance which exceeds the asperity heights. To avoid this, flexible elastic seals have been designed to allow continuous sealing during thermal cycling. Reference 12 discusses some flexible seal designs which have proven to be sound. They include chevron seals, bobbins, bellows and hollow O-ring designs. Of these, the bobbin seal, Reference 12, has shown the most promise

for overall sealing performance. Another possible seal design is that of the internal spring loaded polymeric O-ring seal, (Reference 97). This design is essentially a hollow O-ring formed by bending a helical spring into a circular hoop and covering it with polytetrafluoroethylene. It provides excellent elastic flexibility. Present designs utilize FEP type polytetrafluoroethylene which shows less tolerance to fluorine than TFE. It is recommended that only TFE polytetrafluorine, per Appendix III-1 be used in this design.

3.2.4 Selection

Component serviceability is necessary in any system. This requires a large number of separable joints in a flight system. Flared tube connectors are usually recommended in current aerospace practice, for line sizes of one inch and smaller, although the required preload to effect a seal, and connector material properties could preclude the use of some of the larger sizes. The most common threaded connector used in the aerospace industry is the flared tube type. This type of connector effects a seal between the internal flared surface of the tube and the tapered surface of the connecting union (or other similar connecting member). The AN, MS, and MC connectors have been successfully used in fluorine facility systems with lines sizes up to one inch in diameter. More leak tight connections have been effected when a crush gasket, such as, gaskets of soft aluminum, nickel, or copper were used between the sealing surfaces. Galvanic corrosion will occur when these materials are used with dissimilar connector and/or tubing materials. The rate of this corrosion is unpredictable due to the lack of electro-chemical potential data with fluorine as an electrolyte. Experience has indicated no connection degradation with the use of nickel and copper crush gaskets after six months of connector service in fluorine at pressures up to fifty psig, although some galvanic corrosion was observed. The lines and unions with which these gaskets were used were 316, 321, or 347 austenitic stainless steels. The use of gaskets of different material groups, Table II-3.2a, can be tolerated for short term missions without detrimental results. For longer missions material from the same group is recommended to eliminate electrolytic corrosion.

When the connection preload exceeds the physical properties of the threaded connector, a bolted flange or bobbin type connector must be used. The required preload may be attained by using bolt throughs or ring clamps around the external periphery of the mating flanges. Here again, the use of this type of connection with fluorine requires very little modification. The modification applies only to the gasketing material and not to the structural members of the connection. Crush gaskets of soft metals, such as, copper, aluminum, and nickel, have been successfully used in facility bolted connections (austenitic stainless steel flanges) with only minor galvanic corrosion being observed. Polytetrafluoroethylene, as a flat gasket or O-ring, may be used to effect a seal, if the material meets or exceeds the requirements outlined in Appendix III-1. This material has a high thermal expansion coefficient, therefore it is difficult to effect a good seal at cryogenic temperatures. The prerequisites for a seal are material compatibility (refer to paragraph II-2.0), and that the seal material be sufficiently soft to permit some plastic flow under the preload applied by the loading flanges.

3.2.5 Line Taps

Line taps are necessary for instrumentation purposes. These taps are usually installed by threading an AN, MS, or MC union into an appropriate line or component boss. Whenever possible, the fitting should be permanently welded in place, both internally and externally to provide a reliable, permaent seal. Welding both the internal and external contact surfaces of the fitting to the containing member eliminates cavities which could collect contamination. The fitting material should be of the same electromotive group as the component or line material into which it is assembled to reduce galvanic action, see Table II-3.2a. Where possible, the fitting and boss should be of the same material to facilitate welding. Whenever welding is not possible, the use of a polytetrafluoroethylene O-ring under the external sealing shoulder of the fitting is recommended. This polytetrafluoroethylene should meet or exceed the requirements outlined in Appendix III-1.

For a comprehensive discussion of basic connector design considerations refer to Reference 13.

3.2.6 Conclusions

The conclusions reached are as follows:

1. Welded, silver solder or brazed connections should be used wherever a permanent or semi-permanent connection can be tolerated.
2. Bobbin seals are highly recommended for fluorine service where a separable connection is required.
3. Flared tube connectors of the AN, MS, or MC type may be used for connections up to one inch in diameter.
4. Crush gaskets of nickel or copper should be used with all flared connections.
5. Galvanic corrosion between crush gaskets and flared tubing components can be tolerated.
6. Large connections, over one inch in diameter, should be of the bolted flange type to make use of deformed sealing surfaces.
7. Instrumentation taps should be welded in place and be of the same electromotive group preferably.

3.3 Tankage

The propellant tankage configurations of any stage is selected based upon the required stage performance for the specific vehicle mission requirement being considered and the dimensional constraints which may be imposed upon the stage or vehicle. This preliminary selection is influenced by specific design considerations such as design simplicity, stage inert weight, and many other factors. Typical propellant tankage types are shown in Figure II-3.3a. The use of liquid fluorine as an oxidizer requires only minor modification of any of these specific design considerations.

Two basic tankage configurations are shown in Figure II-3.3a, (1) separate fuel and oxidizer tanks, and (2) single tank, with a common bulkhead separating the fuel from the oxidizer. Either type of tankage configuration is acceptable for fluorine service so long as good design techniques are employed which include material compatibility, material corrosion allowances, and ease of cleaning the fabricated tank.

Most metals of construction are completely compatible with liquid fluorine, refer to paragraph II-2.0. Facility and test tanks which were fabricated from Monel, aluminum alloys, and austenitic stainless steels have been successfully used with liquid fluorine for long periods of time without failure attributed to material incompatibility. Within the normal tank pressure range of the feed system, the tank wall thickness is usually established by the handling and shipping loads rather than tank pressure and flight load requirements. For this reason the material corrosion allowances would not be a major design requirement, except for long term shortage with very thin membranes, since the corroded depth would be very minor, see Tables 2.6a and f through i.

A high level of cleanliness of any surface which contacts fluorine in service is a prerequisite for reliable functional life. Refer to paragraph II-2.6 for a detailed discussion of this subject. This requirement is not unique to fluorine although the degree of cleanliness is greater due to the high reactivity of fluorine with the most common contaminants and its ability to support combustion. In order to provide a clean system it is necessary that the internal contour of the tank should be as smooth as possible and contain a minimum of cracks and cavities in which contaminants could collect. Butt or double fillet (for overlapping joints) welding in an inert atmosphere, such as, Heli-Arc, TIG, or MIG, is the only recommended method of joining tank sections and/or segments. Full penetration of the butt weld and a full fillet of any overlapping joint is essential. The puddled material, of the weld, should be ground smooth to eliminate collection cavities and cracks.

The requirement for slosh baffles is determined using current cryogenic design procedures. No major modification will be required because of their contact with fluorine, provided metal baffles, selected from Table II-2.0b, are used. Here also, the elimination of contamination-collection cavities and cracks is a prime requirement. It is further recommended that the baffle be made of the same material, or of the same electromotive group (Table II-3.2a), as the tank, to reduce galvanic corrosion to an acceptable level.

3.3.1 Conclusions

The conclusions reached are as follows:

1. Common bulkhead or separate oxidizer and fuel tankage designs are adaptable to fluorine stages.
2. Austenitic stainless steel, Monel, and aluminum alloys have been used successfully for long term storage of fluorine containing hydrogen fluoride below the solubility limit, such as, 0.3 percent.

3.4 Insulation

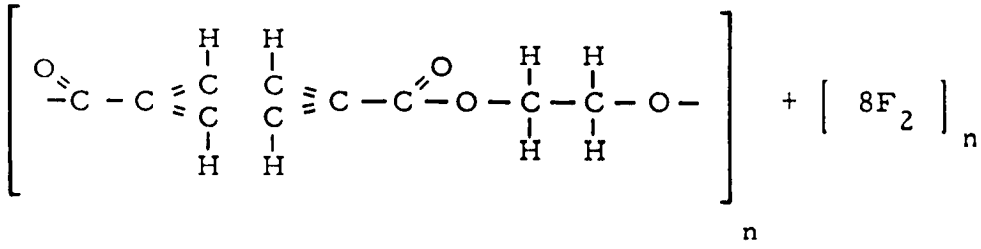
The design techniques currently employed to determine the need, type, and amount of insulation for other cryogenic feed systems applies directly to a liquid fluorine system. Like all cryogens, long term storage of liquid fluorine requires high performance thermal insulation. The time-limit applied to "long term storage" is dependent upon the heat flux into the cryogen, the area through which the flux is conducted to the cryogen, the volumetric quantity and heat of vaporization of the cryogen, and many other factors too numerous to mention. A specific time limit requirement, applicable to "long term storage", will probably vary over wide limits. However, the determination of the need for thermal insulation of oxidizer tanks, lines, and components is irrelevant in the following discussion as well as in the detailed design of a specific system, therefore, it will not be discussed further. The designer is referred to standard aerospace practice to establish the basic design parameters.

The primary concern in the use of any insulating material on fluorine system components, is that of material compatibility. This is due to the high reactivity of fluorine with most organic materials and with vacuum deposited metal platings. Although the insulation would be external to the fluid system, exposure to fluorine is possible should a system leak occur or should fluid be spilled.

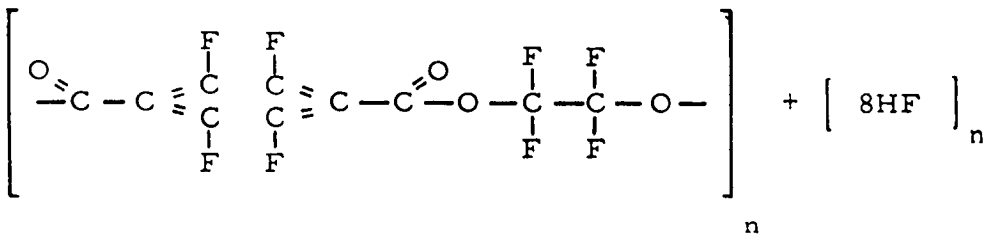
Radiation is the primary means by which heat is transferred to any body operating in space. "High performance insulation," (HPI), is the most efficient insulation under radiation heat fluxes and, therefore, offers the highest performance potential for space use. High performance insulation systems are composed of parallel reflective sheets separated by insulating materials and/or gas voids, viz, vacuum. The thermal performance of this type of insulation is greatly degraded if conduction occurs between the various radiation shields, by direct contact of adjacent shields or the presence of conducting media between the sheets. To obtain the performance of which HPI is capable, the pressure in the gas voids between the sheets, must be maintained at or below 10^{-4} torr. A comprehensive discussion of HPI and some specific analytical design considerations are presented in Reference 280, as well as in many other state-of-the-art publication and therefore, are not discussed further in this volume.

A series of tests were performed to determine the compatibility of some HPI materials in fluorine as described in Reference 149. The first test exposed a specimen of Mylar with a vacuum deposited layer of aluminum (approximately 100 angstroms in thickness) on each side to gaseous fluorine (0.22 volume-percent hydrogen fluoride, maximum) maintained at five psig pressure and ambient temperature. At the end of one and a half hours there was no observed reaction. At this time the fluorine was removed and the specimen vacuum sealed in its container. Immediate, visual inspection disclosed only a slight tarnishing of the aluminum. Visual inspection of the sealed specimen, approximately sixteen hours after sealing, showed that the aluminum coatings had completely disappeared. Electron diffraction analysis of the Mylar substrate revealed the presence of hydrated aluminum fluoride and fluorination of the Mylar surface. The hydration of the fluoride film is assumed to have occurred from atmospheric moisture, after the specimen was removed from the sealed container and prior to its analysis. The initial tarnishing observed, is assumed to be from the formation of surface aluminum fluoride. The disappearance of the aluminum was the result of complete reaction of the coating with fluorine to form transparent anhydrous aluminum fluoride. Analysis of the substrate Mylar indicated fluorination of the polymer surface.

In the reaction which caused this, it is assumed that the hydrogen atoms were replaced by fluorine with the free hydrogen reacting with the fluorine to form hydrogen fluoride. This hydrogen fluoride remained at the Mylar-aluminum bond surface, in microvoids between the materials, even after the fluorine was evacuated. The hydrogen fluoride continued to attack the aluminum until only anhydrous aluminum fluoride, which is transparent, existed on the surface of the Mylar. The surface reaction of the Mylar with the fluorine is assumed to have occurred as follows:



$$+ \left[8F_2 \right]_n$$



$$+ \left[8HF \right]_n + \text{ENERGY}$$

Some oxygen difluoride (OF_2) could also have been formed; however its reactivity is much less than that of hydrogen fluoride and has been ignored in the above discussion.

The aluminum fluoride film thickness formed after two hours of exposure to 80°F gaseous fluorine was approximately five angstroms with a thickness change of less than one angstrom between the exposure times of sixty to one hundred twenty minutes. See Figure II-2.6d. Since hydrogen fluoride will

attack aluminum at a much higher rate than fluorine, it is reasonable to believe that the major portion of the aluminum reacted with this hydrogen fluoride.

Another test exposed a specimen of aluminized Mylar, as described above, to "scrubbed" liquid fluorine containing a maximum of 0.02 percent hydrogen fluoride by volume, at -320°F and ambient pressure for approximately thirty minutes with no observed reaction. The result of this test was the same as the gaseous test discussed above, such as, slight tarnish of the aluminum coatings immediately after test and apparent disappearance of the aluminum after remaining approximately sixteen hours in a vacuum sealed container. The same conclusions made for the gaseous fluorine test above apply equally to this liquid fluorine test.

In order to simulate a leak, a jet of "scrubbed" gaseous fluorine was impinged upon a specimen of aluminized Mylar. There was apparently no reaction from a 1/16 inside diameter glass tube, 1/4 inch from the specimen, and only a slight etching of the aluminum coating was observed.

After the above testing showed that aluminized Mylar high performance insulation would not ignite when exposed to one hundred percent gaseous or liquid fluorine, additional static tests were performed in order to determine the degradation of emissive properties from exposure to low concentrations of gaseous fluorine. During a vehicle ground hold, a dry inert gas plenum purge is required wherever HPI is used. This plenum is defined as the space between the component being insulated and its covering shroud, for example, space between a spherical tank and its aerodynamic or structural shroud. A portion of the plenum void will be occupied by the HPI. The purge gas is circulated through the plenum so as to eliminate, or reduce to an absolute minimum, any air that would be present and which would therefore be liquified by exposure to the cold liquid propellant tank. The condensation temperatures of the major constituents of air are: oxygen 139°R, nitrogen 136°R. It should be noted that the normal boiling temperature of these gases at one atmosphere pressure is 162°R and 139°R respectively.

Additional tests were performed on specimens of NRC-2 and Dimplar (both smooth and dimpled, 0.25 mil thick Mylar aluminized on one side only). These were statically exposed to mixtures of gaseous fluorine and nitrogen of varying fluorine content, such as, 0.1, 0.5, 1.0, 2.0 and 5.0 percent by weight. One specimen of each of the above mentioned materials was exposed to each of the above fluorine concentration mixtures for one hour at ambient temperature and atmospheric pressure. No visible effects were observed upon the specimen during this time. Post test emissivity measurements indicated little or no change in the optical properties of the aluminum coating. Further exposure tests to mixtures of gaseous fluorine and nitrogen were performed with the fluorine concentrations being increased to 10, 20, 40, and 80 percent by weight. The materials tested were again NRC-2 and Dimpler (both smooth and dimpled), but with the Mylar thickness increased to 0.5 mil in lieu of 0.25 mil. Two specimens of each material were exposed to each of the above fluorine concentration mixtures for one hour at ambient temperature and atmospheric pressure. The specimens were visually inspected for gross effects upon the aluminum coating and emissivity measurements were made. The results of these tests, along with the measured emissivity values for unexposed specimens and the 5.0 percent fluorine concentration specimens are presented in Table II-3.4a. The normal emittance values presented were obtained by a reflectance technique using the Gier-Dunkle Heated Cavity Reflectometer. Reference 149 presents a complete discussion of this technique. It should be noted that the emissivity values were determined from measurements of specific points on the various specimens and that the actual values could vary over the measured surface. The indicated values are considered to be representative of what could be expected in practice and therefore may be used for design evaluation. These emittance values, however, should be accepted as qualitative rather than quantitative.

The above described tests were performed only upon the reflective component of an HPI system. Although this component receives the major consideration in the evaluation of such a system, many other components are required to make such a system perform as required. These other components include reflective film separating material, film layer adhesive material, and fastener

components. A gross compatibility test was performed upon each of nine such materials. The tests were performed by pouring five to ten milliliters of "scrubbed" liquid fluorine, a fluorine which had been passed through a sodium fluoride filter to reduce the hydrogen fluoride level, over the specimen which was contained in a 250 milliliter beaker. Initially the specimen temperature was approximately 70°F and they had not been cleaned prior to the exposure to fluorine. This testing procedure subjected each specimen to a high concentration of gaseous fluorine while contact with liquid fluorine may or may not have been made; i.e., the lighter materials bounced around in the beaker due to the rapid evolution of gaseous fluorine. The materials tested and the observed results are presented in Table II-3.4b. Additionally, Figures II-3.4a through II-3.4f show the pre-test and post-test specimens. It is interesting to note the test results of two of the materials tested. The Dexiglas paper and the fiberglass spacer are fibrous and tend to absorb moisture, yet the specimens tested which were desiccated exhibited a higher reactivity than the similar ones tested in the "as received" condition. No explanation has been postulated for these occurences.

3.4.1 Conclusions

The conclusions reached are as follows:

1. Aluminized polyethylene terephthalate (Mylar), a typical high performance insulation, HPI, reflective film, will not ignite when exposed to "scrubbed" liquid or gaseous fluorine. However, the use of Mylar as the carrier for the reflective aluminum coating is questionable due to its reaction with fluorine to form hydrogen fluoride and the subsequent complete fluorination of the aluminum coating.
2. Insufficient information is available to define an HPI system which would be compatible with a fluorine feed system. The foremost prerequisite in the design of any system is the application of specific performance criteria, and their integration into the overall vehicle criteria. To date, no such information is available.
3. In lieu of more design information aluminized Mylar may be used to insulate the fluorine system provided its exposure to fluorine is prevented. If the exposure cannot be prevented, it must be recognized that limited exposure can be tolerated with some degradation in performance.

4. Before specific insulation selections can be made it will be necessary to: (1) establish all of the necessary performance parameters which will define the insulation and (2) perform a test and evaluation program on candidate insulation to define their performance and compatibility in the operating environment.

3.5 Instrumentation

The instrumentation devices which are commonly associated with a feed system, and subsequently exposed, either partially or wholly, to the fluid media, are pressure and temperature sensors, flowmeters, and level sensing devices. The primary considerations of any of these devices for application in a fluorine system are material compatibility and cleanliness.

3.5.1 Pressure Sensors

Various types of pressure sensors are available as shelf hardware. All isolate the sensed medium from the sensing mechanism of the transducer, by means of a diaphram or similar membrane. This diaphram should be welded to the transducer housing, either by a electron-beam or heli-arc method, so as to prevent leakage of the fluorine into the sensing mechanism cavity. The selection of material for those components which will contact fluorine should be made based on the information presented in paragraph II-2.0 and Table II-2.0b.

Cleanliness of the transducer is of paramount importance to the successful operation of the transducer and to maintain integrity of the system within which it operates. Because of the thinness of diaphragm material, entrapment of contaminants and/or moisture on the sensing side of the diaphram could result in accelerated corrosion and ultimate failure of the transducer. Adherence to the cleaning procedure presented in Appendix III-4, "Fluorine Service Cleaning Procedure," should assure the necessary level of cleanliness.

The type of transducers used to measure differential pressure, as well as some absolute pressure transducers, which are commercially available, have the cavity in which the sensing mechanism is located filled with oil. This oil (normally silicon or hydrocarbon base) provides dynamic dampening for the pressure sensitive diaphragm, so as to reduce transient pulsing of the signals from the transducer. To date, refer to Table II-2.7a and paragraph II-2.7.1.1, no known oils are completely compatible with fluorine. Therefore, a diaphragm seal failure, with fluorine contacting this damping fluid, would result in a violent reaction followed by a catastrophic failure of the system. Reference 141 recommends that this damping fluid be a fluoropolymer oil. The rate of

reaction of this type of oil with fluorine is much less than either silicon or hydrocarbon oils, which react violently with fluorine regardless of the fluorine concentration. The primary products of reaction of the fluoropolymers are carbon tetrafluoride and chlorine. This reaction results in heat being released which will result in a pressure increase in the sensing cavity, and if not of sufficient magnitude to cause a failure, will provide erroneous pressure readings.

The use of any oil filled transducers, which will contact a cryogen is not desirable, since at cryogenic temperatures, all known oils freeze. In an application where this condition would exist, the oil should be omitted and the transducer calibrated as a "dry" unit. This procedure is currently being used, on the Saturn S-IVB program, for differential pressure transducers located within the propellant tanks. These transducers operate over a temperature range of +100°F to -423°F with a reported accuracy of two and a half to three percent.

3.5.2 Temperature Sensors

3.5.2.1 Thermocouples

The primary considerations for sensor selection for fluorine service are material compatibility and cleanliness. Completely shrouded thermocouples and thermistors are compatible with fluorine up to the shroud material limitations, as discussed in paragraph II-2.0.

If bare-wire sensors are used for greater response characteristics, sealing of the two lead wires at the point of exit from the fluid container becomes a major problem. The difficulty of sealing is due to the small size of wire around which the seal must be effected. Fired ceramic material should be used as the insulation media, between the wires and the metal containing tube. If the use of this type of sensor is a system prerequisite, the seals should be in accordance with the material recommendations of paragraph II-2.7.1.2. In addition, due to the small mass of the wires, the heat released upon reaction of the metal surface with fluorine could result in

accelerated corrosion of the wire, and ultimate failure, even during the passivation process of such components. Here again, the rate of corrosion is dependent upon the amount of heat released, and the thermodynamic properties of the fluorine and the material. To date, no known analytical method analysis is available by which the thermodynamic state of such a reaction system can be predicted; therefore, from the standpoint of system reliability, the use of bare-wire temperature sensors for fluorine airborne feed system is discouraged.

3.5.3 Level Sensing Devices

There are several methods currently used to determine the fluid level of cryogenic liquids within the airborne propellant tanks throughout the life of the system, such as, capacitance probe, differential pressure tranducers, magnetic switches, flowmeters, and sonic devices.

3.5.3.1 Capacitance Probe

The capacitance probe is a continuous level sensing device which has been used in both liquid hydrogen and oxygen systems. The probe is made up of two concentric tubes rigidly held and spaced apart by nonelectrical conducting materials, thus forming a capacitor. The capacitance varies as the total dielectric strength of the fluid (gas or liquid) between the tubes and therefore is proportional to the liquid level within the tank. This type of liquid level sensing device is usable with fluorine so long as compatible materials, paragraph II-2.0, are used and the component has been cleaned for fluorine service, Appendix III-4.

3.5.3.2 Differential Pressure

Differential pressure transducers determine the liquid level in the tank by measuring the pressure head of the liquid and are continuous-level sensing devices. By connecting one side of the transducer so as to sense pressure at the bottom of the tank and the other side sense pressure in the ullage volume of the tank, the transducer will measure the liquid head. This device is

recommended for use in a fluorine system if compliance to paragraph II-3.5.1, (Pressure Sensors), is maintained.

3.5.3.3 Magnetic

Magnetic switch systems have been used with several fluids other than fluorine and are increment-level sensing devices. This system is made up of several magnetic switches placed at various levels within a sealed tube around which a float containing a permanent magnet travels up and down the tube, as the liquid level changes. No problems are anticipated in the application of this device to a fluorine system so long as compatible materials and fluorine clean end product are used and, therefore, is recommended for fluorine service.

3.5.3.4 Sonic Devices

Two types of sonic level sensors are available. One a continuous sensor and the other a point sensor.

The continuous sensor measures the transit time for a pulse emitted from a piezioelectric crystal to travel to the gas-liquid interface and return. The liquid level is correlated to transit time.

The point sensor measures the difference between the sonic impedance between a covered and uncovered transducer. Both of these sensors have been developed for oxygen and hydrogen. However, the transducer is not compatible with fluorine without modification. The modification consists of isolating the crystal by use of a metal diaphragm. Prototype units have been produced and proved satisfactory.

3.5.4 Flowmeters

Flowmeters can be used to evaluate the liquid level within the tank if the initial volume and vaporization and vent rates are known, by monitoring the amount of liquid leaving the tank. The accuracy of this system is poor because of unpredictable variations in the vaporization and vent rates and lack of the precise initial liquid volume. Of the various types of flowmeters available, three general types have been used in fluorine system to monitor system flow: (1) rotating vane, (2) differential pressure and, (3) rotometers. The rotating

vane (turbine) type flowmeter has been used successfully in several test facilities, for long periods of time, with little or no degradation of performance. Some modification of component materials may be necessary to insure fluorine compatibility. NASA Lewis Research Center, prefers the use of ball bearings in this type of flowmeter, Reference 91, although flowmeters with journal bearings made of chromium carbide (manufactured by Potter Aeronautical Corp.) have been successfully used by Thompson Ramo Woolridge, Inc., and others.

3.5.4.1 Differential Pressure

Two types of differential pressure flowmeters have been successfully used in fluorine systems such as, sharp edge orifice and venturi. Sharp edge orifices made of Monel have been used for long periods of time with little or no performance degradation (Reference 91). Venturis have also been used successfully for long periods of time, (Reference 91). The attractiveness of these devices is the lack of moving parts although their accuracy may be lower than other types. Their use is recommended provided the material constraints of paragraph II-2.0 are observed.

3.5.4.2 Rotometers

Rotometers have been used to monitor low flow rates, such as, leakage across a closed valve seat, but normally require extensive modification for use with fluorine. These devices are not recommended for use with an airborne fluorine feed system.

3.5.5 Feed Throughs

Various electrical feed throughs are required in instrumentation systems. Elastomeric material may be considered as a sealing media provided the limitations of paragraph II-2.3 are observed. The most desirable feed throughs, and those recommended, are those used in vacuum technology, namely, fired aluminum oxide.

3.5.6 Conclusions

The conclusions reached are as follows:

1. Present state-of-the-art instrumentation can be used satisfactorily provided reasonable, discrete rules are observed and judicious selection of specific designs is made.
2. The use of transducers which contain damping fluids is discouraged; however, if used, only fluoropolymer oil damping fluids should be used.
3. Bare wire thermocouples may be used, but their use is discouraged due to possible leakage between the ceramic insulation and the thermocouple wires.
4. Electrical feed throughs should incorporate a combination insulator and mechanical seal of fired aluminum oxide.
5. Commercially available rotating vane, differential pressure, or rotometer flowmeters may be considered for fluorine service. A thorough evaluation of the instruments' materials should be made to ensure compatibility, and all noncompatible materials replaced with compatible ones.
6. Although many level sensing devices may be used with fluorine, in general, the most accurate is the sonic type. Prototype units are presently available which have demonstrated compatibility and their use is recommended.

3.6 Boost Pumps

3.6.1 Application

The function of any propellant supply system is to provide propellant to the engine inlet at a pressure sufficient to prevent pump cavitation. The relative merits of boost-pump and gas-pressurization systems must be assessed for each particular application. This is necessary since the results are highly dependent upon such factors as: total propellant load, number of restarts, length of mission, engine inlet requirements, etc. The boost-pump system will generally appear most competitive for missions requiring many restarts, long coast periods, and stringent engine inlet conditions. If a boost pump is selected for the pressurization system, any external gas pressurization will be precluded because of the excessive weight involved. Therefore, the boost pump must have the capability of operating with a saturated propellant at its inlet (near zero NPSH) and still provide a head rise equal to the required engine-pump NPSH plus friction and acceleration losses. For a comprehensive discussion of boost pumps, refer to References 97 and 299.

3.6.2 Design Options

Several options are available to the designer regarding hydrodynamic design, location, and type of drive. Most boost pumps require an axial-flow (inducer) element which is designed to handle the entering fluid, at or near saturated conditions, without excessive cavitation. Where extremely high flow-rates or pressure rises are required, a secondary impeller element of the mixed-flow or radial-flow type may be required.

Two locations for the boost-pump unit are available; (1) in the tank sump, and (2) in the engine feed line. A variety of pump drives and energy sources are possible regardless of which location is chosen. The pump may be driven by an electric motor (ac or dc) which obtains its power from a turbine-driven generator or it may be driven directly by the turbine. The turbine may derive its power from combustion of the main propellants or auxiliary discharge of the main engine pump. In the following paragraphs, design criteria for fluorine boost-pump systems is presented. A fluorine boost pump failure mode and effect analysis is presented in Table II-3.6a.

3.6.3 Mechanical Design

The design of a liquid fluorine pump requires only limited modification of those considerations used in the design of a pump for other cryogens, for example, liquid oxygen. This modification, in general, would apply in the areas of material compatibility, dynamic sealing, and submerged bearing design. The compatibility of the common materials used in the current design of pumps are discussed in paragraph II-2.0.

3.6.3.1 Housing

Some engine manufacturers have indicated reluctance to use pump housings made of cast aluminum. The primary concern was, in fact, high porosity of the casting which could result in "fluid weeping" at high operational pressures. Casting porosity control is a manufacturing problem and is not unique to aluminum. The tests of cast aluminum alloy A356 (Reference 97) reveal that this material is completely compatible with liquid fluorine. However, if the fluid and material temperatures are greater than -140°F, the "silicon leaching" of the alloy can be expected. Refer to paragraph II-2.0 for a complete discussion of this phenomena. The feed system and maximum operating temperature limit, for most vehicles, is usually specified as approximately +150°F. Therefore, this silicon "leaching out" characteristic of A356 and any subsequent decrease in physical strength properties must be considered in the use of this alloy for a pump housing. The limitations and properties of wrought materials which may be recommended for fluorine service are presented in paragraph II-2.0.

3.6.3.2 Impeller and Shaft

No unique design considerations are required in the design of a pump impeller and shaft if the material limitations discussed in paragraph II-3.0 are adherred to. Special attention may be required in the method used to join the impeller blades to the shaft. This is necessitated in order to assure the formation of a minimum of fluorine reactables at the joint surface which could adversely effect the physical strength of the joint.

3.6.3.3 Bearings

In pump design, it is generally desirable to cool the anti-friction bearings with the fluid being pumped. Liquid fluorine provides an excellent source of heat dissipation, however, the reliable operation of fluorine submerged bearings is still unproven. In normal rolling-contact applications, the only tolerable cause of bearing failure is stress-cycle fatigue. In high-speed operation, however, non-rolling actions become significant and bearing life will be governed by abrasive wear and heating, in the ball contact path, as well as fatigue resistance. The use of non-conventional coolants such as fluorine can be expected to accelerate the detrimental effects of these non-rolling effects. Materials used for the races, balls, and cages of fluorine-cooled bearings must not only be fluorine-compatible, but must also exhibit good bearing-load capacity, and wear and abrasion resistance.

Submerged rolling element bearings have been used in liquid fluorine flowmeters, and References 165 and 236 document tests in which the feasibility of operating rolling-element bearings in liquid fluorine was demonstrated under simulated rocket engine pump conditions. However, these were in flowmeter applications which involved very low loads, and the work consisted of only a limited number of tests under one condition of load and speed. Additional data are required to establish preferred materials, construction techniques, and operating limits.

Two MRC 205-S, 440C stainless steel, bearings and one MRC 305-S Stellite bearing have been tested to determine the feasibility of fluorine cooled bearing operation (Reference 165). The 440C bearings employed a two-piece Monel outer guide ball retainer and the Stellite bearing had a Hastalloy C inner guide ball retainer. Both of the 440C bearings demonstrated the PERT duration at rated loads of one hundred thirty-six pounds radial and fifty pounds axial load. The Stellite bearing failed after an accumulated 2,430 seconds with the same loadings. During tests run by the manufacturer, however, one 440C bearing failed after only eight seconds at 200 pounds radial and 100 pounds axial loading. Another 440C test bearing ran for one and one-half hours at 14,000 rpm and up to two hundred pounds axial load

with all parts remaining in excellent condition at the end of the test. These tests indicate that 440C bearings can withstand the pump dynamic requirements. This stainless steel is compatible with dry liquid fluorine, but will suffer some corrosion attack if hydrogen fluoride is present. Should 440C prove inadequate, titanium carbide races may be considered after a suitable development and evaluation program. Kentanium 162B (TiC) is compatible with fluorine, but is less shock resistant and its higher elastic modulus results in a decreased fatigue life. The material selected for the cage must exhibit low friction in sliding contact with the ball and race material and must be of sufficient strength to permit design for maximum coolant flow through the bearing. Candidate cage materials are Monel and K-162B. The K-162B would probably have to be backed up with a supporting structure, possibly Hastelloy C. It is evident that extensive testing is required in this area before any conclusions can be drawn. If sufficient reliability cannot be demonstrated, it will be necessary to isolate the bearing from fluorine exposure.

3.6.3.4 Dynamic Seals

Effecting a reliable dynamic shaft seal is one of the major problems in designing and producing a liquid fluorine pump. However, it must be recognized that no rotating shaft seal can provide positive sealing, thus some leakage must be expected and therefore tolerated. In all pump applications, the minimum practical leakage becomes the accepted limit; however, due to the high reactivity of fluorine, near zero leakage becomes an absolute requirement.

For the primary liquid fluorine dynamic shaft seal, the requirement for low leakage under static (nonrotating) conditions, imposed by the submerged pump installation, introduces a consideration not normal to conventional rocket engine pumps that have been tested in liquid fluorine. There are two aspects of the problem that require investigation: (1) the behavior during long-term submergence of accepted fluorine dynamic seal materials, many of which rely upon formation of fluoride films for low friction and wear characteristics, and (2) seal loading requirements to achieve low leakage under both rotating and non-rotating conditions.

The first item, seal material behavior, is peculiar to liquid fluorine. Most of the more promising combinations for liquid fluorine seals contain one material that reacts with fluorine at a controlled rate to generate a fluoride film. The film provides a degree of lubrication to the sliding surfaces which may or may not be adequate. In normal rotating service, there is evidence that the film is continually worn off and regenerated. If the materials are to provide a surface capable of good sealing, when exposed statically (no rotation), the film must reach an even equilibrium thickness and the flatness must be maintained. Paragraph II-4.0 presents a detailed discussion of the phenomena and quantitative values involved in effecting an adequate seal.

Use of a dynamic seal arrangement consisting of four elements or individual seals, as shown in Figure II-3.6a is recommended for externally driven boost pumps. This configuration is dictated by the requirement that there be no leakage between the fluorine pump cavity and drive end of the shaft which will probably be exposed to a coolant or lubricant not compatible with fluorine.

The four seal package consists of two primary seals, one on each end, and a pair of secondary seals, back-to-back, in the middle. One primary seal is exposed to fluorine while the other is exposed to the drive coolant. Three cavities are formed by this arrangement; one behind each primary seal and one between the two secondary seals. A vent port is provided for each cavity. For ground test, a low pressure inert gas may be supplied at the central vent (between the secondary seals) to insure separation. Under space conditions all vents could be discharged to vacuum and the propellants would not mix under any single seal failure condition.

Bellows-loaded face seals are recommended for all primary seals. The seal nosepiece must be loaded in a fashion that will permit it to follow axial and lateral shaft movements without breaking the seal. Face seals are prone to torsional vibration or "skipping" if the rotational restraint is inadequate. Multipoint rotational restraint, accomplished with a splined retainer, should be provided.

Circumferential split-ring seals are recommended for the secondary seal locations to reduce the installed length of the package and to facilitate assembly. The rings are loaded both radially and axially to accomplish sealing between the housing and the central rotating disk. Suitable material combinations for seal rubbing elements, both primary and secondary, are shown in Table II-3.6b. It is expected that any of the combinations listed are suitable for anticipated operating conditions; however, investigation of the sealing characteristics under static conditions may reveal a superior combination. Materials recommended for bellows fabrication are presented in paragraph II-3.8.1.

The problem of seal-loading requirements is not unique to fluorine service but rather is a consideration of the submerged application, in which static sealing is of equal importance with dynamic (or rotating) sealing. Unfortunately, there is a paucity of data on the leakage characteristic of dynamic seals under static conditions. It is not anticipated that this will present insurmountable problems, but will probably require developmental work to find an acceptable optimum.

3.6.4 Drive Systems

Several combinations of prime-movers and energy sources are available to drive the pump. Regardless of the combination selected, design parameters which must be considered for any drive system are as follows:

A. Minimum weight consistent with acceptable performance characteristics
B. Simplicity of design and operation for high reliability
C. Use of vehicle propellants
D. Compatibility with space and vehicle environment.

The two most common types of drive systems used are turbine and electric. If a turbine drive is used, its mounting must be external to the propellant tank (although the pump may be submerged) due to the hot propellant gases required to drive the turbine. If the propellant gases used to drive the turbine are derived from the combustion of a propellant system in which fluorine is the oxidizer, a large portion of the gas will be hydrogen

fluoride (HF). This would require the judicious selection of compatible materials as discussed in paragraph II-2.0. If a nonfluorine propellant gas system is used to drive the turbine, no unique design considerations are required unless fluorine is used as a coolant or bearing lubricant. In this event, the same considerations as discussed above for pumps would apply to the drive mechanism.

An electric drive system may be used which is submerged within or mounted external to the propellant tank. If the electric drive system is externally mounted, there are no unique design requirements necessary for use with a fluorine system. Based on current technology, submerged mounting of an electric drive system is not feasible. Presently, there are no known winding insulations which are compatible with fluorine. Further, testing or submerged electric motors in liquid oxygen, a must less reactive oxidizer, is currently only in the feasibility stage and when electrical malfunctions have occurred, in experimental tests, failures are usually catastropic.

3.7 Quick Disconnect Couplings

The design requirements applicable to a fluorine service quick disconnect coupling differ from current cryogenic designs only in consideration of the high toxicity and reactivity of fluorine. For this reason, it is essential that fluorine service couplings be designed for minimum leakage and minimum fluid spillage during disengagement.

A shut-off valve which is automatically closed on disconnection may be built into the coupling in either one or both halves of the coupling. The incorporation of such a valve helps to prevent fluid spillage and leakage when the coupling is separated and it also reduces entry of external contamination. However, the establishment of the need for incorporation of such valves will be dictated by the particular type of vehicle and the program design philosophy. At present, the consensus is that the majority of vehicles to be developed will not require the incorporation of a shut-off feature within the disconnects.

The primary consideration, in the design of a quick disconnect, is the selection of compatible material as discussed in paragraph II-2.0. Although the material selection of most coupling components can be made on the basis of limited contamination from external sources, the effects of high concentrations of hydrogen fluoride must be considered on the internal coupling surfaces which will be exposed to the atmosphere upon disengagement. Upon separation of the coupling, the ground half in particular will be exposed to atmospheric moisture for relatively long periods of time. Except under unusual circumstances there will exist some leakage of fluorine through the separated coupling. This leakage will then be free to react with the atmospheric moisture forming hydrogen fluoride which in turn exposes portions of the coupling to this highly corrosive environment. Further, those metal surfaces which normally contact fluorine will have formed the appropriate fluoride surface film. Subsequent exposure to moisture will hydrolyze this film. These hydrolyzed films are very brittle and upon being subjected to vibration, shock, or other loads can be "flaked off" their respective parent surfaces. Functional utilization of the coupling after formation of the hydrolyzed film can result in transporting this water filled compound into the airborne oxidizer system. Subsequent exposure to fluorine results in the formation of addtional hydrogen fluoride. If this hydrogen fluoride formation is maintained in a localized area, high local corrosion can occur if it is in a gaseous state, or if maintained in a solid state (below -117°F) can result in solid particle contamination of the oxidizer. For these reasons, it is recommended that a continuous inert gas purge be maintained through the separated ground half of the coupling.

The transfer of most cryogens through an uninsulated system results in the formation of frost or liquid air (which freezes at approximately 144°R) on the external portion of the system components. It would be virtually impossible to insulate a quick-disconnect coupling. External shrouds with a continuous inert gas purge through the annulus formed by the external surface of the coupling and the internal surface of the shroud have been used for other cryogens to prevent frost formation. Although ice shows no apparent reactivity with gaseous fluorine, it will react violently when exposed to liquid fluorine. Leakage across the connected coupling seal

would probably be in a gaseous state when contacting the frost; however, upon separation of the coupling halves, spillage of the residual fluid in the line will occur. Contact of the liquid spillage with this frost would result in damage or failure of the contacted component. It is therefore recommended that an external shroud with a continuous inert gas purge be used on all liquid fluorine service couplings. The use with gaseous service couplings should be encouraged even though it is not an essential feature.

As mentioned above, upon separation of the coupling, some liquid fluorine spillage of the residual line fluid will probably occur. This spillage would probably occur through the ground half of the coupling if it did not incorporate a valve or other design feature to prevent or reduce spillage. The umbilical tower line will be a flexible line supported intermittently, and upon separation of the coupling, the ground half and the adjacent section of unsupported line would normally swing back, down, and away from the vehicle. If residual liquid fluorine existed in the umbilical line at the time of separation, some portion of this fluid could be spilled on the vehicle skin. This spillage is highly undesirable because of probable frost buildup on the vehicle outer skin, and the resultant reaction hazard; the reactive effects upon and possible failure of tne control wiring and destruct systems located in external raceways; and the resulting health hazard in the launch pad area. Although the incorporation of a valve would prevent this it is recommended instead, that judicious routing of the line be used to prevent spillage.

The seal between the coupling halves is of major concern and warrants a meticulous design evaluation due to the health hazard resulting from leakage and the reactive environment to which the local components would be subjected. A comprehensive design discussion is presented in paragraph III-4.0 which should be utilized in any such seal design.

Consideration must be made of the wear qualities of those dynamic components of the coupling. No material should be used for those dynamic components which would produce metal chips, etc., which could be dropped or in some manner transported into the fluorine system. A comprehensive discussion of galling and wear characteristics is presented in paragraph II-6.0 which should be consulted to prevent this.

Utilization of current design techniques for cryogenic service supplemented with the above considerations will result in an adequate quick-disconnect coupling for fluorine service. To date, two prototype fluorine service quick-disconnect couplings have been successfully designed, built, and tested. The first of these incorporated a valve into each coupling half and was capable of remote connection and separation. This coupling was approximately 3/4 inch in diameter (equivalent flow area) and is described in Reference 117. The second coupling did not possess internal valves, nor was it capable of remote connection. This is a two inch diameter coupling and is described in Reference 300. Either of these two coupling designs are recommended for fluorine service. It must be recognized, however, that other designs may be considered provided they meet the requirements discussed above.

3.8 Flexible Joints

Flexible joints allow ducting systems to absorb thermal expansion and contraction, installation misalignment, structural deflection, and vibration. A system should be designed so that its flexible joints will be subjected to only one of three types of movement, namely, axial, lateral or angular. Combined motions and/or torsional motion should be avoided to prevent overstressing.

Bellows joints are the most common form of flexible joint and are recommended for fluorine service. Physical restraining devices will be necessary, for some designs, to control and limit the movement of these devices. The recommended designs and fabrication techniques, for bellows, are included in paragraph II-3.8.1. Table II-3.8a contains a summary of the properties of various flexible joints. Specific design selection, for fluorine service, is no different from conventional cryogenic systems. With the exception of the internal link joint all others types are recommended for fluorine service. The internal link joint is not recommended because of an inherent cleaning and potential bearing problems.

3.8.1 Bellows

Metal bellows are common subcomponents used in flexible lines, bellows sealed valves, rotary seals, and other components. The flexure to which they are subjected eventually results in fatigue failure, consequently bellows must be carefully designed to ensure adequate life. At present, bellows are designed empirically, however, an Air Force program USAF Contract No. 04(611)-10532, is presently developing analytical techniques for bellows and diaphram design. Although certain constraints are desirable with fluorine, present empirical state-of-the-art bellows designs are applicable to fluorine systems.

The following design and fabrication constraints must be considered for bellows in fluorine service:

1. Fluorine compatible materials must be used as discussed in paragraph II-2.0.
2. Single-ply walls should be used because there is danger of contamination between laminated sheets, and because adequate cleaning would be difficult.
3. Convoluted hydroformed, spun or rolled bellows are preferred for fluorine service.
4. Welded bellows are not recommended for fluorine service due to the possibility of contamination and the difficulty of cleaning the welded areas.
5. Conventional installation couplings should be used to connect bellows into the system. These couplings should be attached to the bellows stem by inert welding methods as discussed in paragraph III-2.3.
6. The use of internal bellows liners is not recommended due to the difficulty of cleaning and inspecting the enclosed volume. Exposure of the convolutes to flowing fluorine will not cause any problems which are different from those of other cryogens.

A limited number of low cycle fatigue tests were made on sectioned convoluted bellows specimens of AL 6061-T6, Amco 21-6-9 stainless steel, and Inconel 625 (Reference 97). General results were: (1) endurance limits were between 10^4 and 10^5 cycles for both cryogenic and ambient temperatures when cycled to the yield stress of the material, (2) strength was

greater at cryogenic temperatures, (3) failure was caused by fine cracks on the smaller radius convolutes, (4) initial failure was at the edges of the coupons, and (5) welded coupons failed sooner than nonwelded.

These tests indicated a tendency toward some material degradation in fluorine when compared with similar tests in nitrogen. Presently, it is not known whether this degradation trend is the result of intergranular corrosion, surface corrosion, or the flaking of the fluoride film.

Safety factors should be applied to bellows to ensure proper operation and long life. Present knowledge indicates that these factors should be 1.5 for gaseous fluorine and 1.3 for liquid fluorine. The lower factor for liquid is due to the increased material strength at cryogenic temperatures. These factors are considered to be conservative and may be decreased as more empirical experience and good analytical techniques are gained.

Table II-3.1a

FLUORINE VALVE MATERIALS (see also Table II-2.0b)

Table II-3.1a

Valve Type	Closure Element	Seat	Primary Shaft Seal	Secondary Shaft Seal	Gaskets	Body	Shaft	Bearings
Poppet	Stainless Steel (300 series) Monel	Monel Nickel Copper Copper alloys	1. Bellows Armco 21-6-9 Inconel 347 Monel 2. Packing TFE*	None	Plastic Soft Aluminum Soft Copper Tin Elastic Metals TFE*	Monel 304L SS Bronze Brass Aluminum (Low Si for casting)	Same as Poppet	Composite (CaF_2-BaF_2-Ni) Sprayed Ceramic (Al_2O_3, TiC) Bronze
Ball	Monel Aluminum (hard faced) Stainless steel (hard chrome plated)	Cermet Gold plated SS Soft Copper	1. Bellows Inconel SS 2. Bellows Face Seal Cermet/Ceramic	1. None 2. TFE* "O" Ring (spring assist)	Plastic Soft Aluminum Soft Copper Tin Elastic Metals TFE*	Monel 304L SS Bronze Brass Aluminum (Low Si for casting)	Monel SS (300 series)	SS Ball Bearings
Butterfly	Monel Aluminum Copper Alloys	Monel Stainless steels	1. Bellows Face Seal Cermet/Ceramic 2. Bellows	1. TFE* "O" Ring (spring assist) 2. None	Plastic Soft Aluminum Soft Copper Tin Elastic Metals TFE*	Monel 304L SS Bronze Brass Aluminum (Low Si for casting)	Monel SS (300 series)	Composite (CaF_2-BaF_2-Ni) Sprayed Ceramic (Al_2O_3, TiC)
Gate	Stainless Steel (hard chrome plated)	Copper Brass	1. Bellows Inconel SS	None	Plastic Soft Aluminum Soft Copper Tin Elastic Metals TFE*	Monel 304L SS Bronze Brass Aluminum (Low Si for casting)		
Blade (not recommended)	Monel SS (300 series)	Silver Plated SS	1. Bellows Face Seal Cermets/Ceramic	1. TFE* "O" Ring	Plastic Soft Aluminum Soft Copper Tin Elastic Metals TFE*	Monel 304L SS Bronze Brass Aluminum (Low Si for casting)		
Check (simple)	Stainless Steel (300 series) Monel	Copper Alloys Gold plated SS Teflon* TFE			Plastic Soft Aluminum Soft Copper Tin Elastic Metals TFE*	Monel 304L SS Bronze Brass Aluminum (Low Si for casting)		

*Refer to paragraph II-2.3 for limitations in use of polytetrafluoroethylene.

3.9 Filters

The feasibility of using filters in fluorine feed systems was demonstrated during a full scale filter compatibility testing program (Ref. 326). Special consideration must be given to the type of elements used in fluorine filters if satisfactory performance is to be obtained. Two critical areas in filter element design relate to the reactivity of the element material and to the feasibility of cleaning the element to a level suitable for this service. The types of construction used on filter elements in the 10-100 micron size range all incorporate the basic element materials in some form of thin sections. These thin sections result in the element materials having a high surface area compared to the volume of material. A high surface to volume ratio condition is favorable to ignition reactions and is fundamentally undesirable for exposure to fluorine. The effects of the high surface to volume ratio of the exposed material can be minimized by selecting element materials which have high ignition temperature thresholds and which exhibit high thermal conductivity properties. The ignition temperature of various materials in fluorine was presented on Table II-2-6C. Since nickel has the highest listed ignition temperature in fluorine it is recommended for use in filter elements for fluorine service. This selection was verified by testing high purity nickel elements in uncontaminated fluorine and in fluorine containing controlled amounts of contamination. Both sintered nickel particle elements and woven nickel wire type elements (sintered) were tested (Ref. 326).

The sintering process should be used on the nickel wire element for two reasons. The sintering process provides a cleaner material due to the high temperature removal of organic material in the sintering process, and it also provides a screen which is mechanically stronger due to the bonding of the individual strands of wire. This bonding minimizes movement between individual wires and reduces the possibility of exposure of potential contaminant entrapment areas when the element is subjected to pressure loading during the flow process. Since high purity nickel is a soft, ductile material, the increase in strength due to bonding of the wires is desirable.

The characteristics of sintered alumina oxide Al_2O_3 makes this material an alternate candidate for fluorine filter service. This material is sintered at temperatures exceeding 3000°F and, since all reactable materials are affected by the sintering process, the resulting filter element is resistant to further reactions with fluorine or hydrogen fluoride (HF) and a highly inert element is obtained. Consideration must be given to the mechanical strength of porous Al_2O_3 if this material is to be selected for use in filter element service. High purity Al_2O_3 containing the minimum amount of binder consistent with the mechanical strength requirements should be selected. Al_2O_3 with 2% (1.3% SiO_2, .7% MgO) binder was tested and found to be compatible with LF_2. However, the mechanical strength at this binder level was marginal (Ref. 326).

The cleaning requirements for the metal filter elements will vary with the material selection and are presented in Appendix III-4. The nickel metal filter elements are treated the same as Inconel and other high nickel alloys. Particular attention should be given to the cleanliness of the cleaning solutions. The flow passages of typical filter elements are so small that significant restriction of the element can result from contaminated cleaning fluids.

To minimize the problem of filter blockage it is recommended that the normal rinse (which is made after the alkaline cleaning process) include a reverse flush of the element using demineralized water. The suggested cleaning procedure is to follow the normal cleaning procedure (4.1.2) with additional steps:

1. Ultrasonic clean
2. Dry in oven
3. Rinse with filtered Freon (5μ filter)
4. Oven dry for 12 hours at 240° to 260°F

After completion of the complete cleaning process the filter should be packaged per 4.3.1 before leaving the clean room.

Table II-3.2a

MATERIAL GROUPINGS FOR INSTRUMENTATION TAPS*

Magnesium, Magnesium Alloys
Zinc, Galvanized Iron
Aluminum, Alclad, Cadmium
Mild Steel, Wrought Iron, Cast Iron
Lead, Tin
Muntz Metal, Maganese Bronze, Naval Brass
Copper, Copper Alloys, Nickel, Inconel, Monel, 300 Series Stainless Steel
Silver, Gold, Platium

* Inclusion in this table does not imply recommendation for fluorine service. Material recommendations should be obtained from the appropriate paragraph of Section II.

Table II-3.2b

YIELD STRENGTH OF SEAL MATERIALS

Material	High 1000 psi	Low
Martensitic Stainless Steels	275	25
Titanium and Its Alloys	220	40
Nickel--Base Superalloys	154	52
Beryllium--Copper, Hard	150	130
Cr-Ni-Fe Superalloys	142	58
Austenitic Stainless Steels	140	30
Molybdenum, CW	130	120
Nickel and Its Alloys	120	12
Cobalt--Base Superalloys	113	67
Nickel--Silvers, Hard	90	74
Brasses	90	10
Bronzes	88	10
Ferritic Stainless Steels	80	35
Aluminum and Its Alloys	78	4
Columbium, CW	75	65
Coppers	75	10
Cupro--Nickels, Hard	73	-
Beryllium, Ann	55	45
Gilding, 95%, Hard	50	-
Magnesium Alloys	44	8
Silver, CW	44	-
Cobalt (cast)	43	20
Gold, CW	30	-
Nickel Silvers, Ann.	30	18
Platinum, CW	27	-
Cupro--Nickels, Ann.	22	15
Muntz Metal, Ann.	21	-
Gilding, 95%, Ann.	10	-
Silver, Ann.	8	-
Tin and Its Alloys	6	1.3
Platinum, Ann.	5.5	-
Lead and Its Alloys	1.6	0.8

Table II-3.4a (page 1 of 2)
EMISSIVITIES OF REFLECTIVE MATERIALS AFTER EXPOSURE TO GASEOUS FLUORINE--NITROGEN MIXTURES

GF_2 Concentrations in GN_2	Total Normal Emittance	Comments
0%		
NRC-2 Control	0.032	Base values before exposure.
Dimplar Smooth	0.042	
Dimplar Dimpled	-	
5%		
NRC-2	0.043	No visible damage.
Dimplar Smooth	0.042	No visible damage.
Dimplar Dimpled	-	No visible damage.
10%		
NRC-2	0.074; 0.051	Visible pin hole breaks in aluminum film.
Dimplar Smooth	0.050; 0.058	Visible pin hole breaks in aluminum film.
Dimplar Dimpled	- -	Visible pin hole breaks in aluminum film.
20%		
NRC-2	0.041; 0.086	White film visible on part of surface; pin holes.
Dimplar Smooth	0.073; 0.057	White film visible on part of surface; pin holes.
Dimplar Dimpled	- -	White film visible on part of surface; pin holes.
40%		
NRC-2	0.130; 0.041	Larger area coated with white film.
Dimplar Smooth	0.155; 0.052	Some areas void of aluminum.
Dimplar Dimpled	- -	Large area of aluminum deteriorated.

Table II-3.4a (page 2 of 2)

EMISSIVITIES OF REFLECTIVE MATERIALS AFTER EXPOSURE TO GASEOUS FLUORINE--NITROGEN MIXTURES

GF_2 Concentrations in GN_2	Total Normal Emittance	Comments
80%		
NRC-2	0.073; 0.134	Film coating on entire surface. Sheets stuck together.
Dimplar Smooth	0.0727; 0.148	Large areas void of aluminum. Many pin holes.
Dimplar Dimpled	- -	Extensive deterioration of aluminum film.

Table II-3.4b

FLUORINE EXPOSURE RESULTS OF HPI ASSEMBLY AND INSTALLATION COMPONENTS

Material	Observations	Figure Number
1. Velcro Fastener	Ignited	II-4.4f
2. Velcro fastener bonded to aluminum plate	Ignited	II-4.4f
3. Nylon thread	Ignited--violent reaction	II-4.4a
4. Dexiglas paper	No apparent reaction in two tests (same specimen)	II-4.4e
5. Dexiglas paper (desiccated)	Mild reaction with small puff of flame. Sintered to glassy particles.	II-4.4d
6. Scotch 850 tape, transparent	Ignited--violent reaction.	II-4.4d
7. Scotch 850 tape, silvered	Delayed ignition--mild reaction--specimen only partly consumed	II-4.4d
8. Teflon screw and sleeve	No reaction	II-4.4c
9. Silicone impregnated fiber glass spacer	Mild reaction which stopped as soon as fluorine evaporated	II-4.4b
10. Silicone impregnated fiber glass spacer (desiccated)	Mild reaction which stopped as soon as fluorine evaporated	II-4.4b
11. Plexiglas 11	No reaction in two tests (same specimen)	
12. Phenolic impregnated fiber glass	No reaction in two tests (same specimen)	

Table II-3.6a

FLUORINE BOOST PUMP DRIVE TURBINE FAILURE MODE AND EFFECT ANALYSIS

Failure Type	Failure Effect on Subsystem	Failure Effect on Main Engine	Failure Effect on Vehicle	Mission Abort
1. Housing rupture (any housing)	Loss of function	Propellant not supplied to engine at proper conditions. Probable pump cavitation.	Loss of capability	Probable
2. Bearing failure	Rotation at reduced speed is usually allowed with a failed bearing permitting continued operation at reduced output. Some bearing failures could cause rotation to stop.	Propellant not supplied to engine at proper conditions. Probable pump cavitation.	Loss of capability	Probable
3. Turbine structure failure	Partial to full loss of drive function.	Propellant not supplied to engine at proper conditions Possibility of pump cavitations.	Loss of capability	Probable
4. Gear failure	Loss of function	Propellant not supplied to engine at proper conditions. Probable pump cavitation.	Loss of capability	Certain
5. Housing static seal failure	Little or no loss of function	None	Possibility of explosion and damage if fluids accumulate in unvented area with air present.	Possible
6. Shaft face seal failure	Slight reduction of turbine power due to dilution of gas generator products with H_2 in turbine area.	Propellant not supplied to engine at proper conditions. Possibility of pump cavitation.	Possible loss of capability	Possible
7. Gas Generator fails to function	Complete loss of function	Propellant not supplied to engine at proper conditions Probable pump cavitation.	Loss of capability	Certain
8. Loss of H_2 coolant	Overheating of bearings and gears with eventual bearing and gear failures resulting in loss of function.	No effect until bearings and gears fail, then propellant will not be supplied at proper conditions, then probable pump cavitation.	Eventual loss of capability	Probable

Table II-3.6b

LIQUID FLUORINE PUMP DYNAMIC SEAL MATERIALS

Mating Ring (Rotating)	Nosepiece (Stationary)
Primary Seal	
Kentanium K-162B[1]	Beryllia-Solid
Kentanium K-162B	Kentanium K-162B
Alumina-Flameplate	Alumina/15% Nickel-Flameplate
Kentanium K-162B	Alumina-Flameplate
LW-1[2]	Alumina-Flameplate
Secondary Seal	
Mating Ring (Rotating)	Split Rings (Stationary)
Kentanium K-162B	Beryllia-Solid
LW-1	Meehanite
Kentanium K-162B	Alumina-Solid
Kentanium K-162B	Boron Nitride (Hot Pressed)
Alumina-Flameplate	Ilkoloy[3]

(1) Kennametal Corporation, Latrobe Pa., designation for titanium carbide-nickel cermet.

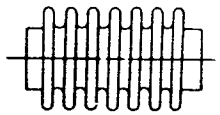
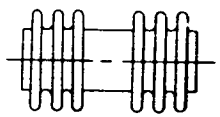
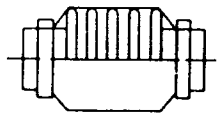
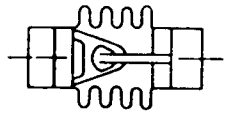
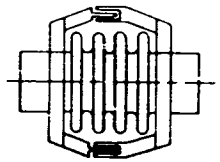
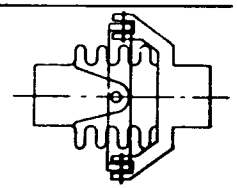
(2) Linde Company, Indianapolis, Indiana, designation for tungsten carbide with 7-10% cobalt flameplated coating.

(3) Ilikon Corporation, Natick, Massachusetts, designation for nickel with 20% dispersed calcium fluoride.

Table II-3.8a

FLEXIBLE JOINT SUMMARY

Table 3.8a
FLEXIBLE JOINT SUMMARY

FLEXIBLE ELEMENT TYPE	PLAIN BELLOWS	OFFSET JOINT	BRAIDED BELLOWS	INTERNAL LINK JOINT	HINGED JOINT	GIMBAL JOINT
CONFIGURATION						
CONSIDERATION						
WEIGHT	EXCELLENT	EXCELLENT	EXCELLENT	GOOD	POOR	POOR
ENVELOPE (EXTERNAL)	EXCELLENT	EXCELLENT	EXCELLENT	EXCELLENT	POOR	FAIR
SPRING RATE	LOW	LOW	HIGH	MEDIUM	LOW	LOW
PRESSURE DROP	LOW	LOW	LOW	HIGH	LOW	LOW
CLEANABILITY	GOOD	GOOD	GOOD	POOR	GOOD	GOOD
VIBRATION RESISTANT	POOR	POOR	FAIR	POOR	GOOD	GOOD
SPRING RATE	LOW	LOW	HIGH	MEDIUM	LOW	LOW
PREDICTABILITY OF END LOAD TRANSMISSION	POOR	POOR	POOR	GOOD	EXCELLENT	EXCELLENT
OPERATING PRESSURE RANGE (SQUIRM FAILURE) 1) HIGH 2) LOW	1) POOR 2) EXCELLENT	1) POOR 2) EXCELLENT	1) GOOD 2) GOOD	1) GOOD 2) GOOD	1) EXCELLENT 2) EXCELLENT	1) EXCELLENT 2) EXCELLENT
MOTION CAPABILITY	1) AXIAL TRAVEL 2) ANGULAR DEFLECTION ALL PLANES 3) LATERAL OFFSET	1) AXIAL TRAVEL 2) ANGULAR DEFLECTION ALL PLANES 3) LARGE LATERAL OFFSET	1) RADIAL OFFSET 2) ANGULATION ALL PLANES	1) ANGULATION ALL PLANES	1) ANGULATION ALL PLANES	1) ANGULATION SINGLE PLANE

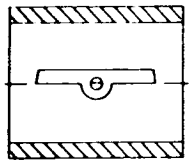
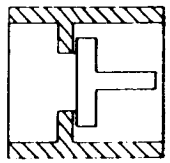
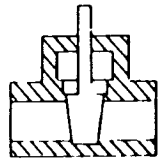
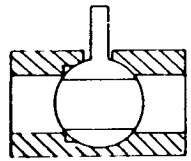
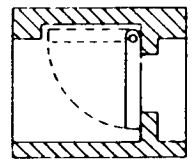
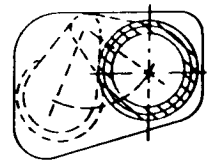
VALVE TYPE	BUTTERFLY	POPPET	GATE	BALL	SWING CHECK	BLADE
CONFIGURATION						
CONSIDERATION						
CLEANABILITY	GOOD	GOOD	POOR	GOOD	GOOD	POOR
PRESSURE DROP	MEDIUM	HIGH	LOW	LOW	LOW	LOW
FLOW PROTUBERANCE	POOR	POOR	GOOD	EXCELLENT	GOOD	EXCELLENT
LIFE CYCLE CAPABILITY	FAIR	EXCELLENT	GOOD	GOOD	EXCELLENT	GOOD
WEIGHT AND ENVELOPE	MINIMUM ENVELOPE EXCELLENT DIAM TO WEIGHT RATIO	LARGE EXTERNAL ENVELOPE IF POPPET IS TO RETRACT OUT OF FLOW PATH. WEIGHT - POOR. PILOT OPERATION REDUCES WEIGHT	LARGE EXTERNAL ENVELOPE FOR GATE TO OPEN. WEIGHT- POOR	MOUNTING FLANGE TO FLANGE (LENGTH) IS LARGE. WEIGHT – GOOD (USE VISOR TYPE IN LIEU OF FULL BALL FOR SIZES OVER 3 IN.)	GOOD EXTERNAL ENVELOPE. MOUNTING FLANGE TO FLANGE DIMENSION IS LARGE. WEIGHT - EXCELLENT	GOOD ENVELOPE MINIMUM MOUNTING DIMENSION WEIGHT - GOOD
SHAFT SEAL TYPE	ROTATING SEAL REQUIRED BELLOWS POSSIBLE ON LINEAR ACTUATOR	LINEAR MOTION WELDED BELLOWS CAN BE USED.	LINEAR MOTION BELLOWS CAN BE USED PROVIDING STROKE IS NOT TOO LONG	ROTATING SEAL REQUIRED BELLOWS POSSIBLE ON LINEAR ACTUATOR	NO EXTERNAL SEALS	ROTATING SEAL REQUIRED
RESPONSE TIME	GOOD SHORT ANGULAR TRAVEL MASS OF DISK MUST BE REDUCED	EXCELLENT SHORT LINEAR MOTION. MINIMUM MASS POPPET	POOR LONG LINEAR MOTION OR LARGE ANGULAR MOTION	GOOD SHORT ANGULAR TRAVEL LARGE BALL MASS. (INVESTIGATE VISOR TYPE FOR DIAM < 3 IN.)	FLUID ACTUATED ONLY RELIEF OR CHECK FUNCTION	FAIR LARGE ANGULAR TRAVEL
CLOSURE SEAL TYPE	LIP TYPE SEAL (METALIC) 1) SEAL IN GATE 2) SEAL IN BODY SEAL IN FLOW STREAM BOTH CASES.	COMPRESSION METAL TO METAL	WEDGE TYPE 1) SEAL IN GATE 2) SEAL IN HOUSING 1) SEAL IS REMOVED FROM FLOW PATH.	METALLIC OR CERAMIC RING TYPE SEAL (BELLOWS LOADED) OUT OF FLOW PATH	METAL TO METAL COMPRESSION SEAL	LIP TYPE SEAL IS REMOVED FROM FLOW PATH
LEAKAGE RATE	FAIR	EXCELLENT	FAIR	GOOD	FAIR	POOR
CLOSURE SEAL ACTION	WIPING & STRETCH POOR	COMPRESSION EXCELLENT	SLIDING-WEDGE POOR	WIPING GOOD	COMPRESSION GOOD	SLIDING FAIR

Figure II-3.1a. Fluorine Valve Design and Selection Criteria

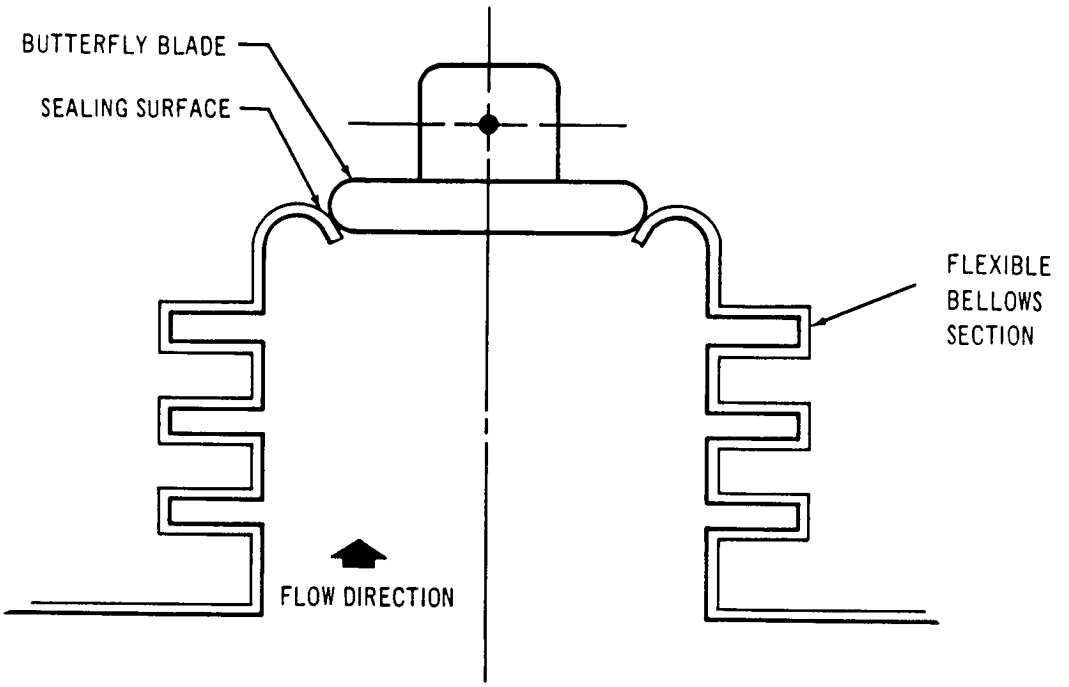


Figure II-3b. Butterfly Valve Floating Seal (Reference 97)

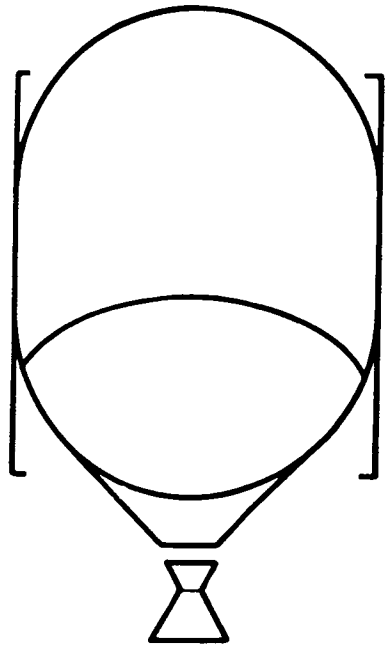
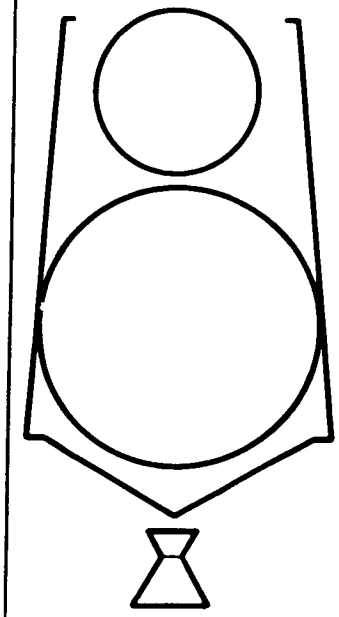
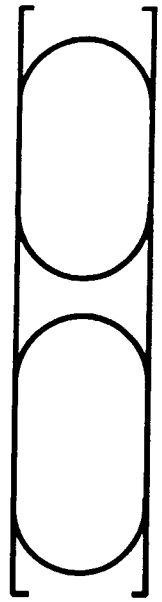
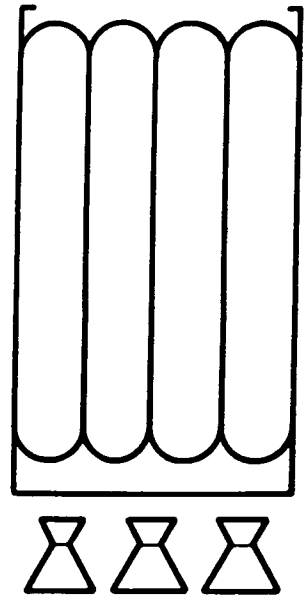
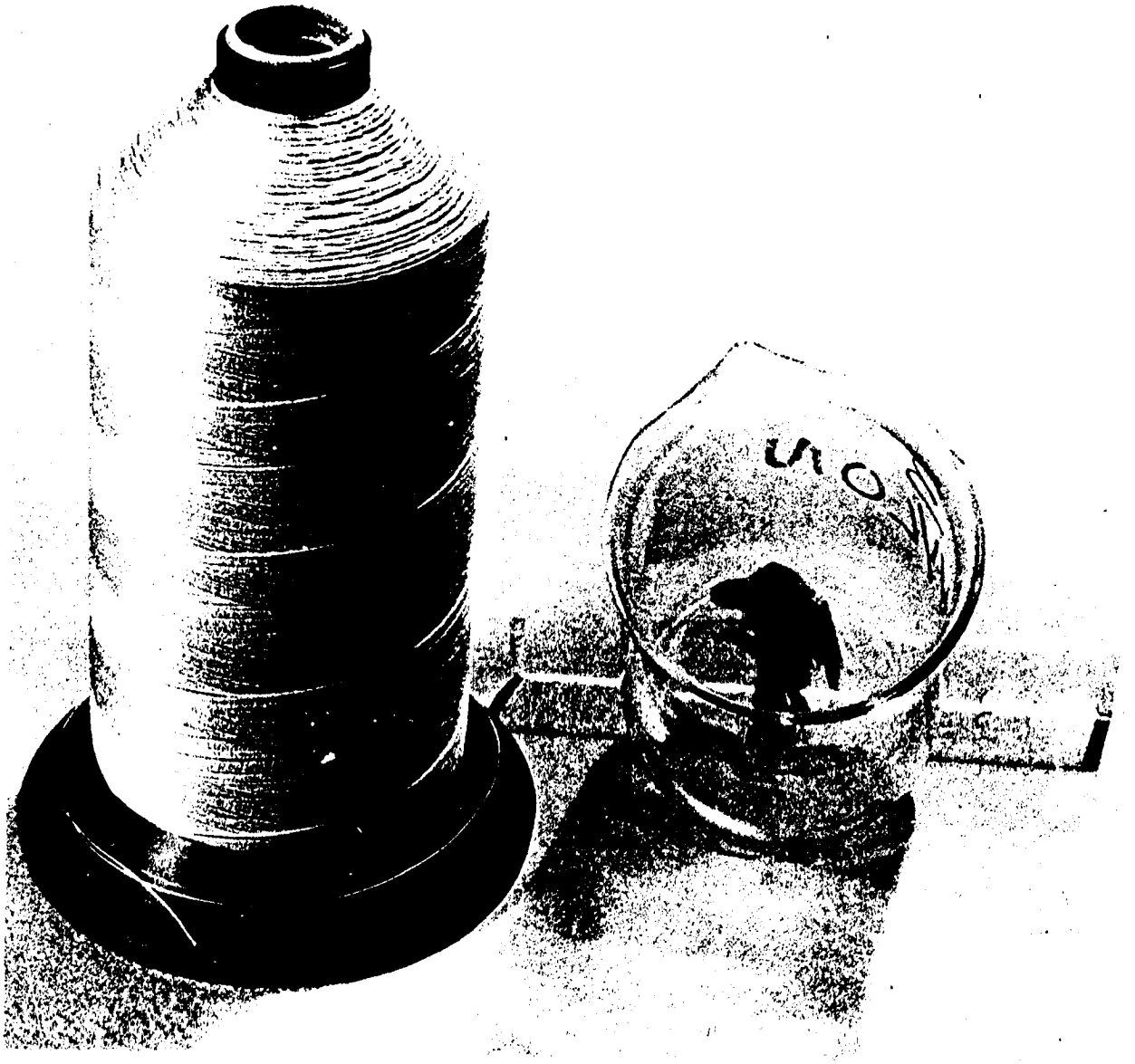
TYPE	CYLINDRICAL TANK COMMON BULKHEAD	INDEPENDENT TANKS SPHERICAL	INDEPENDENT TANKS CYLINDRICAL	CLUSTER
CONFIGURATION				
THERMAL STORABILITY (SURFACE AREA)	GOOD	EXCELLENT	GOOD	POOR
WEIGHT	GOOD	GOOD	FAIR	POOR
FABRICATION - COMPLEXITY	POOR	GOOD	EXCELLENT	EXCELLENT
FEED DUCT ROUTING	EXCELLENT	POOR	POOR	GOOD
CLEANABILITY (ENTRAPMENT AREAS)	GOOD	GOOD	GOOD	GOOD - FOR ENGINE CLUSTER POOR - FOR SINGLE ENGINE

Figure II-3.3a. Fluorine Feed System Tank Configurations Evaluation

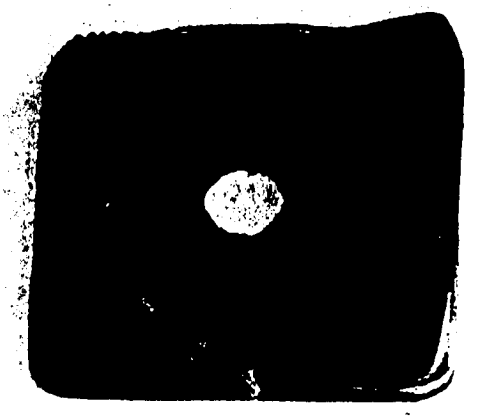


UNEXPOSED EXPOSED

NYLON THREAD

Figure II-3.4a. Nylon Thread--Specimen Exposed to Liquid Fluorine and Comparative Unexposed Specimen

UNEXPOSED FIBER GLASS
SPACER

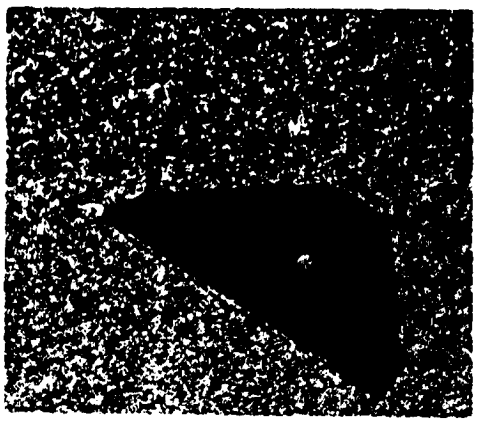


DESICCATED

UNDESICCATED

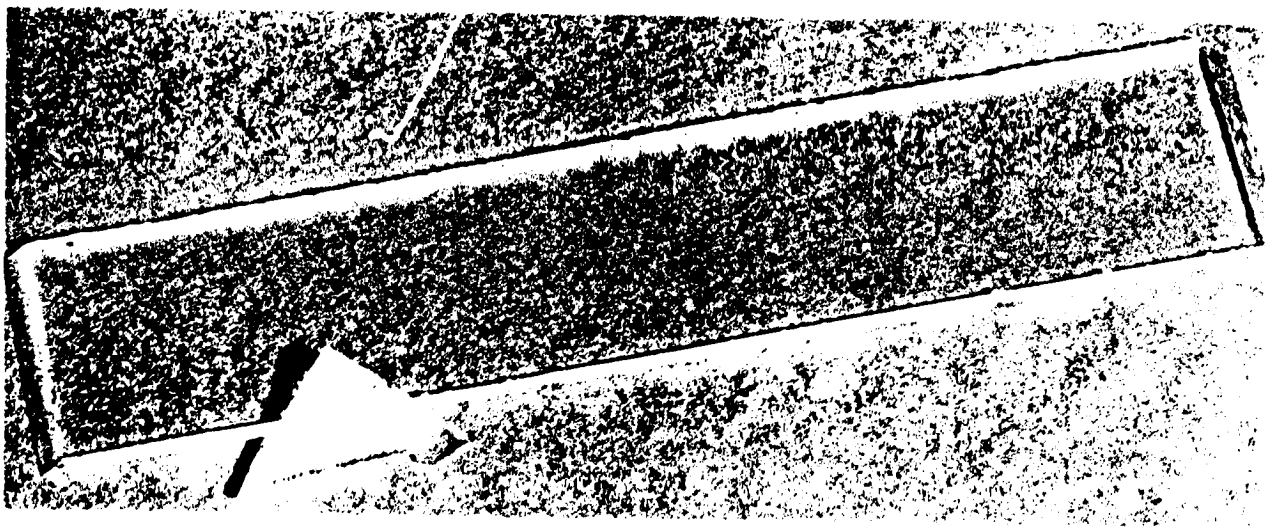
EXPOSED FIBER GLASS
SPACER

Figure II-3.4b. Fiber Glass Spacer – Specimen Exposed to Liquid Fluorine and Comparative Unexposed Specimen



PHENOLIC

TEFLON



EXPOSED LUCITE

UNEXPOSED LUCITE

Figure II-3.4c. Specimens of Phenolic, Teflon, and Lucite Exposed to Liquid Fluorine

SCOTCH 850 CLEAR

850 SILVER

EXPOSED TAPES

850 CLEAR

850 SILVER

UNEXPOSED TAPES

Figure II-3.4d. Scotch 850 Tape – Specimens Exposed to Liquid Fluorine and Comparative Unexposed Specimens

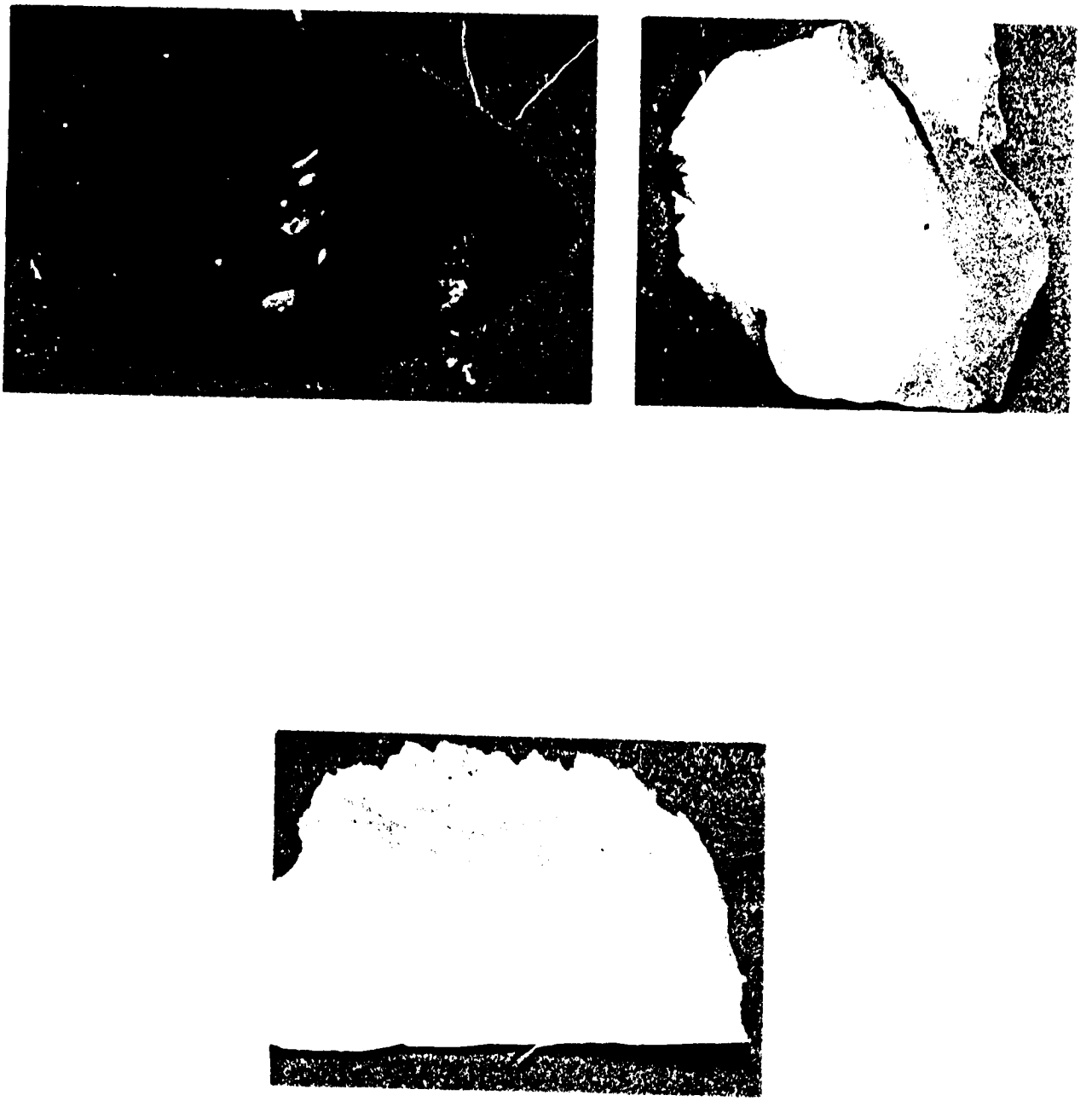
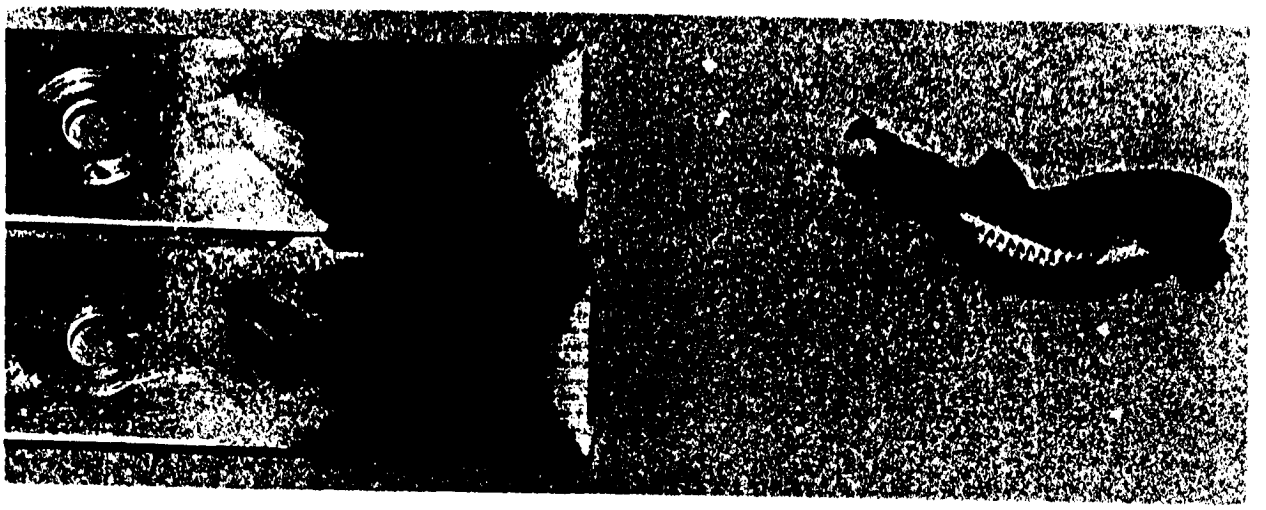
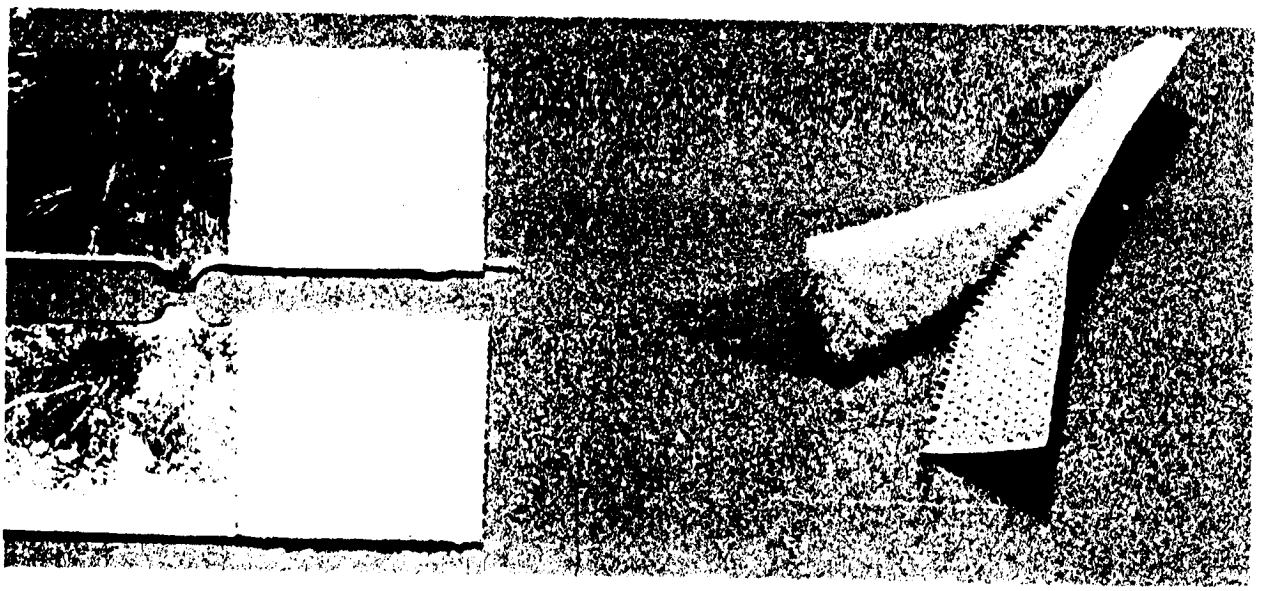


Figure II-3.4e. Dexiglas Paper--Specimen Exposed to Liquid Fluorine and Comparative Unexposed Specimen



BONDED UNBONDED

EXPOSED VELCRO



BONDED UNBONDED

UNEXPOSED VELCRO

Figure II-3.4f. Velcro Fastener--Specimens Exposed to Liquid Fluorine and Comparative Unexposed Specimens

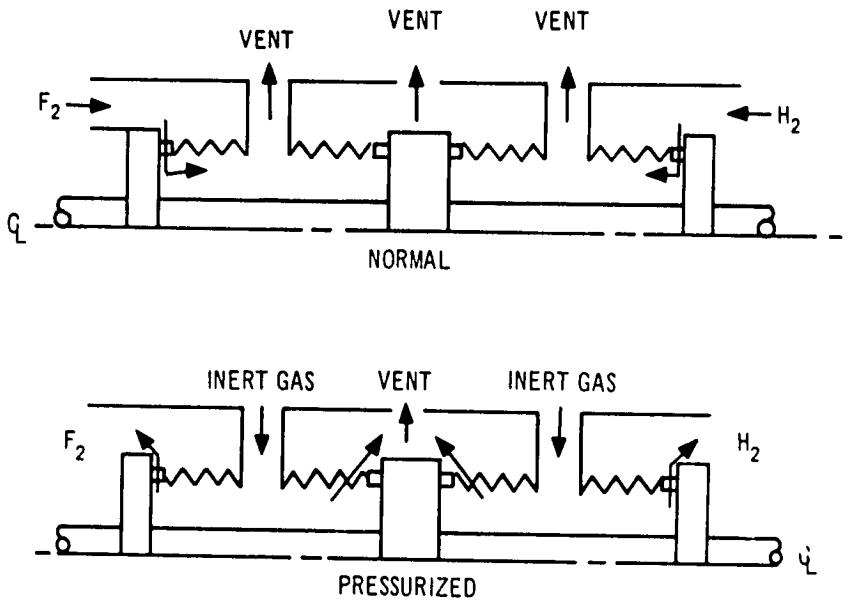


Figure II-3.6a. Boost Pump Dynamic Seal

4.0 LEAKAGE CONSIDERATIONS AND CALCULATION METHODS

4.1 Nomenclature

a	$\frac{E_1}{1-\nu_1^2} + \frac{E_2}{1-\nu_2^2}$, psi
B	$1/a^2$ or $\frac{9\alpha^2}{128}$ when $\theta = 90°$ or $0 < \theta < 90°$, respectively
C_1	compression coefficient when $\theta = 90°$
C_2	compression coefficient when $0 < \theta < 90°$
D	diameter of sine wave's equivalent cylinder - λ^2/h, inch
E_L	modulus of elasticity, psi
E_P	modulus of plasticity, psi
F	load, lbs
g	gravitational constant, ft/sec^2
h	asperity height, inch
h_p	equivalent flat plate spacing = $M_L h$ or $M_M h$, inch
L	valve seat perimeter, inch
M_L	surface coefficient for laminar flow
M_M	surface coefficient for molecular flow
P_1	internal pressure, psia
P_2	external pressure, psia
p	load per linear inch, lb/in.
R	universal gas constant, ft/°R
S	apparent seat stress, psi
T	gas temperature, °R
W	seat width, inch
w	fluid flow rate, lb/sec

α	$\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$, 1/psi
β	experimental molecular flow factor
γ	surface factor in determining C_2
δ	combined deformation of two surfaces, inch
ϵ	deformation coefficient
θ	orientation angle of contacting surfaces, degrees
λ	wavelength, inch
μ	fluid viscosity, lb-min/in.^{2}
ν	Poisson's ratio
ρ	liquid density, lb/ft^3
ϕ	asperity angle, radians

Undefined subscripts

1	valve seat
2	valve poppet

4.2 Background: Analytical, Empirical

4.2.1 Zero Leakage

It is recognized that a definition of zero fluorine leakage is required in the preparation of component specifications and to evaluate test data. At present no standard is recognized and therefore, zero fluorine leakage is defined as a leakage of 5×10^{-10} pounds per second or less. The leakage analysis of Reference 97 showed that fluorine leak rates as low as 5×10^{-10} pounds per second of fluorine can be attained by using surfaces lapped to one micro-inch roughness and by applying seat stresses of about ten thousand psi, Figures II-4.3f thru II4.3k. Since finer surface finishes are difficult to attain, and higher

stress levels are not desirable, this leak rate represents an obtainable, but still practical definition for "zero" leakage of fluorine. Reference 84 defines zero leakage as 10^{-4} standard cubic centimeters per second or 10^{-6} pounds of air per hour. This value was established by evaluating the threshold where no bubbles could be detected in half an hour of leakage. When converted to the same basis, the fluorine leak rate of 5×10^{-10} pounds per second is nearly equivalent to that of 10^{-6} pounds per hour of air.

4.2.2 Analytical

The analytical prediction of leakage through valves and fittings is so difficult a task that it has been traditionally abandoned in favor of empirical results in systems design. But, in space applications, particularly those using very reactive cryogenic propellants, acceptable leakage levels are many orders of magnitude below those of the conventional systems, making a thorough analytical approach especially desirable. The "cut and try" approach to seal design could be very costly and the results unrewarding when applied to these propellant systems. The leakage levels necessary in toxic propellant systems requires a more technical foundation than these antiquated, but proven methods. Present day analysis can easily eliminate laborious manipulations of data, etc., by use of digital computing machines.

Rocketdyne, under an Air Force contract (Reference 244), studied the problem and developed valve poppet and seat design data, which was published in May 1964. The analytical model, developed under this contract, was fairly simple yet their test results correlated rather well with the calculated leakage values. Basically, it was assumed that sealing surfaces resemble regular waveforms, the shapes of which depend upon the finishing method, and that the flow field could be evaluated as that between two flat plates. Further simplification was attained by assuming that both surfaces have identical waveforms which are oriented at right angles. This is the basis for the analytical leakage model of this handbook.

Another study, which did not directly affect the leakage equations, but did contribute to these criteria, was made by General Electric Co., for NASA (Reference 24). Their analytical leakage solution was not complete at this

writing, but a unique approach to define surfaces was developed early in their study and was reported in May 1965. Since no finishing technique can completely destroy the random asperities characteristic of all surfaces, General Electric chose not to over-simplify their model by neglecting these irregularities. Instead, they developed a computer program which generated random asperity heights, the distribution of which can be forced to agree with that of a real surface. Once generated, the arithmetic surface can be altered to duplicate finishing marks, such as waveforms and scratches. The program generates two distinct surfaces and compresses them arithmetically until all leakage paths through them are blocked.

The present work used the analytical leakage model of Rocketdyne, and the computer program of General Electric to establish design criteria for feed system sealing surfaces. The Rocketdyne geometric model was made more general by allowing the contacting waveforms to be of different wavelengths and amplitudes, and by accounting for the orientation of the surfaces and its effect on flat plate leakage theory. These refinements produced more complicated surface deformation equations, but they are as straightforward as the simpler equations.

Preliminary parametric studies involve the plotting of numerous solutions to equations. Since there are so many significant variables in leakage equations, a FORTRAN IV program was written, by Douglas, to solve the equations and automatically plot the results, (Reference 97).

The modification of a seal design is often all that is required, and design curves showing the relative effects of the significant variables should be adequate for this purpose. Figures II-4.31 thru II-4.3t show the effects of nine variables on the leakage rate through a seal. They do not include those variables with which leakage varies directly, because their effects are obvious. The values selected for the independent variables are realistic for a fluorine feed system. Further details are included in paragraph II-4.3.4.2.

Figures II-4.3u thru II-4.3z provide an insight into the relative effects of certain surface features on leakage. The random surface generator program was used, by Douglas, to generate these curves, which show the amount of

compression required to reduce leakage to an acceptable level. In its present form, the program only compresses the surface arithmetically, calculates the increase in contact area, and determines the existence of leak paths across the seal.

A leakage flow analysis and the stress-deformation relationship should be added to the random surface generator program. General Electric is involved in the flow analysis, which will be based on capillary flow theory coupled with the channel flow already discussed, but a completion date cannot be estimated as of this writing. It will necessarily be more involved than the simplified waveform deformation analysis.

4.2.3 Empirical

The bulk of the work done by both Rocketdyne and General Electric was empirical, and it correlated well with theory. Rocketdyne used both profile measurements and interference microscope inspection to define the parameters for their sinusoidal model, then tested the specimens using gaseous nitrogen. General Electric's test procedure was similar, except that helium was used instead of nitrogen. The theory which General Electric used was for channel flow, Reference 84, the equations for which are almost the same as those of the flat plate flow used by Rocketdyne. Both found good correlations with test data.

Douglas used one of several valve tests, Reference 97, to verify the validity of the revised deformation and orientation equations. Good correlation was obtained, as explained in paragraph II-4.4.2.

4.3 Analysis

4.3.1 Geometric Model

4.3.1.1 The geometric model used to represent two finely finished surfaces in contact was derived from that generated in Reference 244. Basic to the analysis is the assumption that surfaces which are finished to the degree of

smoothness needed for good sealing will approximate very flat waveforms, such as those shown in Figure II-4.3a. Of these, the sinusoidal waveform is most nearly representative of a sealing surface because the sharp points which are characteristic of the other surfaces are rounded (flattened) in the finishing process. Therefore, the sinusoidal waveform represents the most logical form which allows reasonable analysis and will give satisfactory results. The defining equations for the waveform model are shown in Figure II-4.3b.

The simplest deformation equations assume that both surfaces have identical characteristics and that their points of contact approximate two contacting spheres, as in Reference 244. This model is depicted in Figure II-4.3c. However, to allow the designer a more flexible parametric study, the model was expanded so as not to be restricted to identical surfaces only; that is, the two surfaces may have different asperity heights and asperity angles. It is more realistic to compare the contact points of intersecting sine waves with those of contacting cylinders, rather than of spheres. In so doing, the deformation analysis becomes more involved, because the angle between the axes of the hypothetical cylinders becomes a factor, but that is not restrictive.

Again, the most realistic model is one in which both surfaces are sinusoidal but need not be identical. They may intersect at any angle and their points of contact are represented by contacting cylinders. This may be visualized as two very flat waveformed, corrugated surfaces in contact. This represents the simplest model which will yield the required analytical results and it is recommended for usage.

4.3.1.2 No surface can be completely devoid of the random asperities which are characteristic of any finish, no matter how smooth, so a computer program was written, Reference 82, to generate such a random surface numerically. A real surface can be simulated very accurately because the generated surface map is dependent upon a probability table which is determined by measuring the real surface contour. This program also allows the designer to superimpose other surface features on the random map, such as lapping, grinding

marks, scratches, etc. The versatility of the model generated by this program gives it great potential, but it is not used here because at present it can only compress two surfaces together numerically. When the deformation-stress relationship is developed and a leakage analysis can be applied to the model, this program will probably prove to be better than the more limited one described above, and it should be considered for use at that time.

4.3.2 Deformation

4.3.2.1 A point of contact in the sinusoidal model is assumed to behave the same as that of two contacting cylinders. The amount of deformation at such a point under an applied load is a function of material properties, the diameters of the cylinders and the angle between the cylinders. The properties and the contact angle are straightforward parameters, but selecting a diameter which will relate a cylinder to a sine wave, with its varying radius of curvature, is arbitrary. In Reference 244 the diameters of the contacting spheres were defined as λ^2/h, the square of the wavelength divided by the amplitude. It is not clear what led to this definition of equivalent diameters, but it has been verified as being reasonable, and is used to define the diameters of the cylinders in the recommended leakage analysis.

In Reference 141, Roark presents equations for the deformation of two cylinders at right angles and for the deformation of two cylinders in parallel, but he does not derive that for two cylinders at intermediate angles. There is a general case, however, from which this latter equation was derived for this analysis. For perpendicular, acute and parallel intersections, respectively, these equations are

$$\delta = C_1 \sqrt[3]{\frac{F_2}{\left(\frac{E_{L1}}{1-\nu_1^2} + \frac{E_{L2}}{1-\nu_2^2}\right)} \frac{(D_1 + D_2)}{D_1 D_2}} \qquad \text{(Eq. 1)}$$

$$\delta = C_2 \sqrt[3]{\frac{9}{64} F^2 \left(\frac{1 - \nu_1^2}{E_{L1}} + \frac{1 - \nu_2^2}{E_{L2}}\right) \frac{(D_1 + D_2)}{2 D_1 D_2}} \qquad \text{(Eq. 2)}$$

and

$$\delta = \left(\frac{1 V_1^2}{E_{L1}} + \frac{1 - V_2^2}{E_{L2}}\right) \left(\frac{p}{\pi}\right) \left(\frac{2}{3} + \ell n \frac{2D_1}{b} + \ell n \frac{2D_2}{b}\right) \qquad \text{(Eq. 3)}$$

where

$$b = 1.6 \sqrt{p \frac{D_1 D_2}{D_1 + D_2} \left[\frac{1 - \nu_1^2}{E_{L2}} + \frac{1 - \nu_2^2}{E_{L2}}\right]}$$

and C_1 and C_2 are functions of the diameters and angle of contact of the cylinders, as shown in the following tables, where θ = angle between the axes of the cylinders and

$$\gamma = \text{arc cos} \frac{D_1 D_2}{D_1 + D_2} \sqrt{\left(\frac{1}{D_1}\right)^2 + \left(\frac{1}{D_2}\right)^2 + \frac{2}{D_1 D_2} \cos 2\theta} \qquad \text{(Eq. 4)}$$

To allow calculation by computer, these tables were approximated by curves. Table II-4.3a is virtually a straight line, and Table II-4.3b can be matched very closely by two ellipses. The equation for the straight line is

$$C_1 = 2.13 - 0.0536 \left(\frac{D_{max}}{D_{min}}\right) \qquad \text{(Eq. 5)}$$

Although it is unlikely that two sealing surfaces will differ greatly, it is conceivable that the value of the ratio of equivalent diameters (D_{max}/D_{min}) could exceed that required to make C_1 attain a value less than 1.0. This would be unrealistic, so the computer program will use a value of 1.04 if the calculated value is less than 1.04. This is an arbitrary limit. The equations of the ellipses are

$$C_2 = 1.807 \sqrt{1 - \frac{(\cos\gamma - 0.526)^2}{3.27}} \quad \text{when } 0 < \gamma < 53° \qquad \text{(Eq. 6)}$$

and

$$C_2 = 2 \sqrt{1 - \frac{\cos^2\gamma}{2}} \quad \text{when } 53° < \gamma < 90° \qquad \text{(Eq. 7)}$$

The above equations apply only to elastic deformation, and no equivalent ones exist for plastic deformation because of the complexity of the plastic phenomenon. However, it is important to be able to predict leakage through seals when one or both surfaces deforms plastically. There are only two material properties in the above equations, and if these could be defined in the plastic region the same equations may be utilized for plastic deformation. A search of the literature revealed that no data is available to define a Poisson's ratio or a plastic modulus for a material in plastic compression. Since Poisson's ratio is nearly the same for all metals and would be very difficult to measure in plastic compression, it may be assumed that it does not change in the plastic region.

A stress-strain diagram for compressive loading of the candidate valve material must be obtained to define a plastic modulus for use in the deformation equations. Materials are not generally tested in compression, so the designer will likely be unable to find such a diagram available. If not, he will need to determine the curve himself. Significantly, it was found that strain-hardening

from alternately loading and unloading a specimen does not have much effect on the slope of the plastic portion of the curve and can be ignored. In other words, a specimen may be loaded to its ultimate stress, without cycling, to obtain its stress-strain characteristics. Figures II-4.4a and II-4.4b are compressive stress-strain diagrams for six important valve seal materials, namely, aluminum 6061-T0, 6061-T4, and 6061-T6, 304 stainless steel, K-Monel, and phosphorous deoxidized copper. These curves are explained in paragraph II-4.4.1. The point at which ultimate failure occurs in compression is difficult to define, however, for numerical calculations it may be assumed that it has approximately the same numerical value as that measured in tension. These curves can be approximated by three straight lines, as in Figure II-4.3e, the slopes of which represent moduli of elasticity or plasticity. Physically, these lines define the elastic region, a transition region, and the plastic region. The designer can now calculate the deformation for whichever operating region is applicable to the specific design. For the computer solution, the transition slope is simply calculated to be the average of the elastic and plastic slopes input by the designer. This is a satisfactory approximation because the transition region is very small or non-existent, and because a seal will seldom be designed to operate in that region. A computer program is described fully in paragraph II-4.3.4 which allows this calculation to be made and plotted with a minimum of effort.

So far, it has been assumed in this discussion, that deformed material simply disappears into the substrate, leaving everything undisturbed outside the actual contact areas. In reality, some degree of "flow" will take place with material displacement occurring elsewhere. The easiest way to cope with this problem is to introduce a factor which accounts for the shifting of this matter. This factor, ϵ, simply allows some fraction of the compressed peak material to appear as a rise in the valleys, remembering that the model is a pure sine wave. On one extreme ($\epsilon = 1$) none of the material appears in the valleys, and on the other ($\epsilon = 2$) all the compressed material appears in the valleys. This factor allows the designer to "tailor" his analysis to conform to empirical data, if necessary, by interpretation of the factor ϵ.

4.3.3 Leakage

4.3.3.1 Theoretical Leakage

The leakage equations used here are those of Reference 244, which are based on the theory of fluid flow between two parallel flat plates. The fact that the surface are not perfectly flat is accounted for by a multiplication factor which gives an equivalent flat plate spacing when applied to the actual asperity heights of the surfaces. Two such factors are needed; M_L for laminar flow and M_M for molecular flow. These factors are shown in Figure II-4.3a, and have the values of 0.678 and 0.612, respectively, for the sinusoidal model. Some simplifying assumptions can be made to derive a flow equation for a leaking seal. First, it is not necessary to consider turbulent flow because we are attempting to design for "zero" leakage, which implies very low flow rates, such as, laminar and/or molecular flow only. Second, the molecular contribution to liquid leakage may be ignored because the mean free path of a liquid molecule is very small compared to the hydraulic diameter of the leak path. The final two assumptions are that the flow is isothermal and that fluid momentum effects are negligible.

These assumptions lead to the Poiseuille equation for laminar flow through stationary flat plates which, when combined with the continuity equation, reduces to the following equations for incompressible and compressible flow, respectively,

$$w = \frac{\rho L h_p^{\,3} (P_1 - P_2)}{1.244 \times 10^6 \, \mu W} \text{ (liquid)} \qquad \text{(Eq. 8)}$$

and

$$w_\ell = \frac{L h_p^{\,3} \left(P_1^{\,2} - P_2^{\,2}\right)}{1.728 \times 10^4 \, \mu WRT} \text{ (gas)} \qquad \text{(Eq. 9)}$$

The second equation assumes a perfect gas and an average gas density across the seat. These equations apply to rectangular plates of length L and width W, whereas a valve seat must necessarily close on itself, and is usually circular. However, the ratio of perimeter-to-width is generally so great that divergence effects can be neglected. For a circular seat, to which the remainder of this analysis will apply, radial divergence can be ignored when r_o/r_i is less than 1.4. If that ratio is greater than 1.4, the following substitution should be made:

$$\frac{L}{w} = \frac{\pi 2}{\ell n\, r_o/r_i} \qquad \text{(Eq. 10)}$$

If the ratio of gaseous molecular mean free path to plate height is less than 0.01, Equation (9) will determine the total gaseous flow between the plates. However, molecular flow will nearly always be a significant factor in the flow regimes in which we are interested; that is, we will be operating in the transition region between pure viscous flow and pure molecular flow. Transitional flow exists when the ratio of molecular mean free path to plate height lies between 0.01 and 1.0. Above 1.0, the flow is purely molecular. The equation for molecular flow was derived using the kinetic theory of gases and it relates flow to mean molecular speed, differential pressure and geometry.

$$\dot{w}_m = \frac{4}{3}\,\frac{Lh_p^2}{W}\,\frac{(P_1 - P_2)}{\sqrt{\pi RT/2g}} \qquad \text{(Eq. 11)}$$

In the transition region, the total flow will be the sum of the viscous and molecular contributions. In Reference 12 a relationship of the form

$$\dot{w} = \dot{w}\ell + \beta\,\dot{w}_m \qquad \text{(Eq. 12)}$$

is used, where β is an experimentally determined constant with the values of approximately 0.9 for single gases and 0.66 for mixtures of gases. Therefore, the equation for total gaseous leakage flow rate is

$$\dot{w} = \frac{Lh_p^3 \quad P_1^2 - P_2^2}{1.728 \times 10^4 \mu WRT} + \beta \frac{4\,Lh_p^2}{3W} \frac{(P_1 - P_2)}{\sqrt{\pi RT/2g}} \qquad \text{(Eq. 13)}$$

and, repeating, that for a liquid is

$$\dot{w} = \frac{\rho Lh_p^3 (P_1 - P_2)}{1.244 \times 10^6 \mu W} . \qquad \text{(Eq. 8)}$$

The equivalent flat plate spacing, h_p, is the sum of the asperity heights of the two surfaces times and equivalence coefficient, M_L or M_M. Further, the sum of the asperity heights under load is equal to the unloaded sum minus the deformation of the surfaces.

$$h_p = M_{L(M)} (h_1 + h_2 - \epsilon\delta) \qquad \text{(Eq. 14)}$$

4.3.3.2 Physical Constraints on Leakage

The theoretical leakage equations derived above should be multiplied by the sine of the orientation angle, θ, to account for the physical orientation of the sealing surfaces. If θ is 90°, as in Figure II-4.3c, the correction factor is 1.0 because the flow area is independent of the direction of flow and the equivalence coefficients are sufficient to account for the deviation from flat surfaces. But, as θ approaches 0°, the restriction to flow becomes more and more a function of the direction of flow.

Valve seats and poppets will usually be finished circumferentially so that the leakage occurs across the peaks rather than through them, so it can be assumed that the flow is always directed across the peaks of at least one of the two surfaces. Then θ can be defined to account for the actual orientation of the second surface with respect to the first, since they would never be finished precisely enough to be perfectly circumferential.

The effect of the correction factor, **sin θ**, on the leakage flow rate is shown in Figure II-4.3d, which compares the uncorrected flat plate solution with the corrected result on the basis of relative leakage. Absolute zero leakage cannot be attained in practice, and as we approach small values of θ, the idealized model becomes less acceptable. However, the solution does correlate well for angles greater than about 10°, which is probably as small as θ would ever be.

4.3.4 Solution of Leakage Equations by Computer

4.3.4.1 Absolute Leakage

The general equations for liquid and gaseous leakage through a circular valve seal are obtained by combining the deformation equations for the sinusoidal model and the flat plate leakage equations, with their appropriate equivalence coefficients. These general equations then become:

$$w_{liq} = \sin\phi \frac{\rho L (P_1 - P_2)}{1.244 \times 10^6 \mu W} \left[M_L \left(h_1 + h_2 - \epsilon C \sqrt[3]{BS^2 \left(\lambda_1^2 h_2 + \lambda_2^2 h_1 \right)} \right) \right]^3$$

(Eq. 15)

and

$$w_{gas} = \sin\theta \frac{L \; P_1^2 - P_2^2}{1.728 \times 10^4 \mu WRT} \left[M_L \left(h_1 + h_2 - \epsilon C \sqrt[3]{BS^2 \left(\lambda_1^2 h_2 + \lambda_2^2 h_1 \right)} \right) \right]^3$$

$$+ \frac{4\beta L (P_1 - P_2)}{3W \quad \pi RT/2g} \left[M_M \left(h_1 + h_2 - \epsilon C \sqrt[3]{BS^2 \left(\lambda_1^2 h^2 + \lambda_2^2 h_1 \right)} \right) \right]^2$$

(Eq. 16)

for liquid and gaseous leakage, respectively.

Although unwieldy, these equations are straightforward and the leakage through a given valve can be predicted by hand. They are most valuable when used to make preliminary design parametric studies.

Several variables must be defined to make use of these equations; that is, the surface finishes and the compressive properties of the surface materials. Profilometer traces of surfaces must be obtained for any finishing techniques under consideration, and these must be related to equivalent sine waves by defining the variables θ and h. This will require some engineering judgment, but the profiles should prove to be very regular for the very fine finishes that are being considered. Table II-4.3c indicates approximate values for these variables.

Although these values will allow calculation of approximate leakage, specific calculations should depend upon profilometric measurements of surfaces which have been finished by applicable production methods.

The required compressive properties of the materials can be obtained from stress versus strain areas in the following manner. Referring to Figure II-4.3e, the curve represents three phases of surface deformation; namely, elastic, elastoplastic and plastic. The elastic region is linear, the plastic region is nearly linear and can be represented by a straight line, and the elasto-plastic region is a transition curve connecting the other two. The information required for solution is: (1) the slope of the elastic curve; (2) the slope of the plastic curve; (3) the stress at point A; (4) the stress at point B, and (5) the stress at which ultimate failure occurs (not shown in figure). Points A and B must be selected such that the slope of a straight line connecting them will be the average of the elastic and plastic slopes, as this elasto-plastic approximation has proven to be adequate for these calculations. The ultimate strength in tension should be used if the compressive strength is not known. This is the usual situation because material failure in compression is difficult to determine.

Figures II-4.3f thru II-4.3k are typical computer program output curves and are the results of a parametric study that was made in Reference 97. The leakage is based upon a "unit" seal perimeter to seal width ratio, L/W, of 100. Since the leakage, based on this model, is a direct linear function of L/W, the values scale directly for other ratios. The other pertinent design values are shown in Table II-4.3d.

4.3.4.2 Relative Leakage

The ability to quickly evaluate the affects of the many variables in the leakage equations would be a valuable design tool. Such a tool is provided in Figures II-4.3l thru II-4.3t, which are curves of relative leakage versus the parameters with which leakage does not scale directly. These curves were generated by defining a typical design situation as a baseline, and then varying each parameter over a reasonable range. The baseline values are listed in Table II-4.3e. This was done for both liquid fluorine and gaseous fluorine in the first six curves, but it was found that the curves were identical for both fluids except when wavelength was varied. Therefore, Figure II-4.3m includes a curve for both fluids, although the difference between them is very small. The last three curves apply to the gaseous equation only, because the affects of the variables P_1, ∇P, and T are not obvious in that equation.

The affects of some surface features on seal behavior are shown in Figures II-4.3u thru II-4.3z. The curves in Figures II-4.3u thru II-4.3w show the decrease in leakage for "unit" increments of compression, whereas those in Figures II-4.3x thru II-4.3z show the increase in actual contact area for these same increments. The latter curves do not extend beyond the point at which leakage presumably stops. These figures were generated for twenty-five surface combinations by the random surface computer program (paragraph II-4.3.1.2), which simply compresses two surfaces arithmetically. One hundred percent leakage is the leakage rate when the two surfaces just touch each other without compression. The contact areas are effectively zero at this point. The wave angle is defined as zero when the flow is across the peaks and as ninety degrees when the flow is between the peaks.

4.4 Empirical

4.4.1 Stress-Strain Data

Compression data was needed for the materials being recommended for use in fluorine, so stress-strain curves were obtained for six important candidate materials; namely, aluminums 6061-T0, 6061-T4 and 6061-T6, 304 stainless steel, K-Monel and phosphorous deoxidized copper. One inch specimens were cut from tube stock and tested under four different conditions; ambient uncycled, ambient cycled, cryogenic uncycled and cryogenic cycled. Although there are other equally good procedures for obtaining this data, this procedure is included to document what has proven to be adequate.

The ambient temperature was about 70°F and the cryogenic temperature was that of liquid nitrogen, about -321°F. In the uncycled tests, the specimens were compressed steadily until strain-gage failure occurred or until the limit of the recorder was reached, whereas the cycled samples were compressed into the plastic range, relaxed, recompressed into the plastic range, relaxed, etc. This was done to determine the affects of strain hardening on the slope of the plastic portion of the curve and to see if the cycled and uncycled stress levels at a given deformation could be correlated.

All the specimens showed signs of buckling at their ends, but the traces gave no indication of ultimate material failure. It would be very difficult to define a failure point in compression and no attempt was made to do so; that is, the stress-strain curves were traced until the strain gages failed or until the plotter mechanical limit was reached, and the specimens were not compressed further.

The uncycled curves for the six candidate materials at both ambient and cryogenic temperatures are reproduced as Figures II-4.4a and II-4.4b. The cycled curves are not included because the results showed that only slight differences existed between the uncycled and cycled curves, and surprisingly, the cycled work hardening affect was not always more severe than the noncycled. The slight variations fell within the tolerances of the test procedure

and were therefore ignored. That is, at a given temperature, the stress-strain curve for an uncycled specimen defines the properties of a material sufficiently to be used for design. The values for the elastic and plastic moduli from these curves are shown in Table II-4.4a, and may be substituted directly into the leakage equations (paragraph II-4.3.4.1).

4.4.2 Valve Leakage Correlation

Good correlation between leakage flow theory and leakage test results was established by both Rocketdyne and General Electric (paragraph II-4.2.2). The present work used the results of one of several valve tests to check the validity of the surface deformation and orientation equations which were revised by this analysis. The valve selected for this check was a poppet valve with both sealing surfaces of K-Monel lapped to a "5" finish. The test was conducted using helium at ambient temperature with a 50 psi pressure drop across the valve and yielded a leakage rate of 1.6×10^{-8} lb/sec.

The gaseous leakage equation, paragraph 4.3.4.1, was used to generate Figure II-4.4c. Average asperity heights for a "5" finish could range from one-half to five micro-inches, with asperity angles of 1/2 to 1.5 degrees being common. This matrix is bounded by the two curves in the figure. The measured leakage is included in the resultant range of reasonable leakage rates, as shown by the dashed line, thereby providing correlation between the calculated and measured values.

4.4.3 Surface Fracture

Profilometer and roughness measurements alone are not usually sufficient to detect plastic deformation, or surface fracture of a sealing surface, but electron microscopic examination of a surface replica will reveal this phenomenon. Figure II-4.4d shows fractographs of a contact surface area after being tested in fluorine. There was no visible evidence of plastic deformation, but this figure clearly shows that such deformation did occur. All the surface features shown would have gone undetected if this valuable tool had not been employed. The groove in the first picture was caused by

the seating of the poppet, whereas the scratch and the surface debris of the others were probably due to handling the valve after testing. The other two pictures show evidence of mild surface fracture, as indicated by the equiaxed dimples.

Trans-granular surface fracture may occur whenever two surfaces are pressed together with sufficient pressure. One or both surfaces may suffer fracture, depending upon their relative hardnesses. The fracture may be one of three types, which are depicted in Figure II-4.4e, depending upon the type of valve, or seal closure. The equiaxed dimples of the valve seat above indicate that the fracture as that of type (a), such as, tension, which is characteristic of poppet valves and others whose sealing surfaces close squarely on each other. Shear and tensile tear types of fracture would likely occur in designs which feature a sliding type of closure, such as butterfly valves. Since this surface plastic deformation is microscopic it does not preclude further use of the surfaces as seals, but it may reduce the life of the seal.

Table II-4.3a
VALUES OF C_1 FOR USE IN LEAKAGE CALCULATIONS

$\theta = 90°$							
D_1/D_2	1	1.5	2	3	4	6	10
C_1	2.08	2.06	2.03	1.95	1.88	1.77	1.61

Table II-4.3b
VALUES OF C_2 FOR USE IN LEAKAGE CALCULATIONS

$0° < \theta < 90°$									
γ	10°	20°	30°	40°	50°	60°	70°	80°	90°
C_2	0.85	1.22	1.45	1.64	1.77	1.88	1.94	1.99	2.00

Table II-4.3c
TYPICAL ASPERITY HEIGHTS AND ANGLES FOR COMMON FINISHING TECHNIQUES

Method	Asperity Heights	Asperity Angles
Diamond Burnishing	1-20 μ-in.	1/2°-2°
Tapping	1-20	1/2°-2°
Honing	4-30	1°-4°
Grinding	8-40	1°-4°
Machining	30-250	1°-8°
Casting, sand	300+	1°-15°

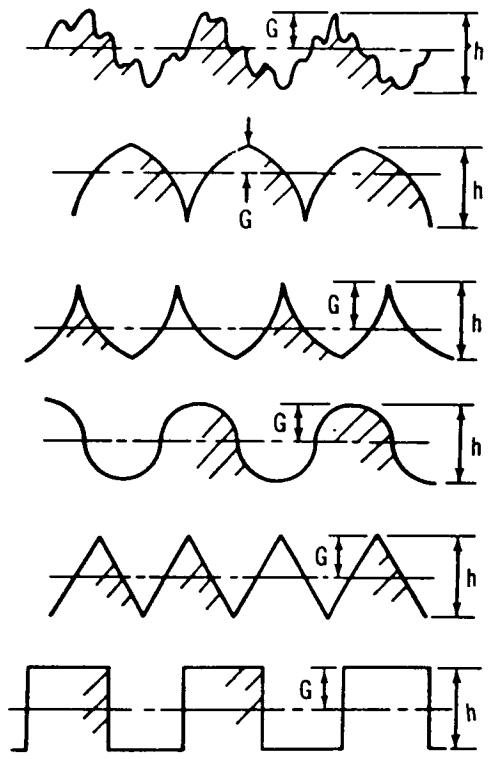
Table II-4.3d
CONDITIONS FOR FLUORINE VALVE DESIGN STUDY

Liquid temperature	-310°F	Internal pressure	65 psia
Gas temperature	70°F	External pressure	15 psia
L/W	100	ϵ	1.5
M_L	0.68	ϕ	1/4°
M_M	0.61	θ	90°

Table II-4.3e
BASELINE VALUES FOR INFLUENCE CURVES

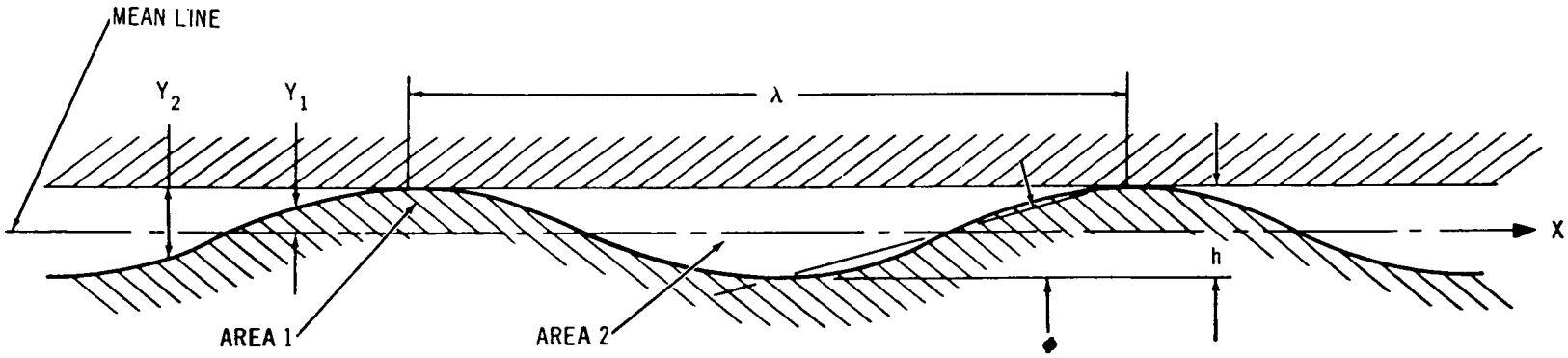
h	λ	ϵ	δ	θ	E	P_1	∇P	T_{gas}
5×10^{-6} in.	5×10^{-4} in.	1.5	2000 psi	45°	25×10^{6} psi	65 psia	50 psi	60°F

WAVE FORM: h = 1	M_L^*	M_M^*	AA	rms	$\frac{h}{AA}$	$\frac{h}{rms}$	$\frac{G}{h}$	$\frac{G}{AA}$	$\frac{rms}{AA}$
UNIFORMLY RANDOM			0.2	0.25	5.0	4.0	0.5	2.5	1.25
ROUND CRESTED PARABOLIC	0.523		0.256	0.298	3.91	3.36	0.333	1.29	1.16
SHARP CRESTED PARABOLIC	0.770		0.256	0.298	3.91	3.36	0.667	2.60	1.16
SINUSOIDAL	0.678	0.612	0.318	0.353	3.14	2.83	0.5	1.57	1.11
SAW TOOTH	0.630	0.578	0.25	0.289	4.0	3.46	0.5	2.0	1.16
SQUARE	1.0	1.0	0.5	0.5	2.0	2.0	0.5	1.0	1.0



*$h_{eL} = M_L h$; $h_{eM} = M_M h$

Figure II-4.3a. Average Height Values for Various Wave Forms



$$AA = \frac{1}{\lambda}\int_0^{\lambda} |y1|\, dx; \quad rms = \left[\frac{1}{\lambda}\int_0^{\lambda} y_1^2 \, dx\right]^{1/2}$$

$$h_{eL} = \left[\frac{1}{\lambda}\int_0^{\lambda} y_2^3 \, dx\right]^{1/3} ; \quad h_{eM} = \left[\frac{1}{\lambda}\int_0^{\lambda} y_2^2 \, dx\right]^{1/2}$$

AVERAGE ASPERITY ANGLE $\Phi \cong \frac{2h}{\lambda}$

LOCATION OF MEAN LINE DEFINED BY AREA 1 = AREA 2

Figure II-4.3b. Model Surface Geometry with Defining Equations

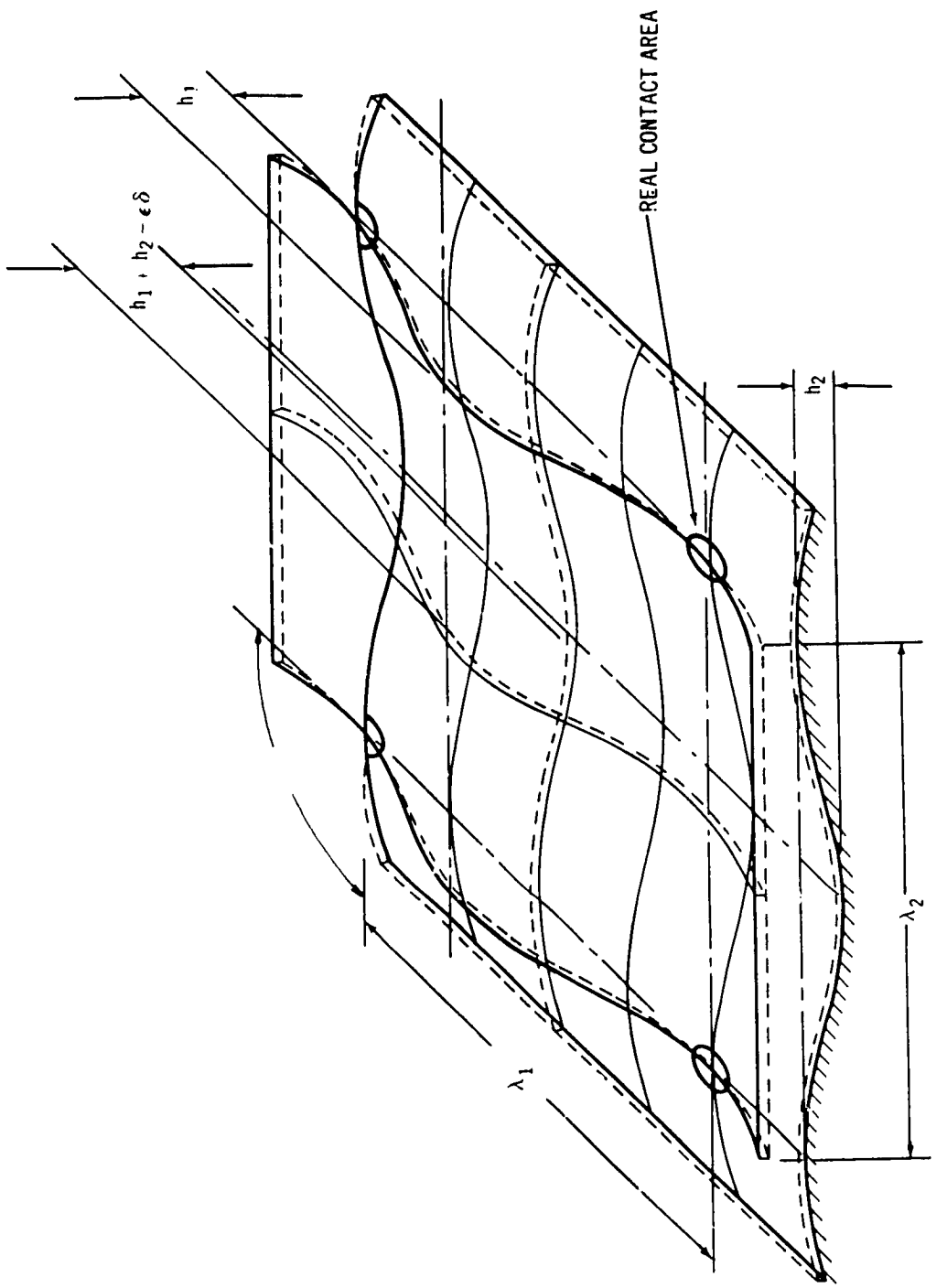


Figure II-4.3c. Sinusoidal Model Surfaces

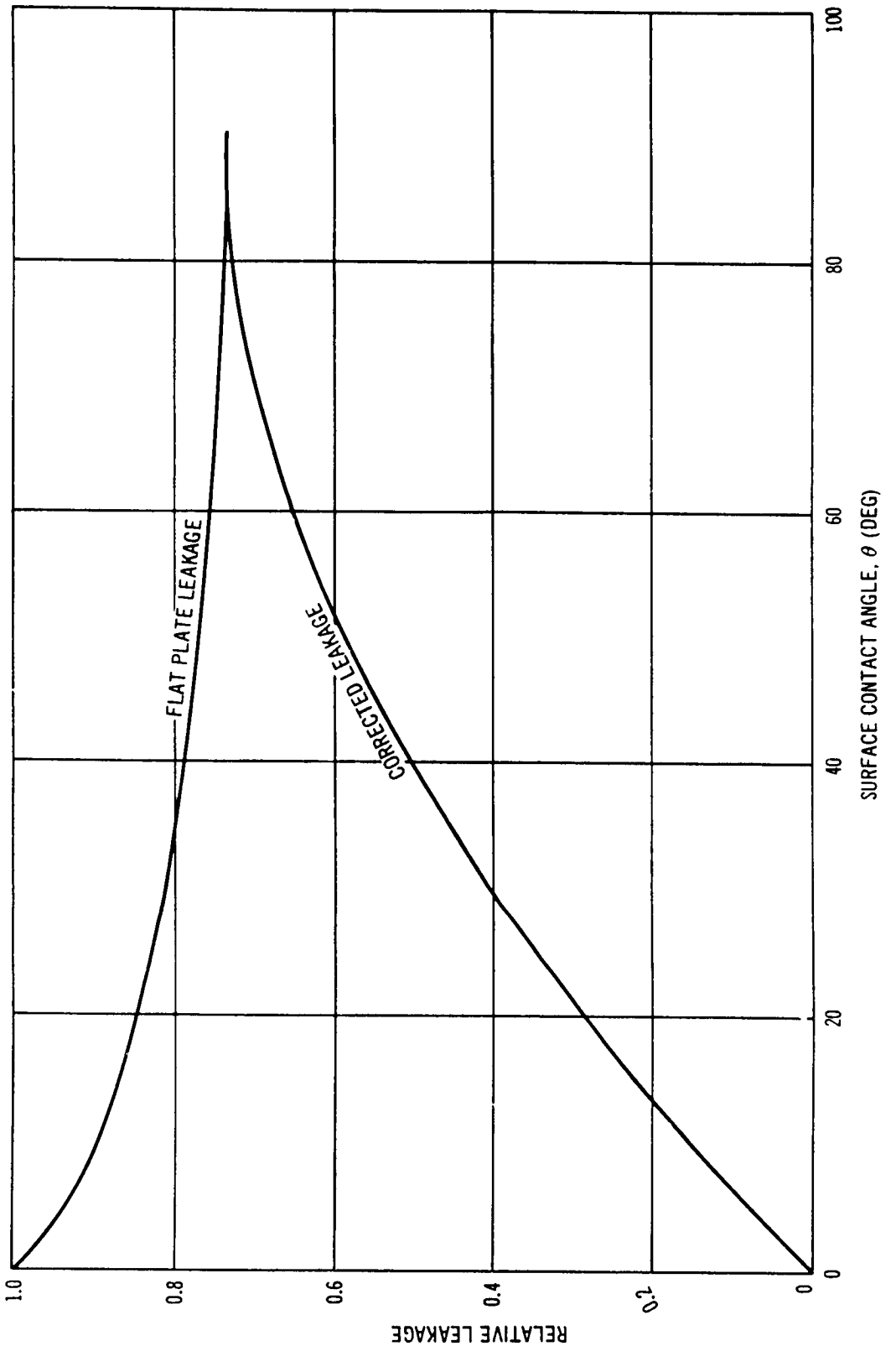


Figure II-4.3d. Effect of Contact Angle Correction Factor on Leakage

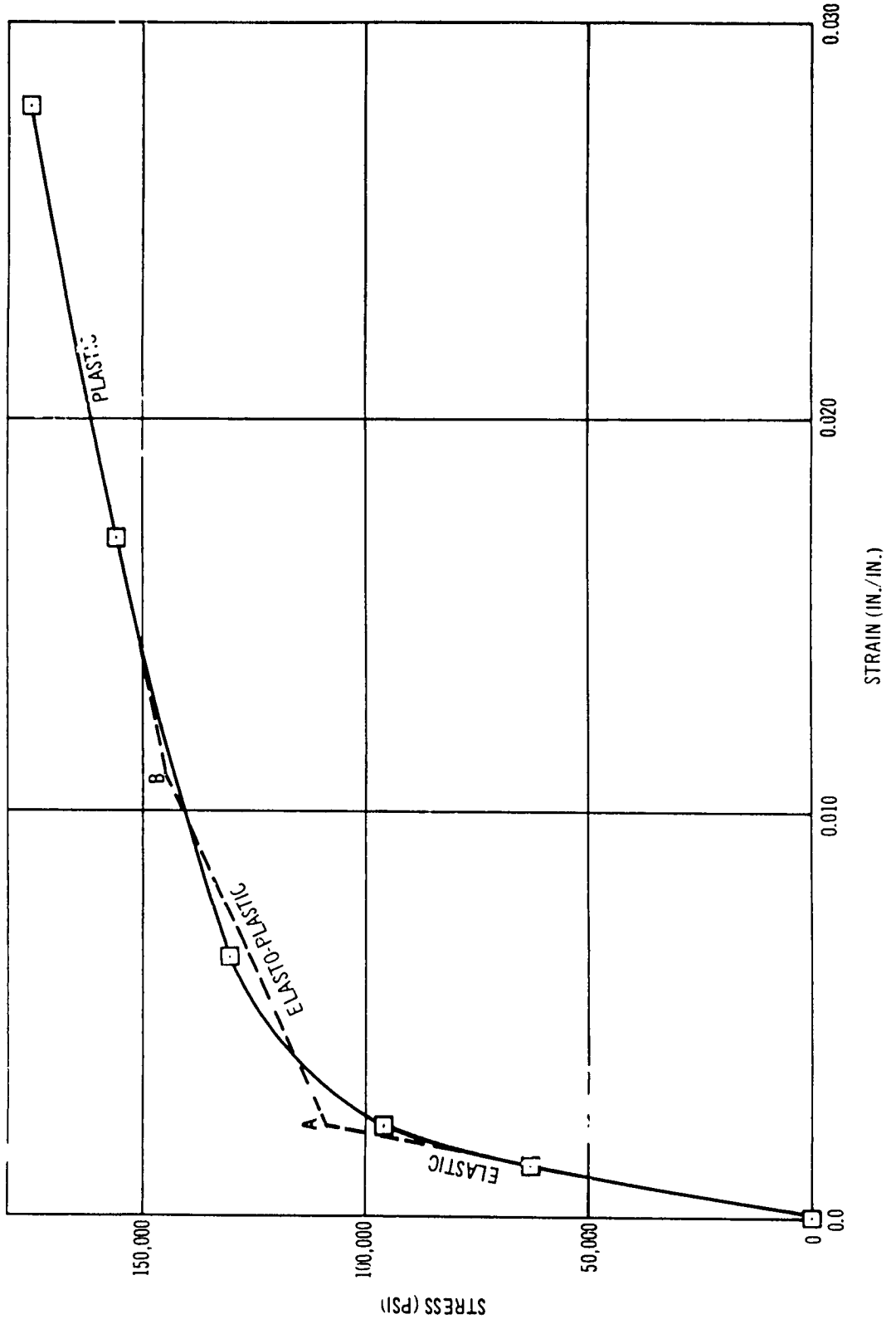


Figure II-4.3e. Compressive Stress-Strain Diagram for 304 S.S. Showing Three Phases of Compression

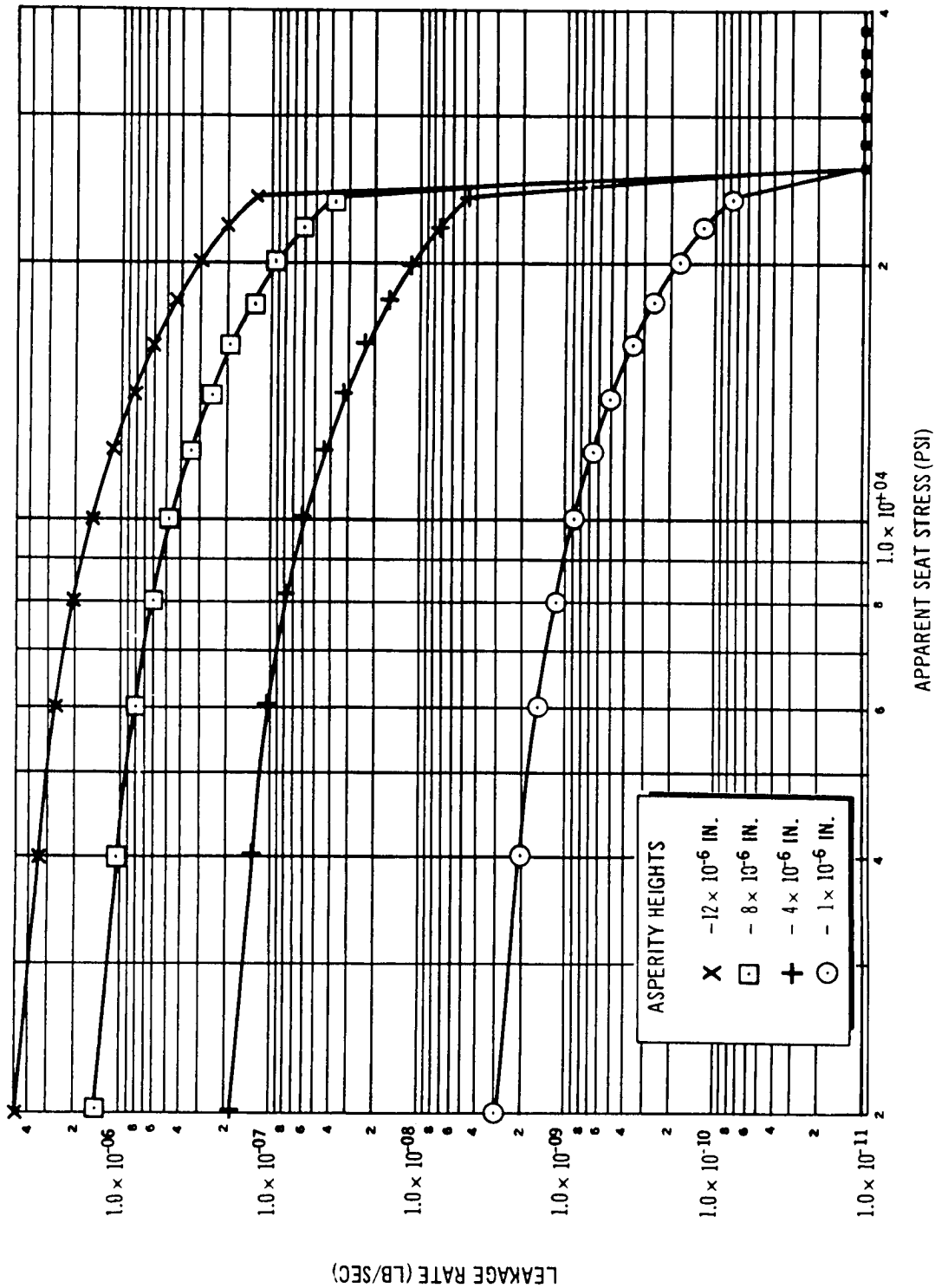


Figure II-4.3f. GF2 Seal Leakage (Monel/Monel)

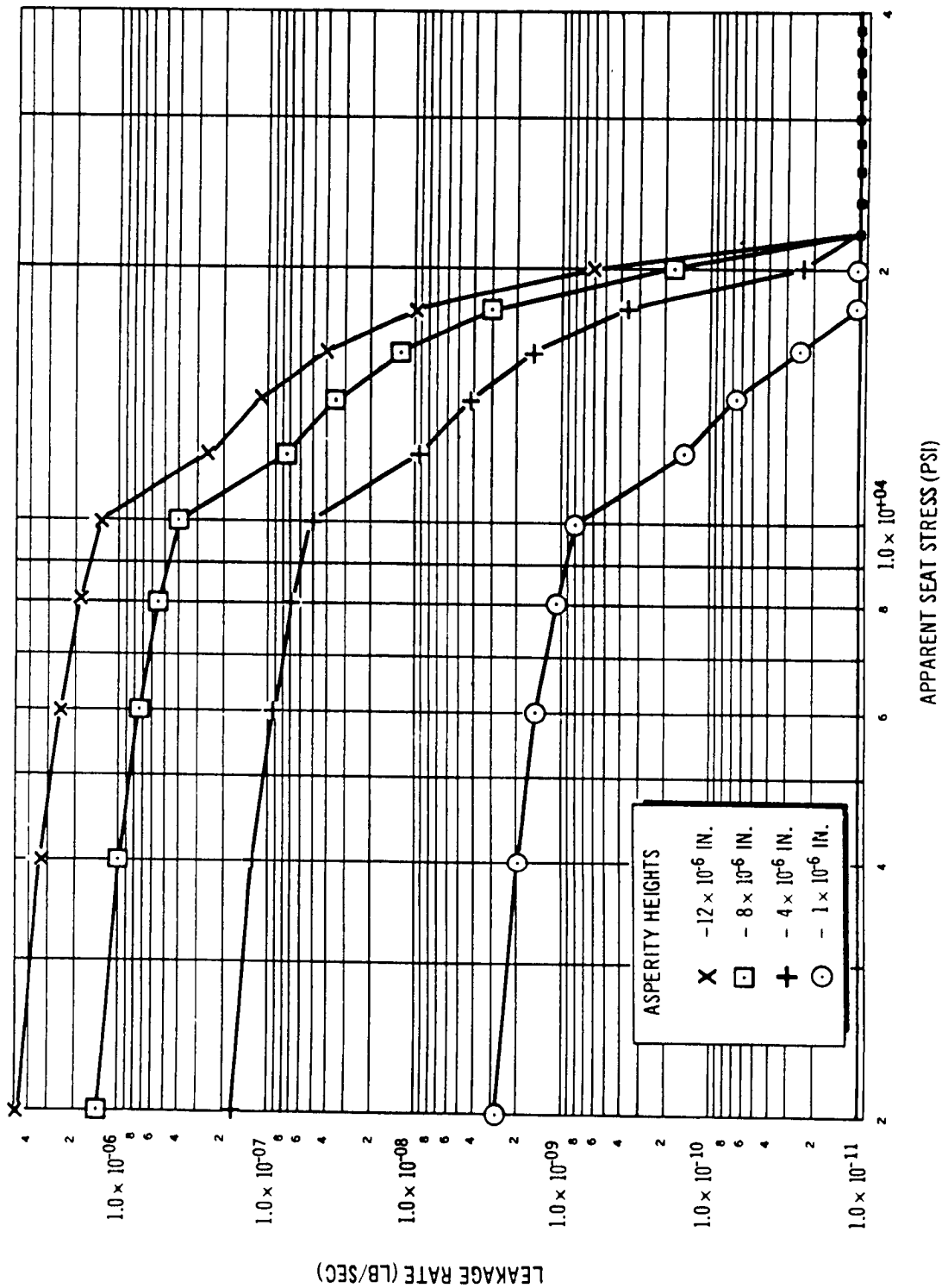


Figure II-4.3g. GF2 Seal Leakage (Steel/Copper)

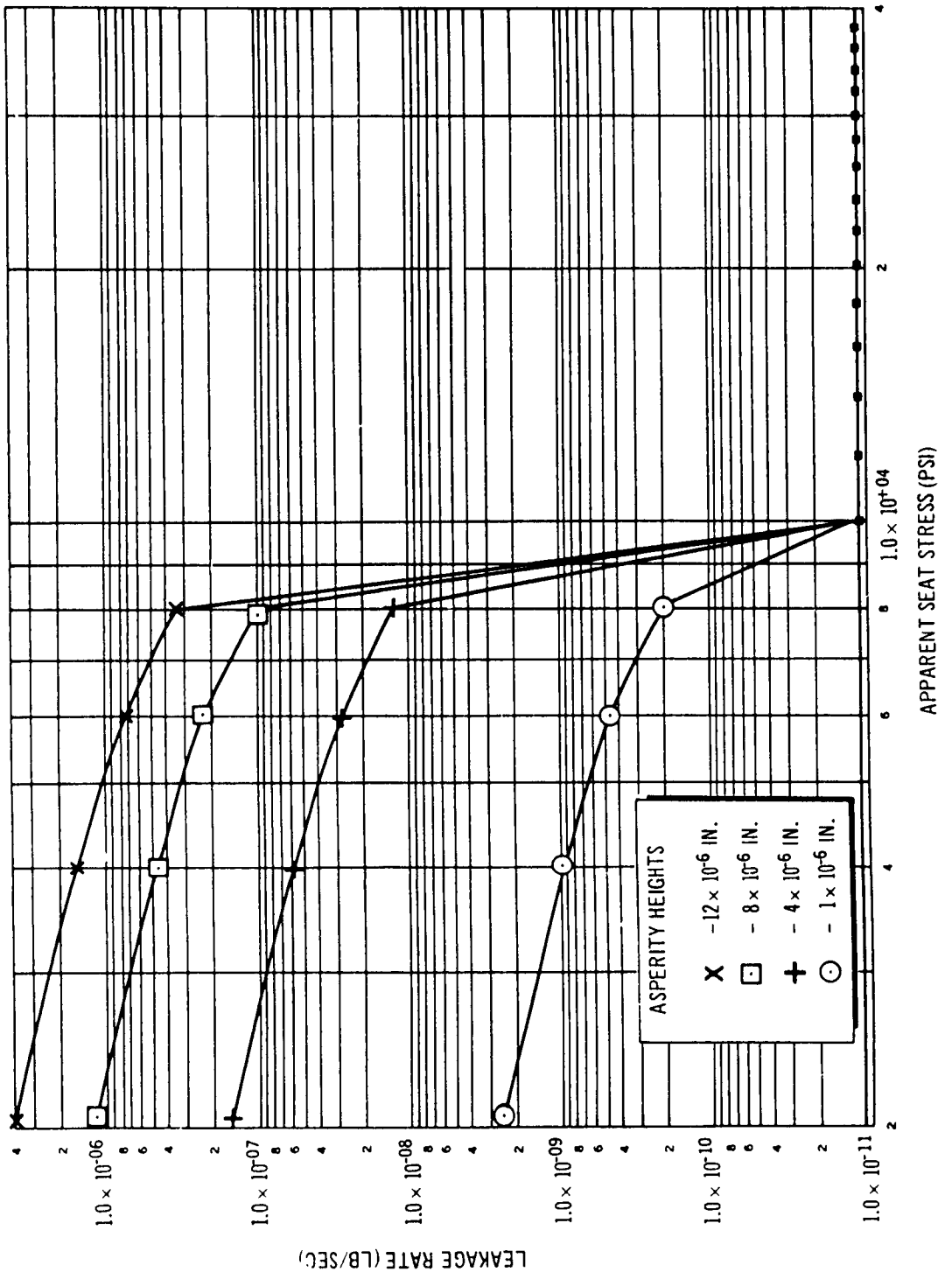


Figure II-4.3h. GF2 Seal Leakage (Steel/Aluminum)

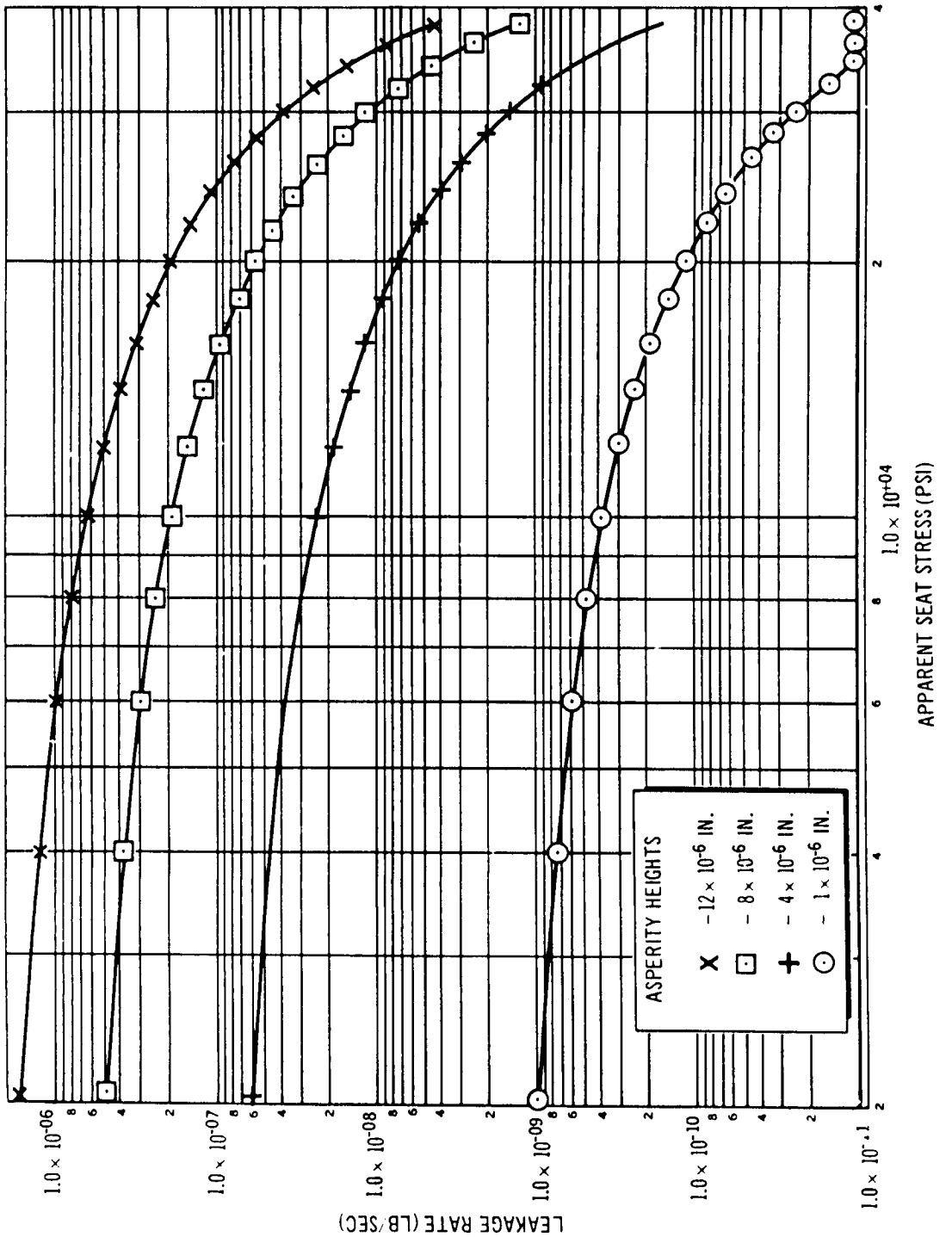


Figure II-4.3i. LF2 Seal Leakage (Monel/Monel)

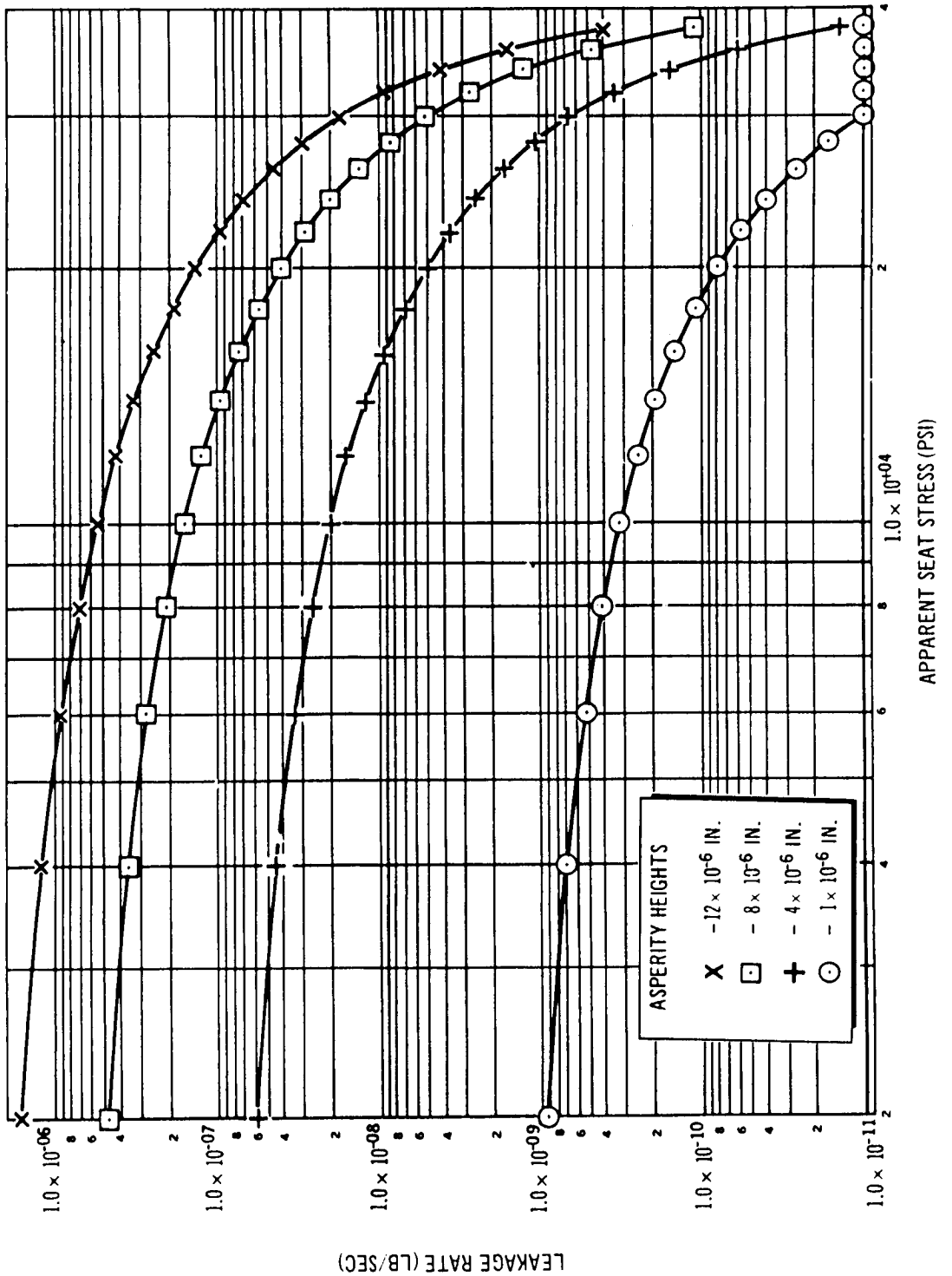


Figure II-4.3j. LF2 Seal Leakage (Steel/Copper)

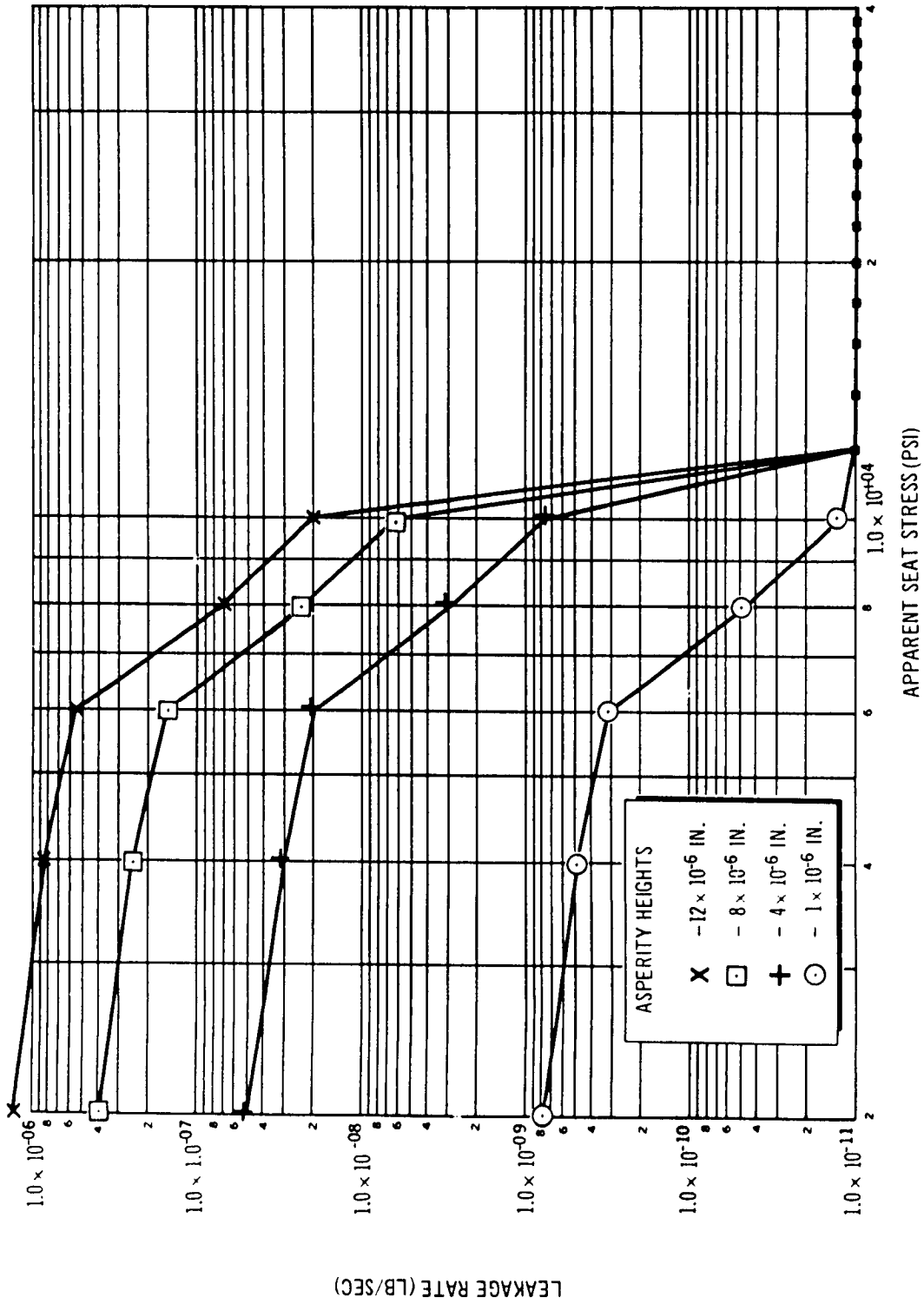


Figure II-4.3k. LF2 Seal Leakage (Steel/Aluminum)

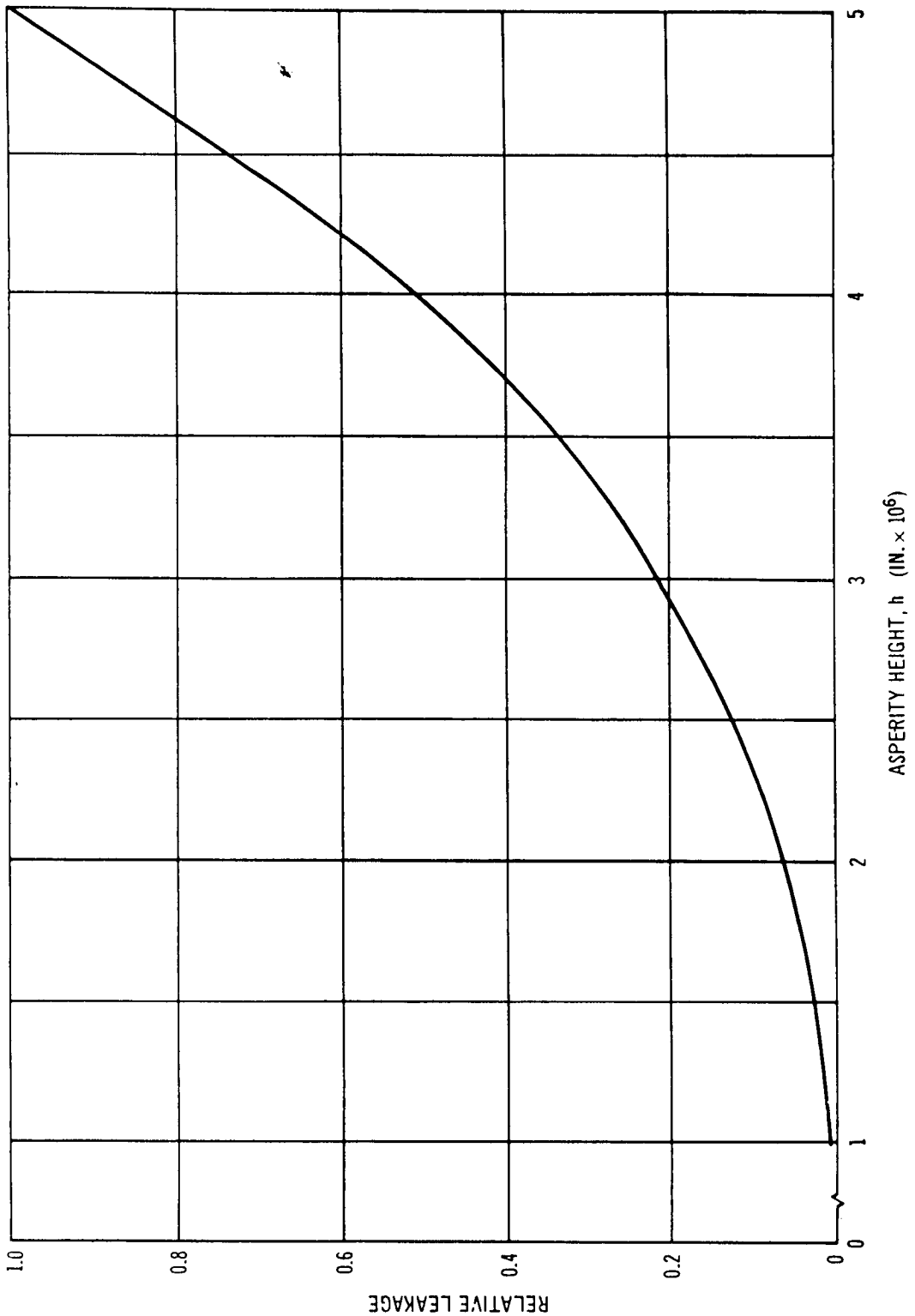


Figure II-4.3ℓ. Effect of Asperity Height on Leakage

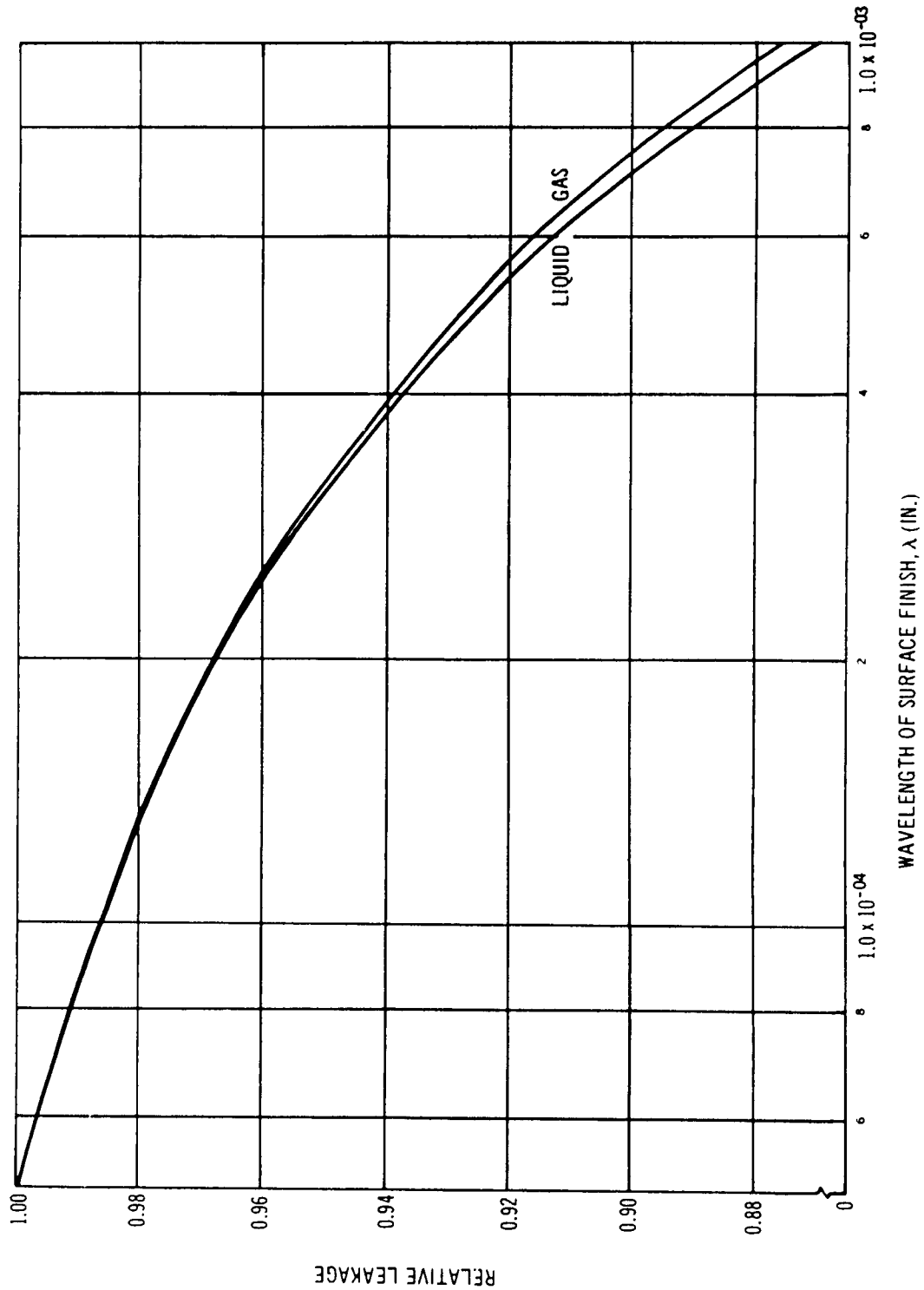


Figure II-4.3m. Effect of Surface Finish Wavelength on Leakage

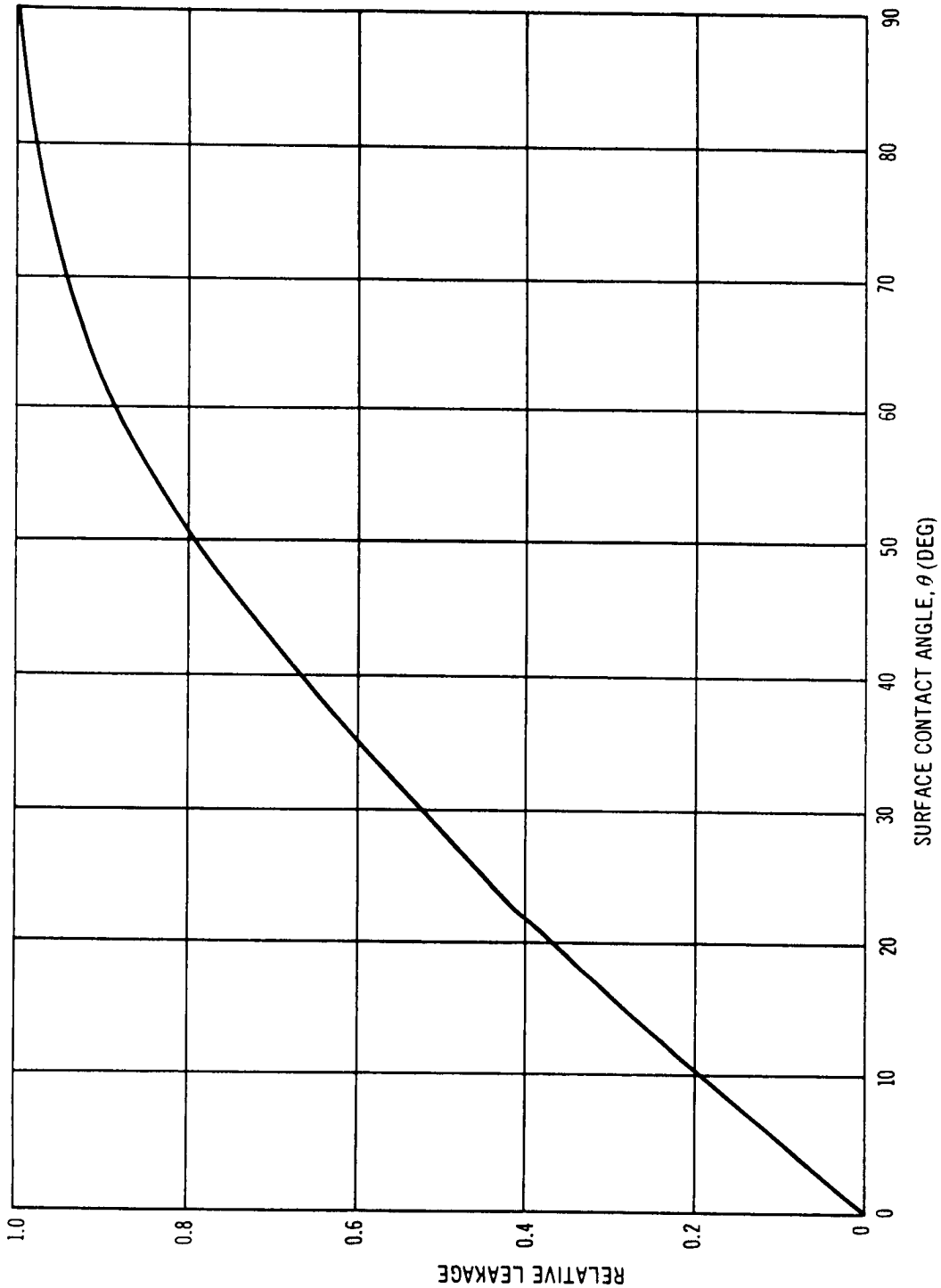


Figure II-4.3n. Effect of Surface Contact Angle on Leakage

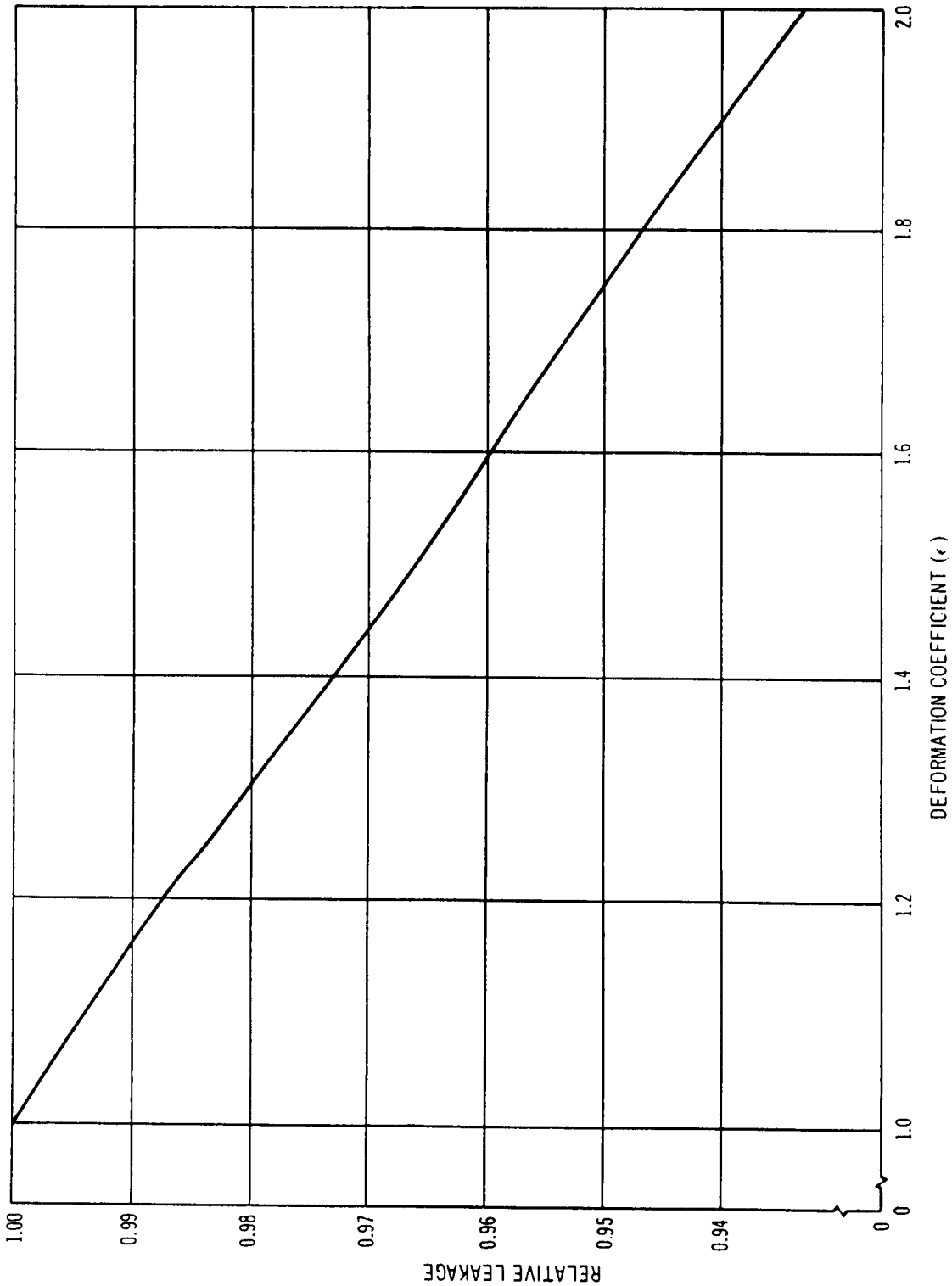


Figure II-4.3o. Effect of Deformation Coefficient on Leakage

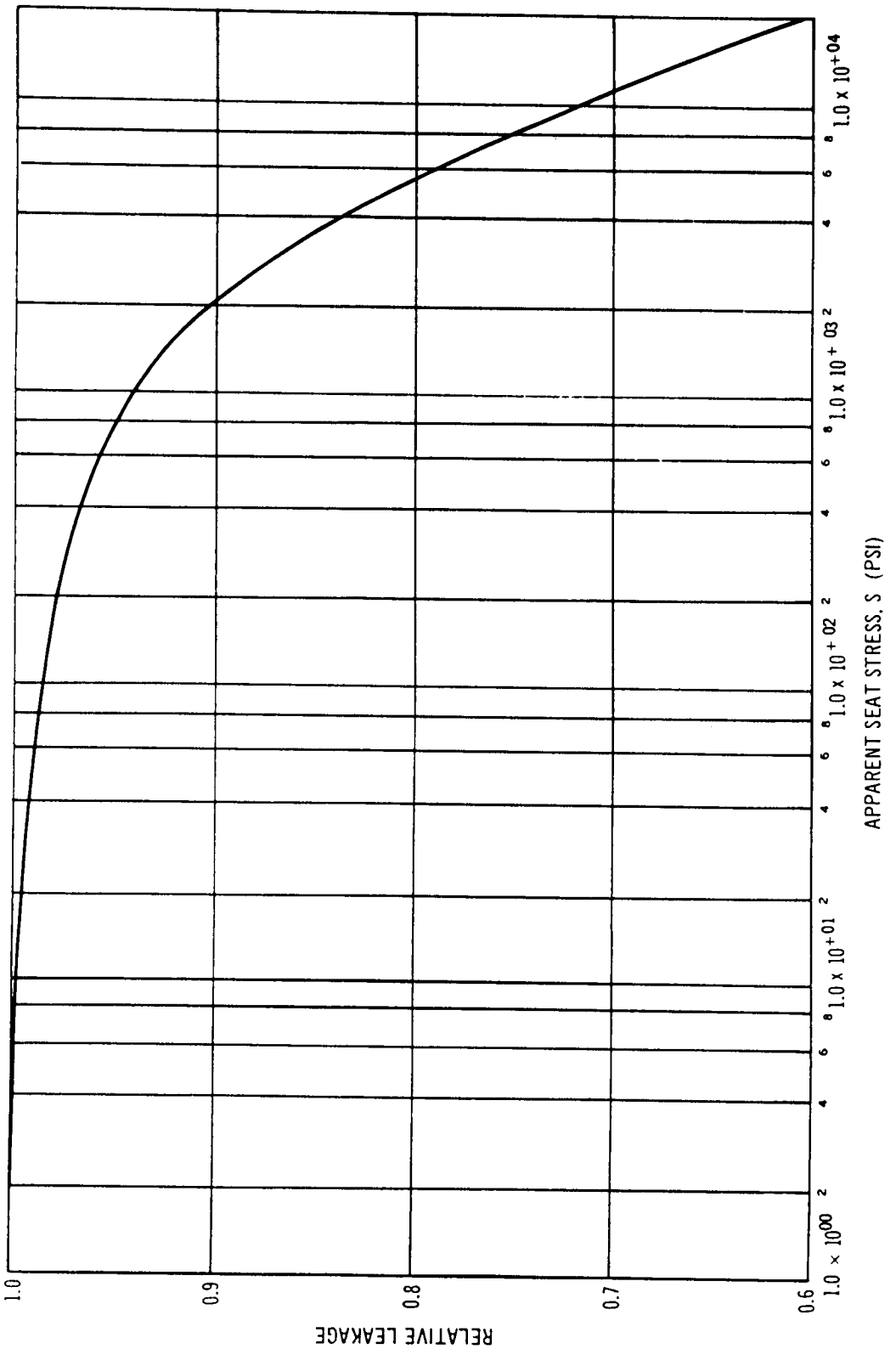


Figure II-4.3p. Effect of Apparent Seat Stress on Leakage

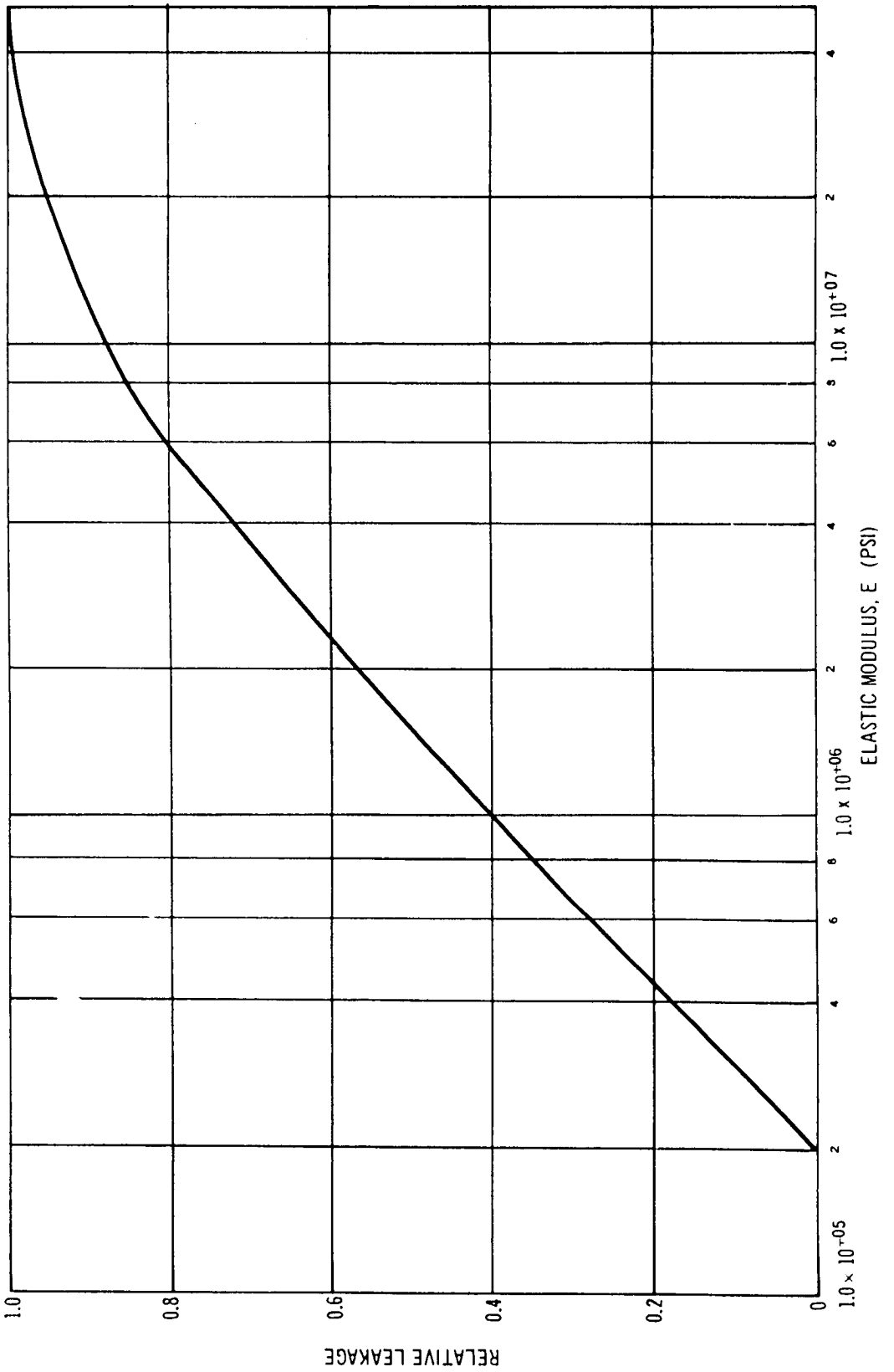


Figure II-4.3q. Effect of Elastic Modulus on Leakage

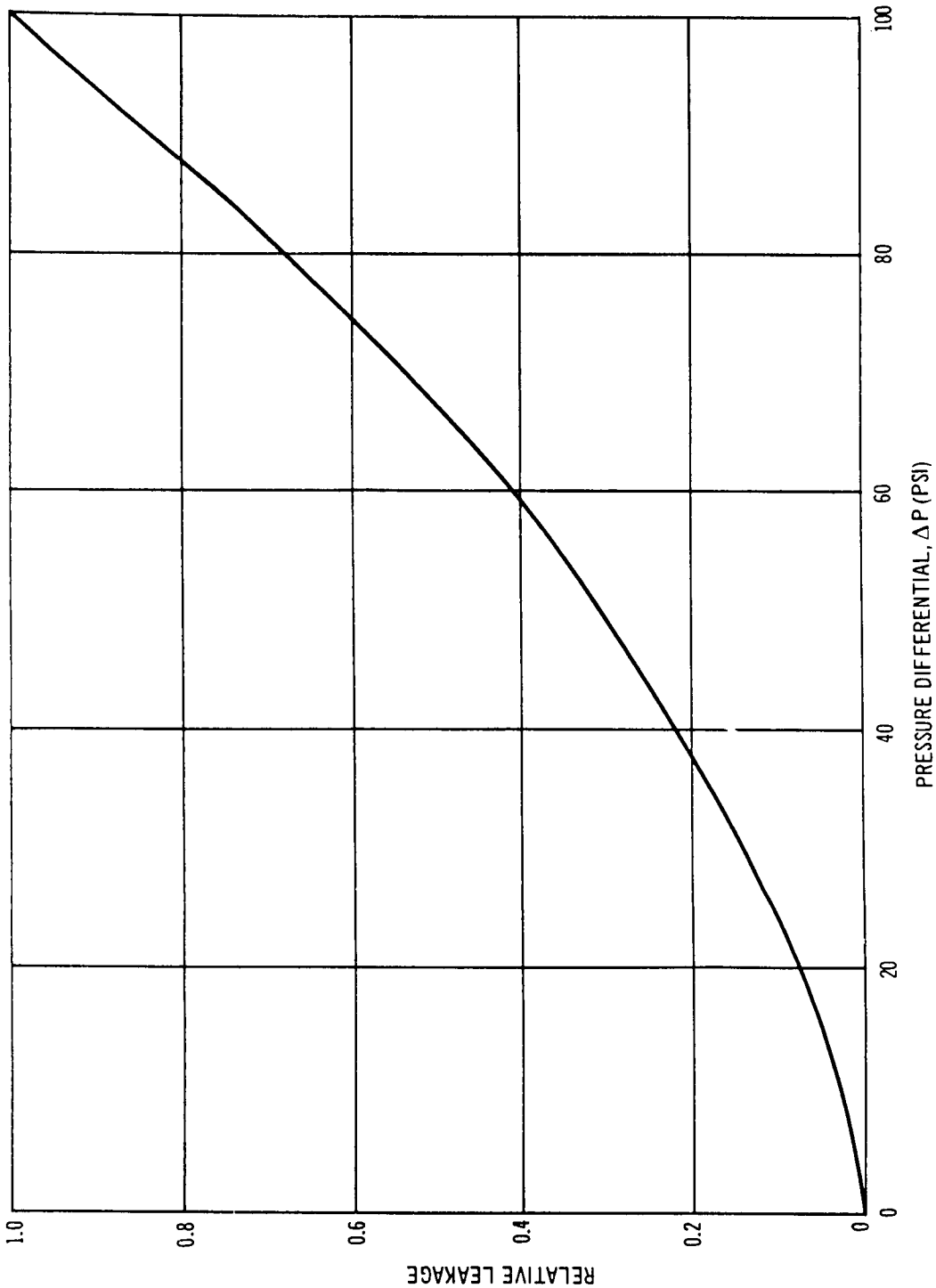


Figure II-4.3r Effect of Pressure Differential on Leakage

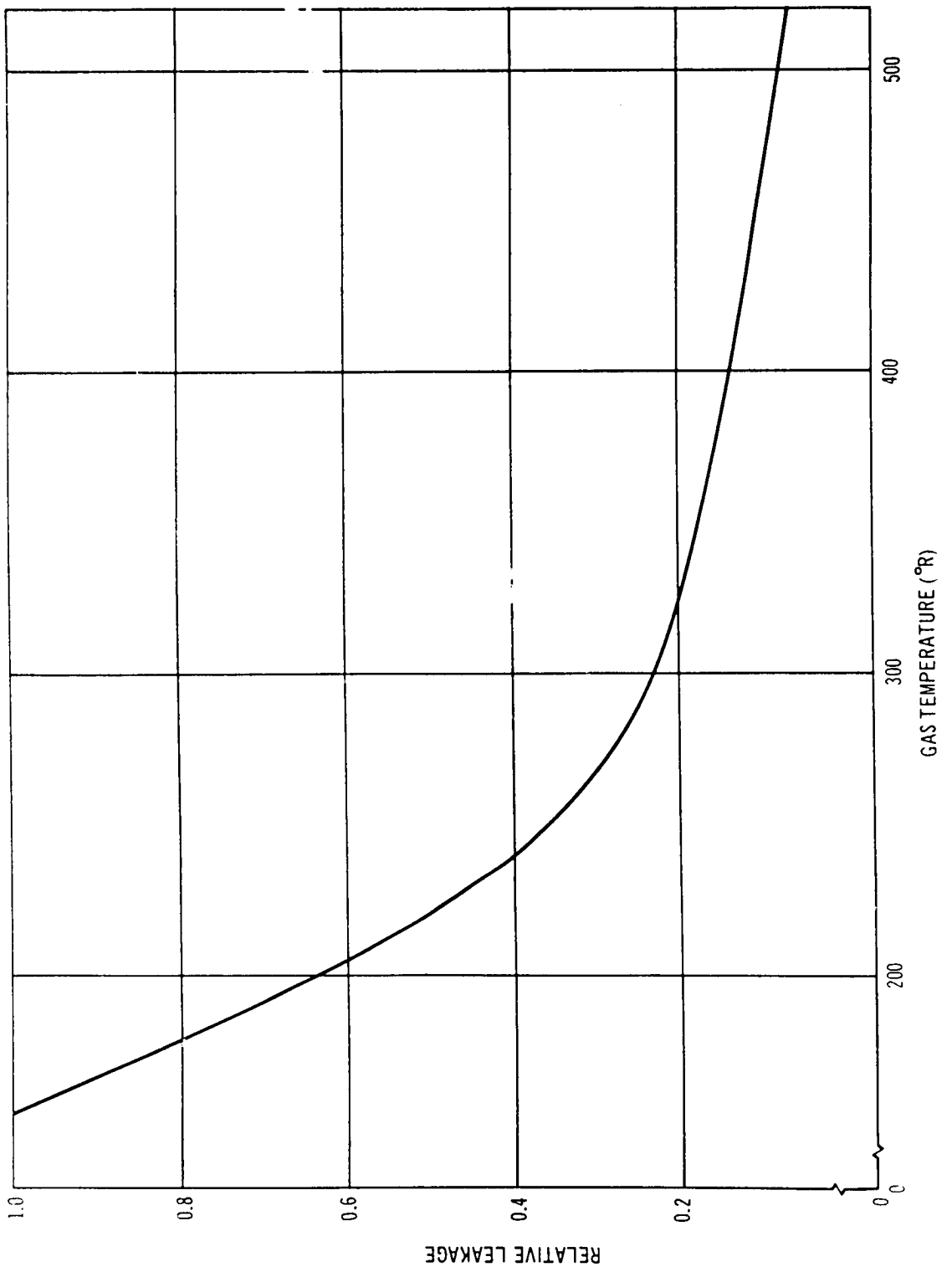


Figure II-4.3s. Effect of Gas Temperature on Leakage

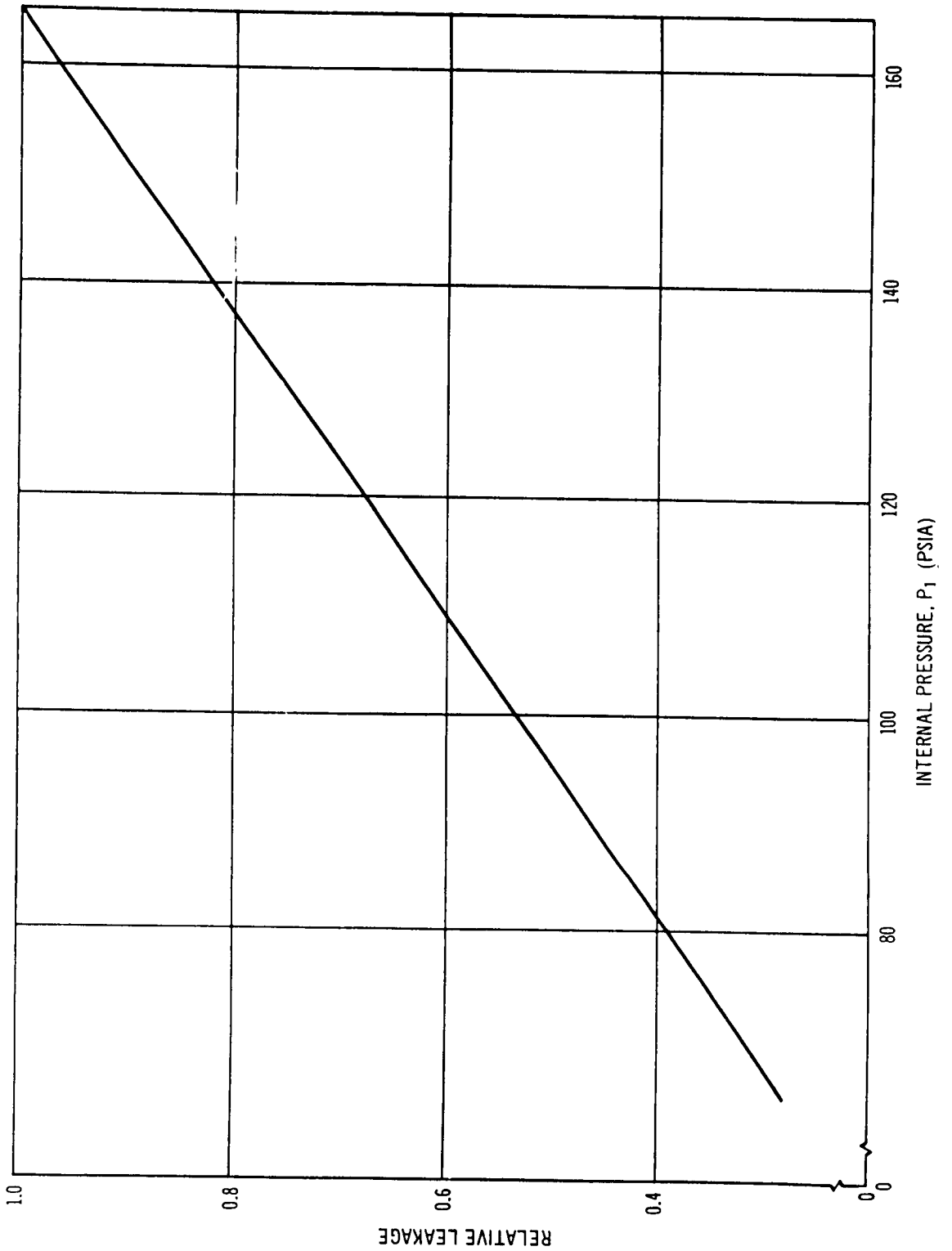


Figure II-4.3t. Effect of Absolute Pressure on Leakage

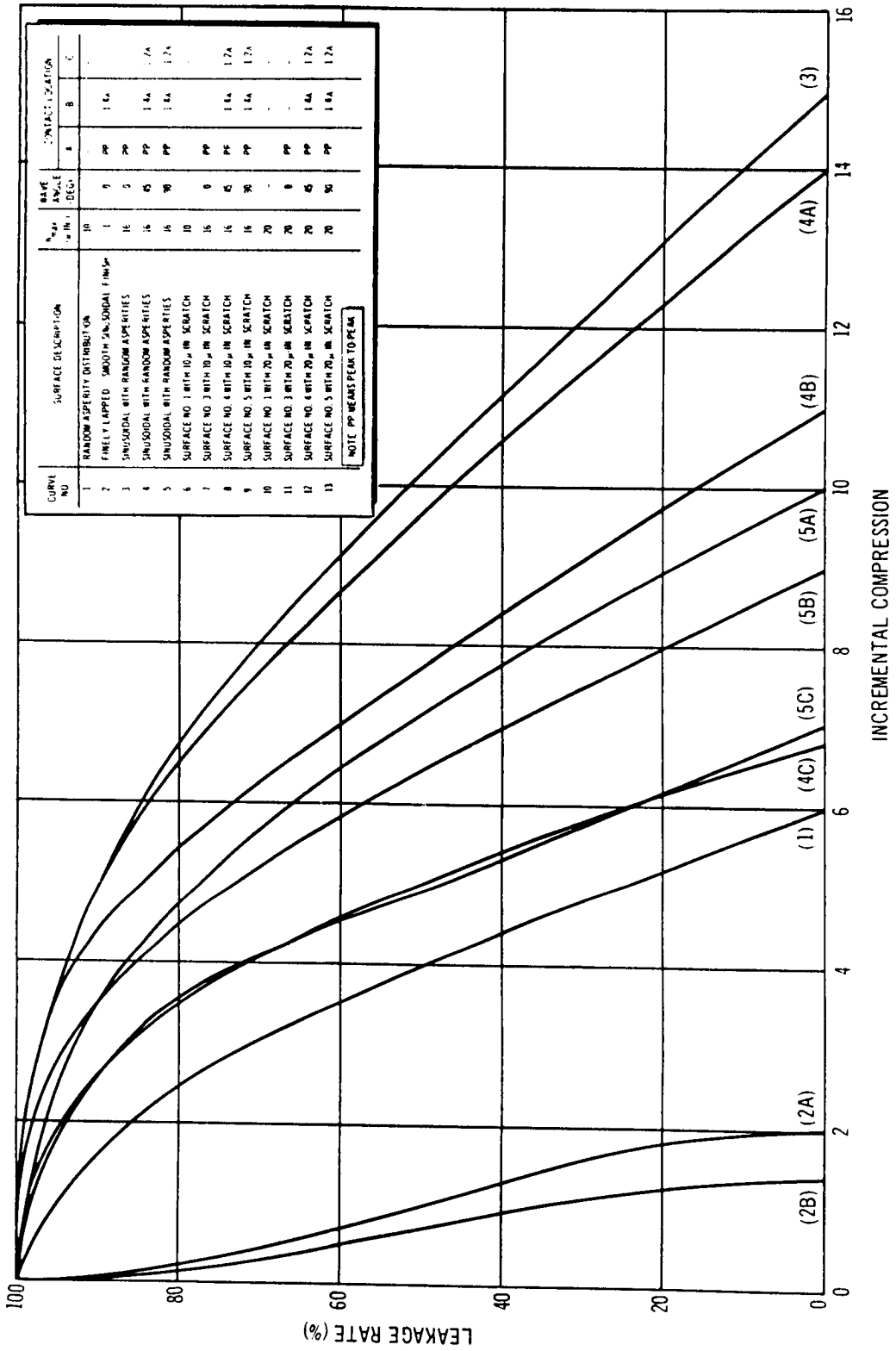


Figure II-4.3u. Leakage Flow Through Seals Compressed Elastically

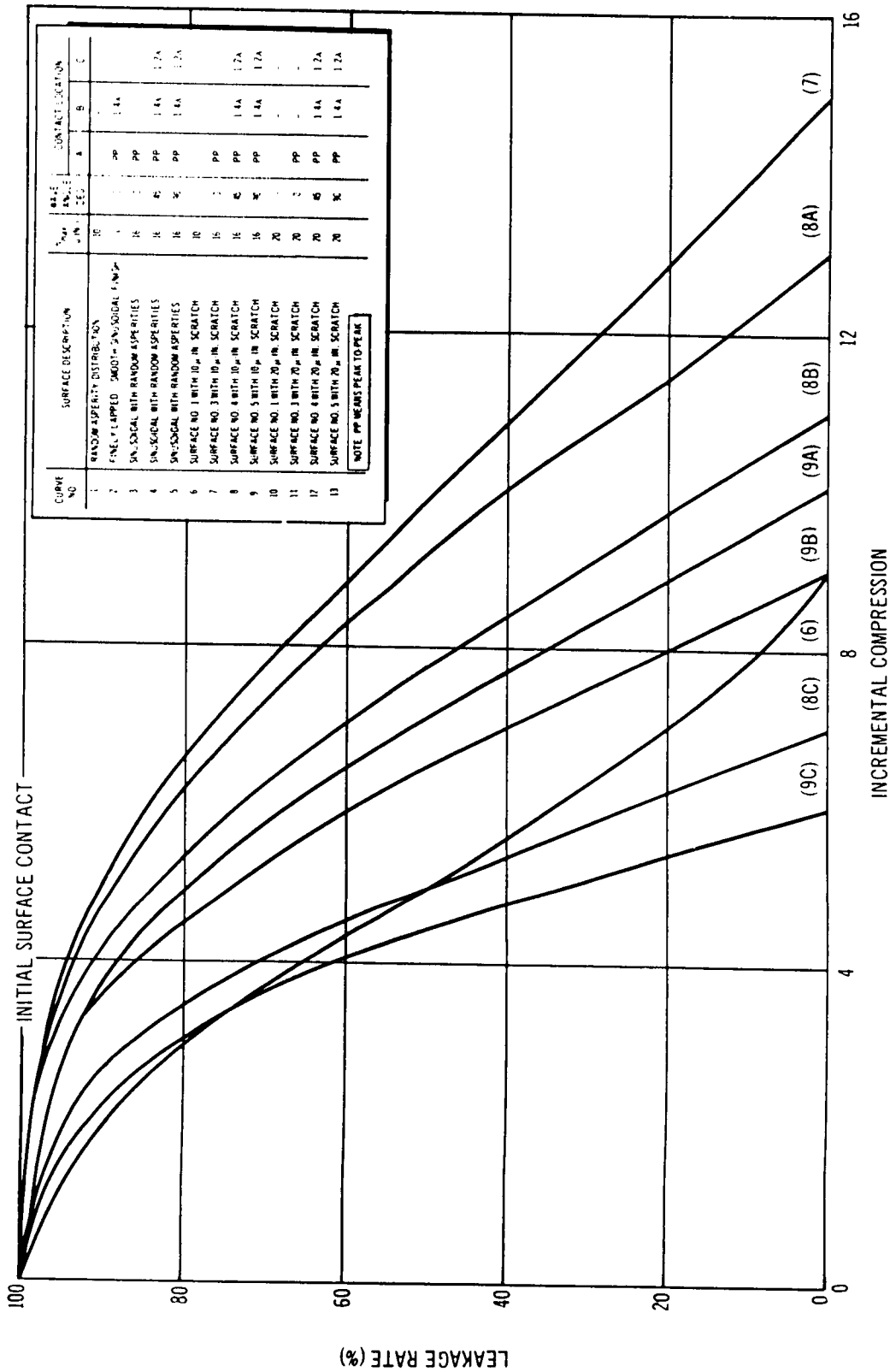


Figure II-4.3v. Leakage Flow Through Seals Compressed Elastically

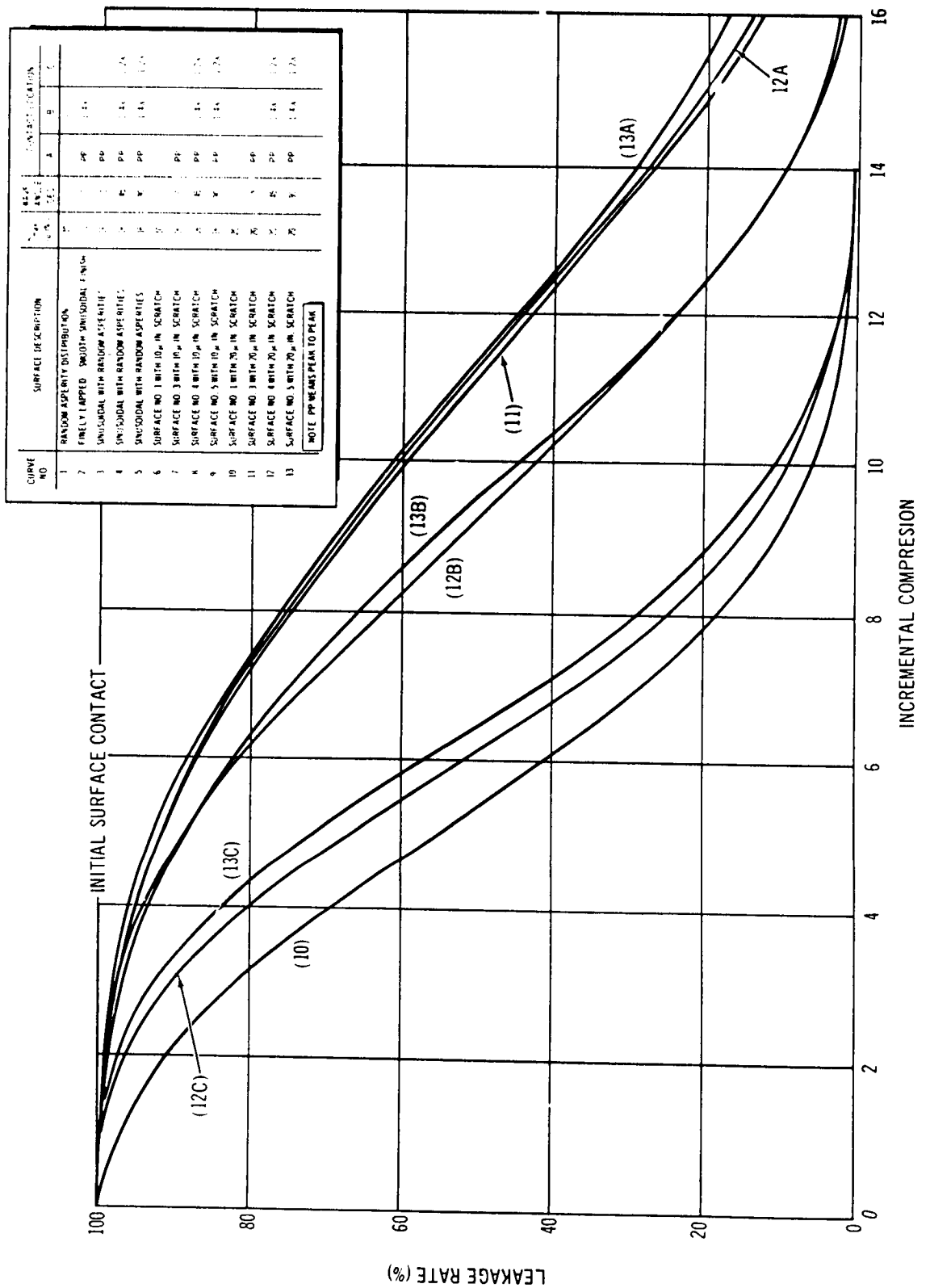


Figure II-4.3w. Leakage Flow Through Seals Compressed Elastically

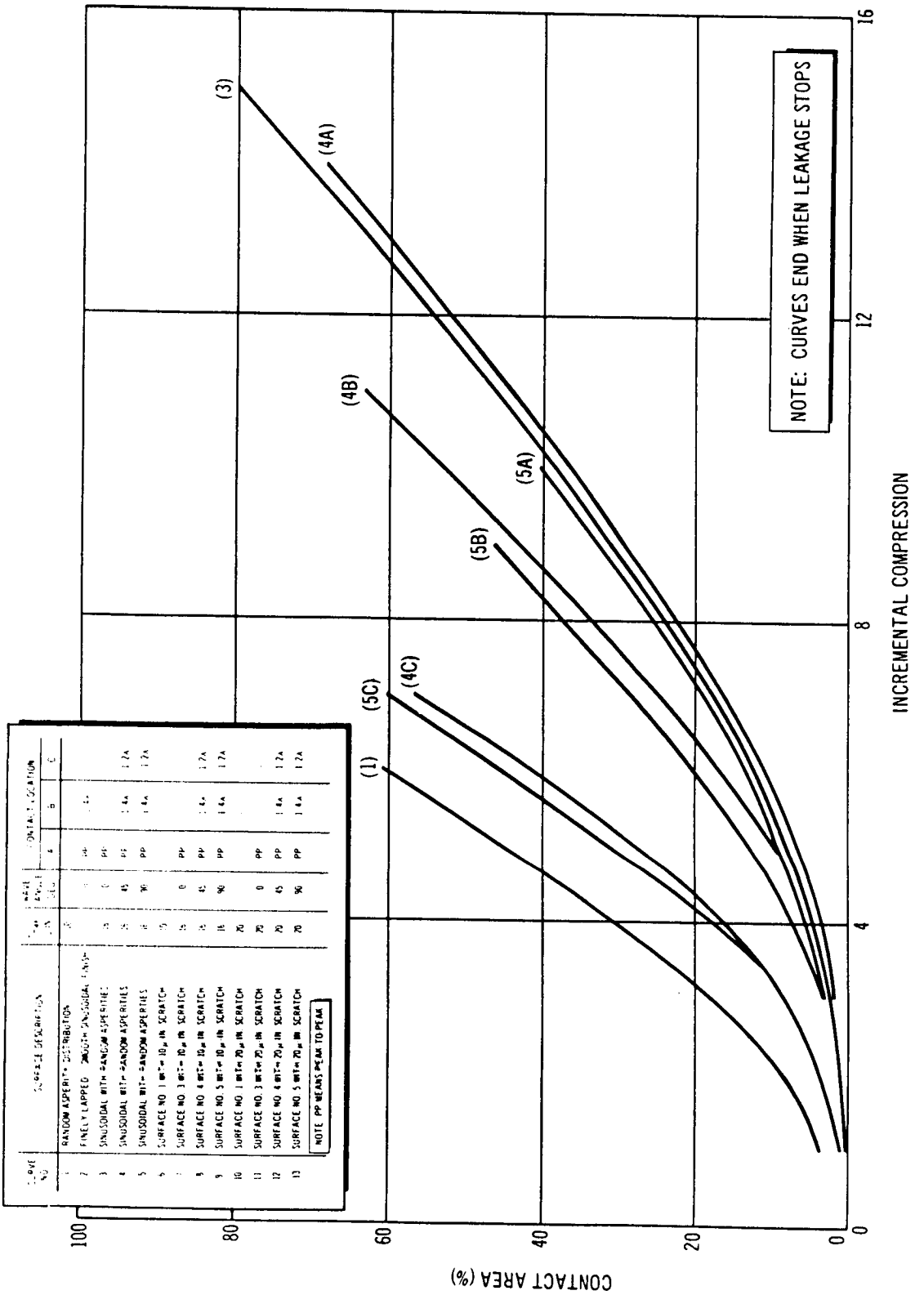


Figure II-4.3x. Seal Contract Area in Elastic Compression

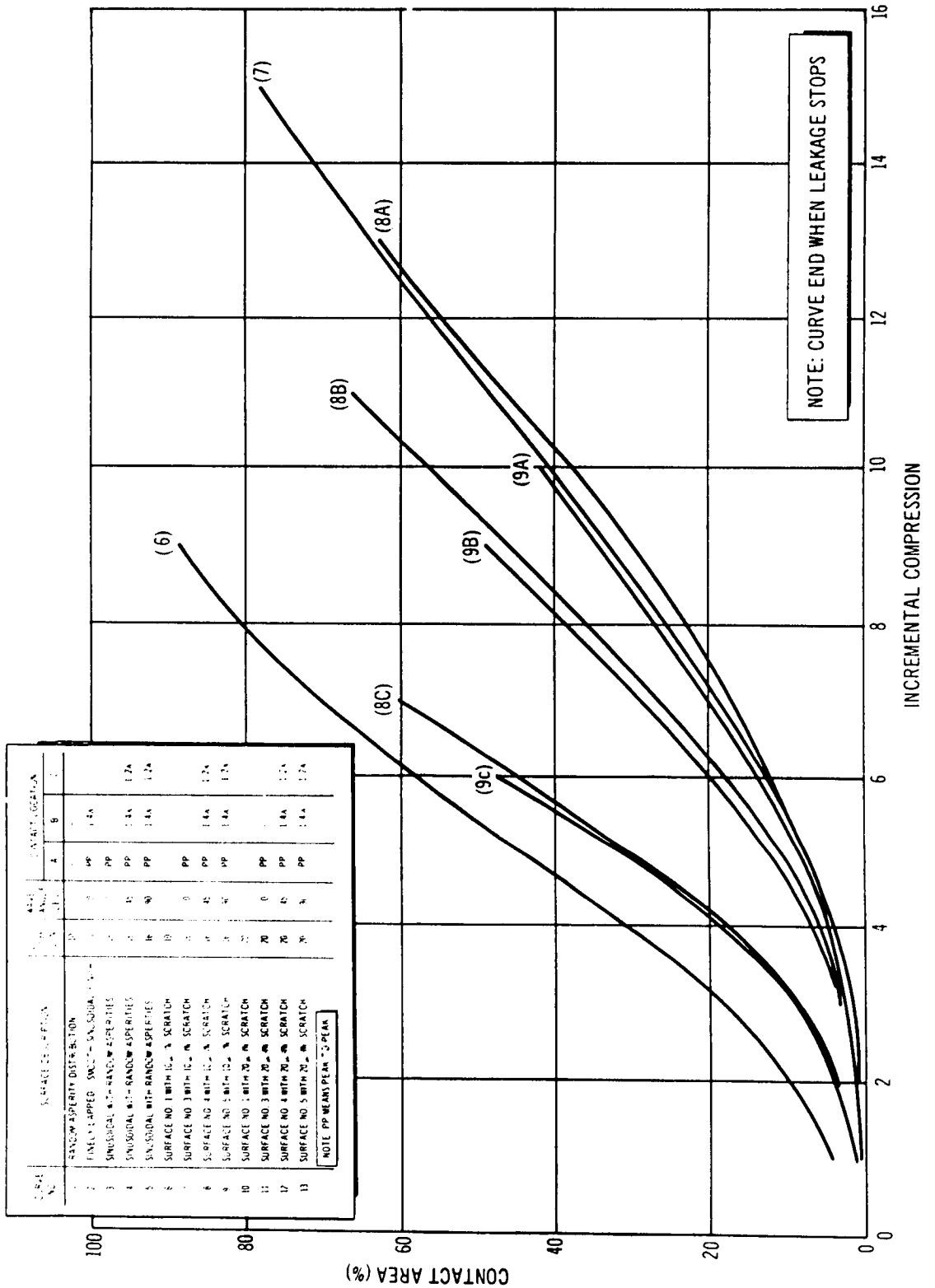


Figure II-4.3y. Seal Contact Area in Elastic Compression

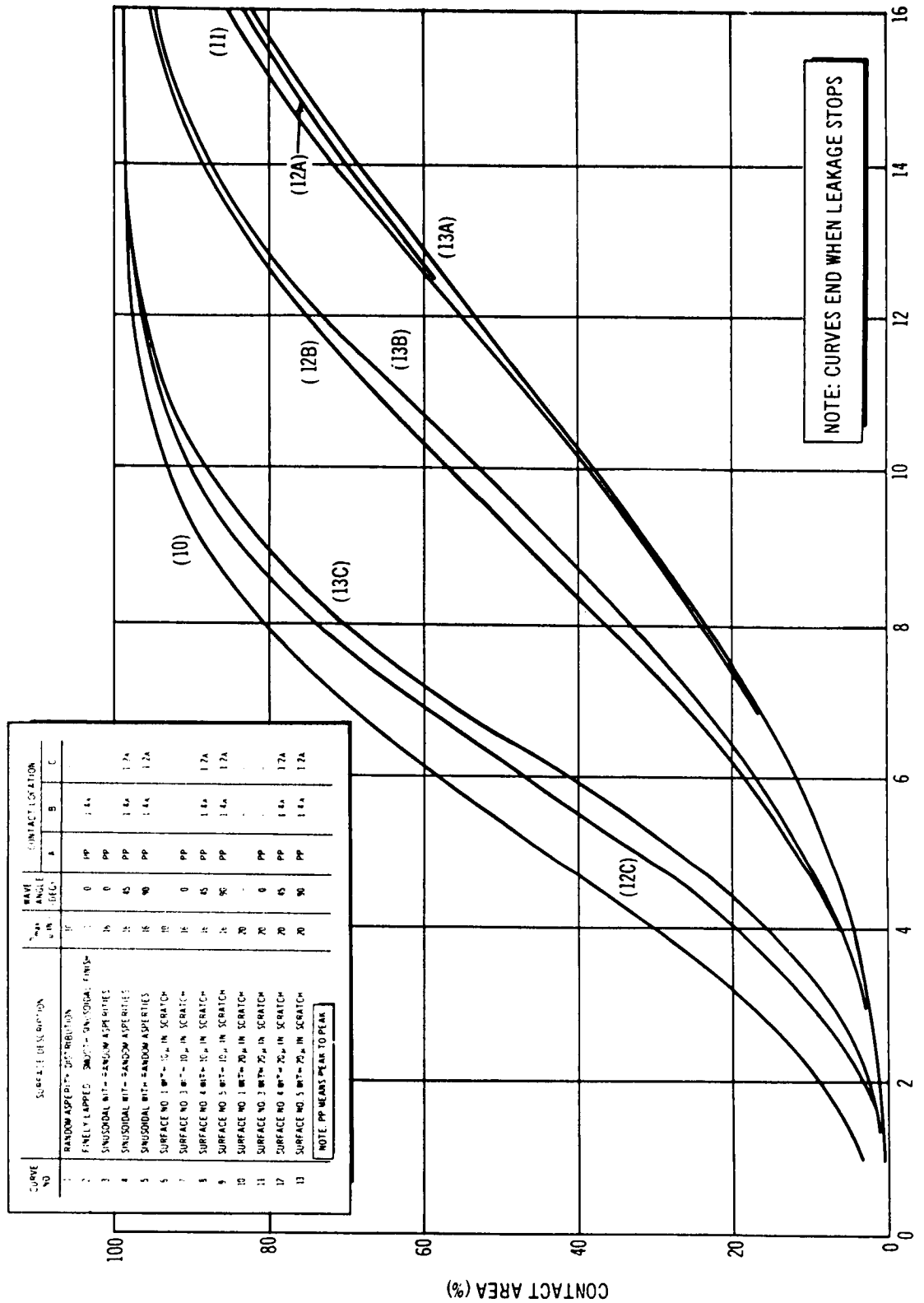


Figure II-4.3z. Seal Contact Area in Elastic Compression

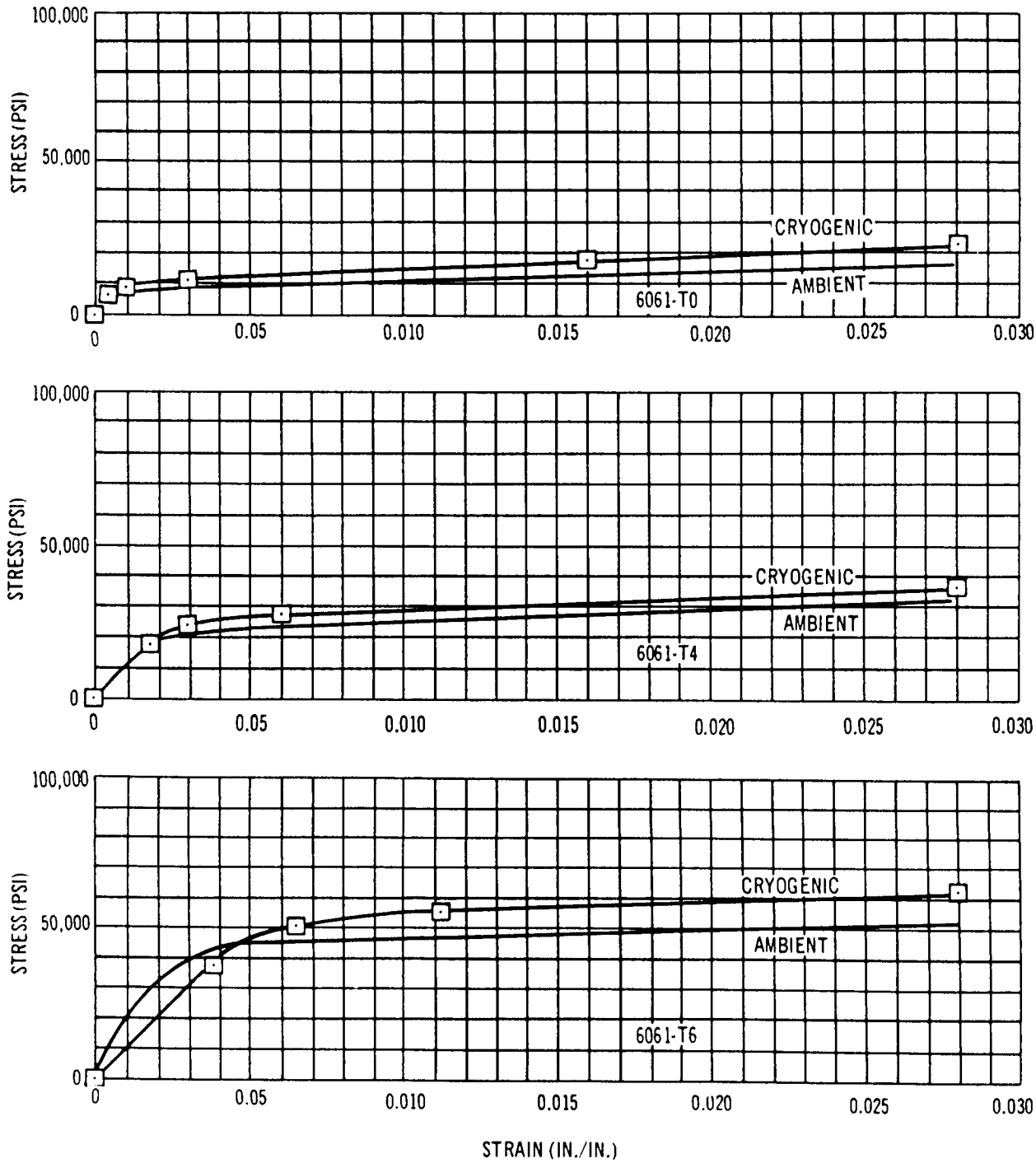


Figure II-4.4a. Compressive Stress-Strain Diagrams for Several Heat Treated Aluminum Alloys

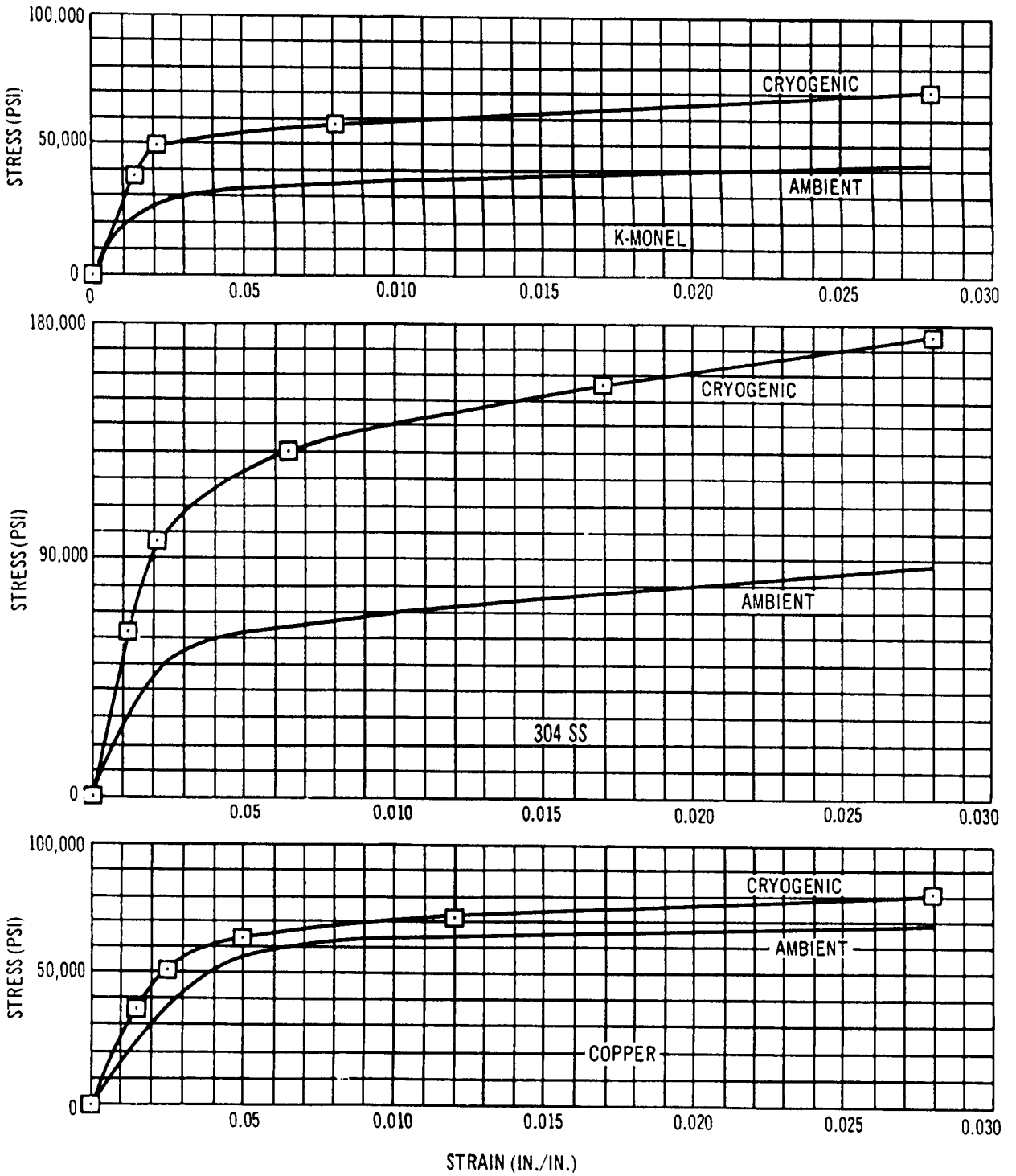


Figure II-4.4b. Compressive Stress-Strain Diagram Copper, 304 SS and K-Monel

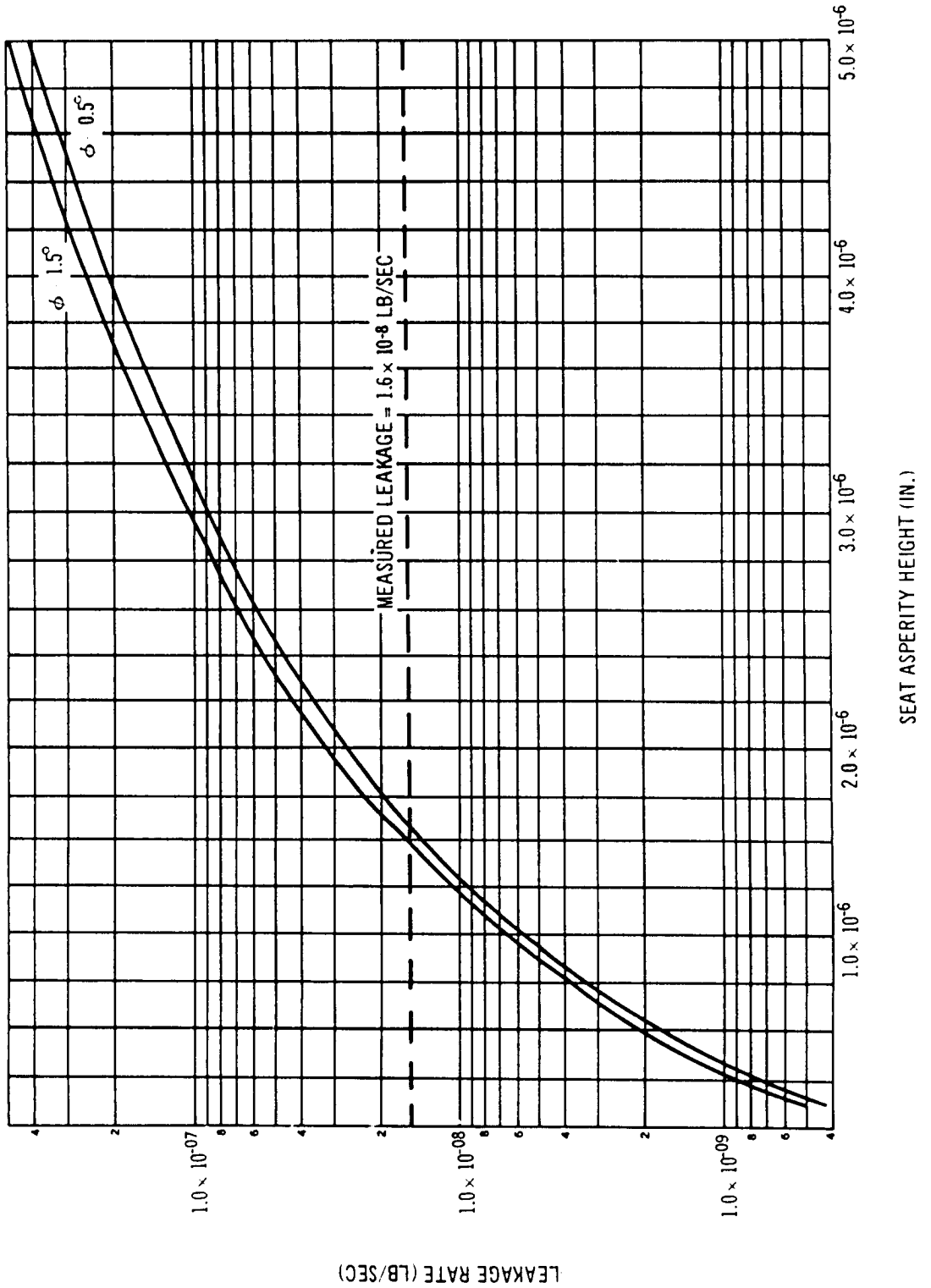
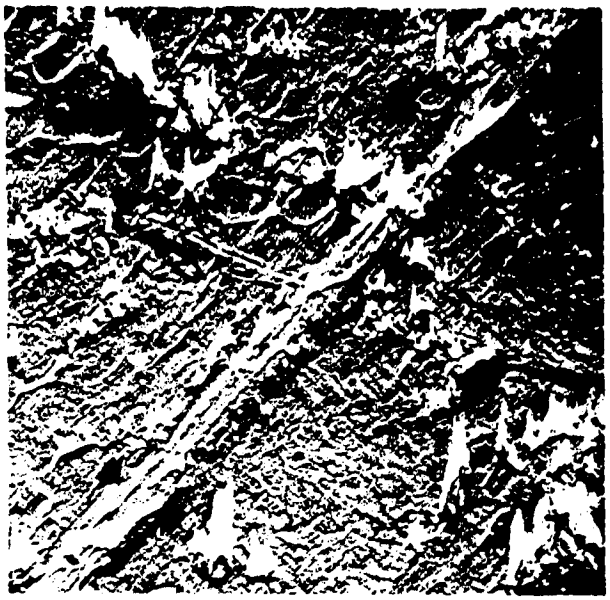
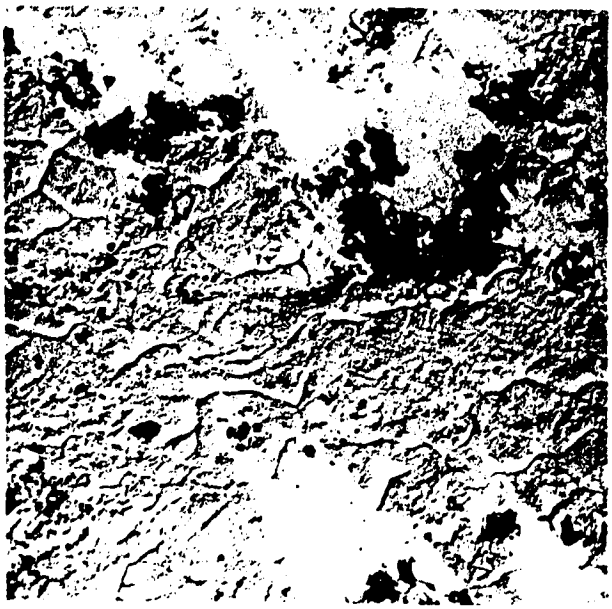


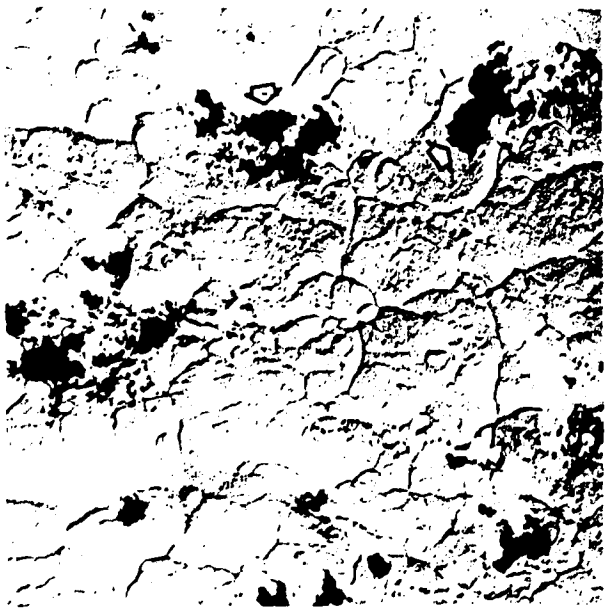
Figure II-4.4c. Seal Leakage, GHE (Monel/Monel)



SOLID ARROWS INDICATE MICRO-
SCOPIC GROVES. OPEN ARROWS
OPEN ARROWS POINT TO A SCRATCH



EVIDENCE OF EQUIAXED DIMPLES.
OPEN ARROWS POINT TO SURFACE
DEBRIS.



EVIDENCE OF EQUIAXED DIMPLES.
OPEN ARROWS POINT TO SURFACE
DEBRIS

Figure II-4.4d. Fractographs of Contact Surface Area After Fluorine Test

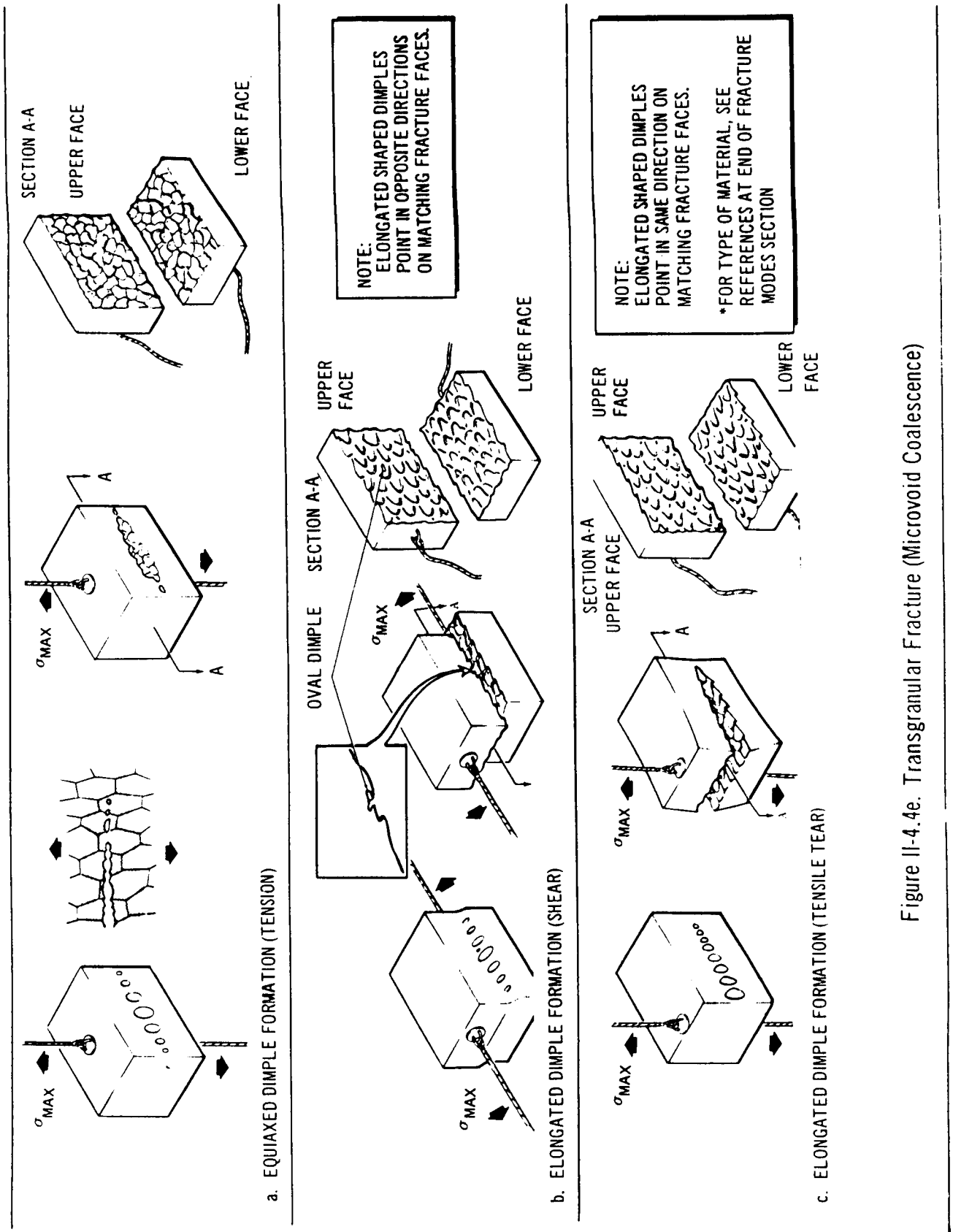


Figure II-4.4e. Transgranular Fracture (Microvoid Coalescence)

5.0 Energy Sensitivity

Energy can be introduced into a system component by four means: (1) external heating, (2) chemical reaction of the system fluid and the materials which it contacts, (3) impacting one component upon another, such as a valve poppet striking the seat during closing of the valve, and (4) fluid impact upon system components, fluid scouring of components, and fluid friction and cavitation at the fluid-component material interface. The major portion of this energy is converted into heat which raises the temperature of the material affected zone and the immediate surrounding fluid. This temperature increase is dependent upon the thermodynamic properties and masses of the affected material and fluid. Prediction of the material temperature plateau which can result from any one or combination of the above energy additions ranges from very good to outright guesswork.

5.1 External Heating

Energy additions due to external heating, such as, aerodynamic heating, solar radiation, etc., can be analytically predicted with a high degree of accuracy. The analytical techniques currently used to determine this heat flux are applicable to a fluorine feed system. The insulation required to maintain the heat input at the desired level will necessitate consideration of the insulation compatibility with fluorine, discussed in paragraph II-3.4.

5.2 Chemical Reaction

The energy additions due to exothermic reactions of fluorine and the materials with which it contacts is not predictable with any reliable degree of accuracy. The energy released from chemical reaction of fluorine and most elements or compounds are known quantities having been determined in the laboratory by actual test. Unfortunately the quantities and concentrations of the element and compound constitutents of the material surface which would contact fluorine is at best only grossly predictable. Further, contaminants will undoubtably be lodged on the material surface, the composition, quantity, and concentraction of which will be unknown. Passivating the components per Appendix III-5 prior to the functional operation of the system permits the

addition of the exothermoic chemical heat energy with a minimum addition of the other types of energy inputs listed above. By permitting this individual energy addition, there is sufficient time for any heat input to be dissipated and any resultant material increased temperature can revert back to its initial temperature level before system operation. If this passivation is performed per Appendix III-5, and recontamination of the system is prevented, this type of energy addition can be discounted in any evaluation of the functional operation of the system. It should be noted, however, that any structural failure of a component (one which does not compromise the system) which is contacted by fluorine, or leakage of reactive contaminants into the system, locally provides additional energy to itself and the surrounding fluid and components. Evaluation of such additions is difficult if not impossible.

5.3 Component Impacting

Some materials which will not spontaneously ignite when in contact with specific fluids, will ignite or explode when subjected to certain levels of impact or shock while in contact with or immersed in the same fluid. The need for determining which materials would exhibit such characteristics in liquid oxygen resulted in development of the Army Ballistic Missile Agency (ABMA) impact sensitivity test, (Reference 293). This test consists of impacting a test specimen, placed in a metal cup filled with liquid oxygen which is supported on a flat anvil, with a weight dropped from a known height. Because of the variation of test results obtained by various contractors using the ABMA test methods, the Air Force Wright Air Development Command, issued a specification, (Reference 294), to standardize the impact test procedures, using the ABMA test equipment. The Air Force primary acceptable impact-insensitivity level for any material, to be used in a liquid oxygen system, is "no reaction" of the material in twenty consecutive impact tests at seventy foot pounds of potential energy, (per Reference 294) while submerged in the cryogen. The NASA specification, (Reference 296) is primarily the same as described above except that the potential energy of the impacting weight is seventy-two foot pounds instead of seventy. To date, no such test procedures or acceptable insensitivity levels have been established for evaluation of materials subjected to impact in a fluorine environment. Until

this is done it is recommended that the ABMA impact sensitivity test be used to compare various materials for fluorine service. The user of the results of such tests, must be cautioned that the results may have no quantitative meaning. In general, no reaction means compatible while a reaction may not mean incompatibility.

In order to evaluate material sensitivity in liquid fluorine, various investigations have employed the use of a modified ABMA tester. One of the modifications of the tester, was made only in the anvil area and permits the specimen and liquid fluorine, and the cup in which they are contained, to be maintained at a temperature of -320°F by surrounding the specimen cup with liquid nitrogen. Figure II-5.3a diagrams this tester. This cooling is necessary since the application of the liquid oxygen technique, simply pouring a large excess of liquid oxygen on the entire anvil assembly, is uneconomical and, more important presents a health and safety hazard due to the high toxicity of fluorine. The acceptable insensitivity level using this modified tester has been assumed to be the same as described in Reference 296.

With this basis of acceptability, a series of seventy-two foot pound impact tests were performed with specimens of case aluminum alloy A356 in a T6 heat treated condition using the above described modified ABMA tester, (Reference 97). A total of thirty-eight tests were performed with no reaction of the aluminum and fluorine. The test specimens were made up of three different levels of material porosity; Grade I-F, III-F, and IV-F, as defined in NASA specification MSFC-STD-100. Of this total of thirty-eight, twenty-six specimens were classified as Grade III-F and six each as Grade I-F and IV-F. The results of these tests indicate that uncontaminated case aluminum A356 possessing a porosity level no greater than III-F is acceptable for use in any airborne fluorine feed system as far as compatibility is concerned. Surface degradation and silicon leaching may preclude its use however. Paragraph II-2.6.1.1.4, presents a detailed discussion of this phenomena.

Additional tests were performed on A356-T6 case material after having a dye penetrant applied to the surface and then cleaned for fluorine service prior to being impacted. Two types of dye penetrants were used; (1) oil base, Penetrex Z1-22 (Magnaflux Corp.), and (2) water soluble, SKL-4

Penetrant and SKD-W Developer (3M Co.). Six specimens each of Grade I-F, II-F, and IV-F levels were tested with the oil base penetrant. One reaction occurred in each of the grade levels tested (one in six). Twenty specimens of Grade IV-F were tested with the water soluble penetrant with one reaction occurring (one in twenty). Based on the assumed acceptability limit (no reactions in twenty consecutive tests), the use of dye penetrants as an inspection tool is not recommended for use with fluorine service components until further testing results show more positive data.

Some impact testing was performed in liquid fluorine and described in Reference 47. These tests were performed primarily using Monel striker pins on titanium samples. A few tests were conducted with titanium striker pins on titanium samples and aluminum and stainless steel striker pin on aluminum samples. The energy transfer surfaces of the striker pins used were of various shapes; flat, conical (sharply pointed), hollow pointed (small flat tip had 1/16 inch diameter hole drilled in center), chisel pointed (1/4 inch knife edge), round; with the impact level ranging from 2.6 to 65 foot pounds. The results of this testing were not very reproducible and in no case was ignition generally observed with liquid fluorine. The lack of reproducible results indicates that these data would be questionable in the direct application within a fluorine system.

Several types of dynamic tests were performed in liquid fluorine and described in Reference 42. One series of tests, impacted specimens of 1100-0 aluminum and 347 stainless steel with seventy-two foot pounds of energy using the modified ABMA specification. No specimen ignition occurred in any test when the test cell air had previously been dehumidified. The number of tests performed on either of the above materials is unknown.

It should be borne in mind that any of the test data obtained from such impact testing is solely qualitative and not directly applicable to a specific design problem. This type of test is actually a "go-no-go" test based solely upon past performance and experience. There is no agreement upon what particular mechanism causes a material to react under the test conditions nor a means of predicting the impact level at which a reaction might occur. One theory of the reaction mechanism, (Reference 298) attributes the ignition source to localized hot spots resulting from the adiabatic compression of trapped gas

bubbles or surface defects. If the dissipation of heat does not quickly lower the temperature of the localized region, a reaction may be initiated from the hot spot and the reaction zone grows by a normal thermal process. Another theory, the maximum-rate theory, (reference 295) assumes that nearly all of the plummet energy goes into elastic strain energy of the impacted specimen, ignoring the elastic strains of the striker pin, cup, anvil, and plummets.

The reaction is attributed to the assumption that the impacted specimen material is not solely homogeneous as assumed by Hooke's law. The variations in different crystals and impurities in them require a series of adjustments as the material strain is increased. The adjustments (slip-intervals) are discontinuous enough to provide trigger-actions interrupting the smooth transfer to elastic energy and to release a small portion of the impact and internal bond energy directly into increased vibrational energy or temperature of the affected surface atoms. This action, amplified by interaction with pressure shock waves and natural frequencies in the system, is concluded to be the source of later occurring localized hot spots. Several other theories have been postulated, but the point is, the mechanism of reaction remains unknown. Further, the elastic characteristics of the impact tester system differs greatly from the elastic characteristics of any airborne feed system component which might experience impact loads in service, such as a valve. Therefore, since the material reaction mechanism is not known and because of the large system elastic characteristics differences between the tester and any airborne component, there is no known method of impact test data application to component design.

5.4 Fluid Impact

Energy additions resulting from fluid impact, fluid scouring, and fluid friction and cavitation occur whenever the fluid is in a dynamic state. The available data from this type of fluid condition are discussed in paragraphs II-2.6.2 and II-2.7.2.

5.5 Conclusions

The conclusions reached are as follows:

1. The mechanism of reaction under impact is unknown.
2. The modified ABMA impact test is adaptable to fluorine testing, however, the results must be used with caution.
3. Basically the ABMA impact test is useful only to compare various materials. Materials which react under this test cannot, catagorically, be rejected from fluorine service.

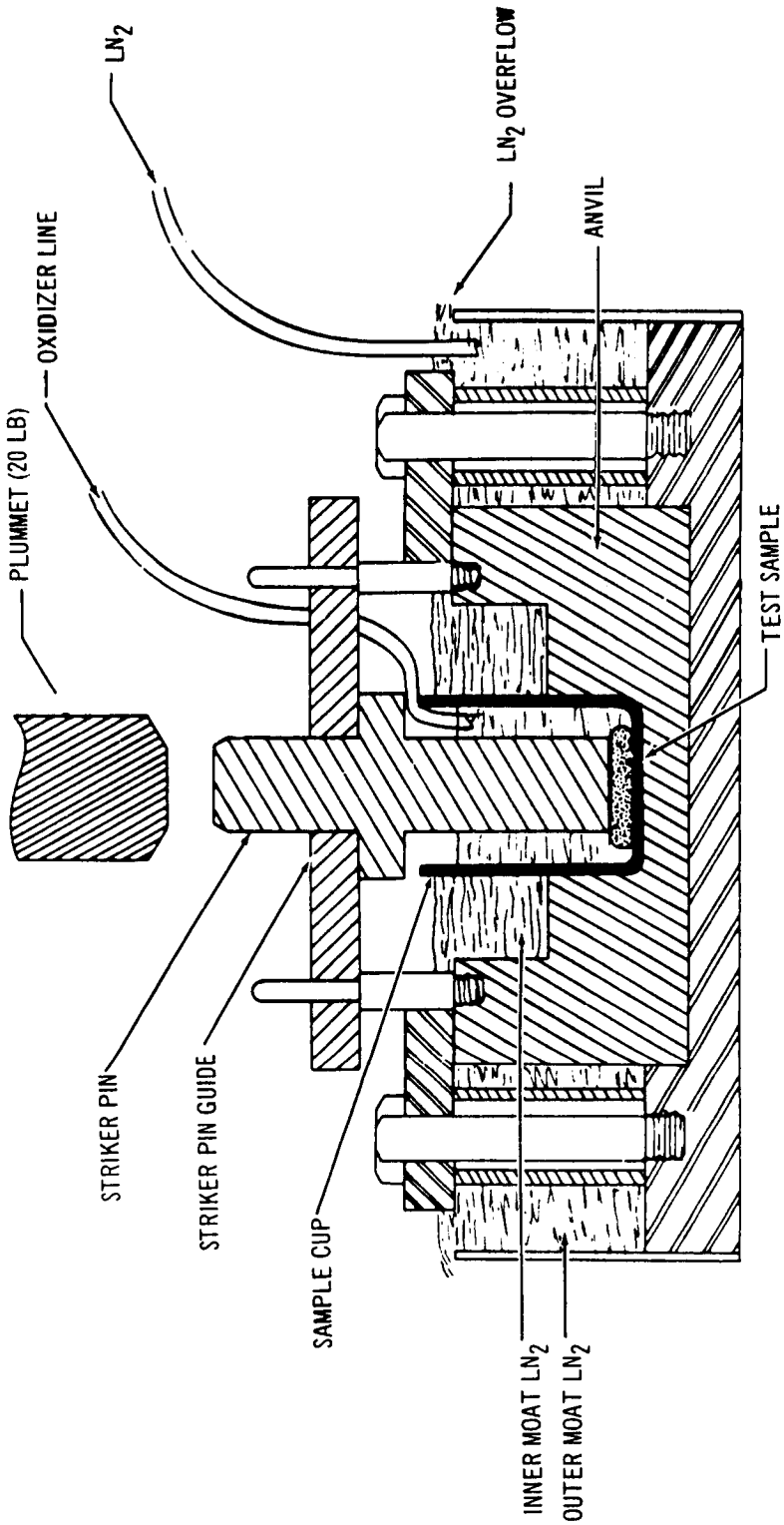


Figure II-5.3a. Details of Anvil Region Assembly of ABMA Type Impact Testing Device

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6.0 Galling and Wear of Unlubricated Surfaces

6.1 Adhesive-Wear Theory

The atoms and molecules of a metal are held together by a mutual affinity (cohesion), which is satisfied in all directions except at its surface. This surface affinity seeks to be satisified and, for this reason, a clean metal surface tends to acquire a tenacious coating, even of air or water vapor. Such a film, water vapor for instance, stays put in spite of reduced pressure and high temperature, far above the normal boiling point of water.

Not only does the surface have an affinity for gases, but for solids also. The greatest affinity is between similar materials; however, even metals which are not alloyable in the usual sense possess an attraction for each other. The primary conditions for adhesion of the materials are; freedom of both surfaces from film or foreign matter, and intimate contact of the surface atoms. In the case of extremely hard surfaces, elevation of temperature is often necessary before bonding will occur.

When these conditions exist between surfaces in relative motion, a phenomenon known as adhesive wear or "galling" may occur. This phenomenon is quite different from ordinary frictional wear, as atomic rather than mechanical (shearing) forces are dominant. As the surfaces slide over each other in direct contact, the abrasive action scours off the surface films, thus forcing the clean metallic surfaces together. Pressure welding then takes place at the points where the surface asperities come into contact. If only small areas are joined, the motion will not be arrested and the "joint" is forced apart. Instead of separating smoothly, metal chunks are torn out from beneath the surface at the welded locations. The surfaces have galled. The resultant projections will then proceed to cause scoring or excessive local wear. The surface temperature is thereby increased by friction, enhancing the conditions for welding, and complete seizure may result. Incipient welding at a few minute locations, may not matter if the rough spots can be smoothed out during proper "wearing in" under low initial loading.

At those regions where intimate contact occurs, the deformation will first be elastic; but, with metals and other ductile materials, the smallest loads will produce stresses exceeding the elastic limit and plastic deformation will take place. As the load is increased the asperities crush down plastically until they are large enough to support the load. Thus, the area of real contact is proportional to the load and inversely proportional to the hardness or yield pressure of the metal. Although the regions of real contact are plastically deformed, the stresses are supported by elastic strains in the underlying material. The greater the area of real contact, the greater is the tendency of the surfaces to seize due to adhesive forces.

6.2 Surface Chemistry and Crystal Structure

The adhesive force between surfaces is also proportional to their interface surface energy. Since it has been found that hard metals are characterized by high surface energies, an apparent paradox arises. Will increase hardness result in higher or lower adhesive force? In order to avoid confusion, it is necessary to evaluate the surface energy effect with respect to the dominant mode of adhesion; mechanical or physico-chemical. The mechanical aspect of adhesion involves the attainment of clean and conforming surfaces, whereas the physico-chemical aspect involves satisfying the surface energy requirements for the formation of atomic bonds between these surfaces.

The pure physico-chemical mode would be attained only at high vacuum, with atomically smooth surfaces devoid of contamination, brought together with no energy addition. Under these conditions, hard mating surfaces, having higher surface energies, will exhibit greater adhesion than softer surfaces, all other factors being equal. These conditions are rather unlikely, however, and in most practical applications the mechanical aspects related to surface energy will dominate the physico-chemical aspects. Thus, when external normal and tangential (sliding) forces enter the picture, the ability of the surfaces to resist adhesion increases with their hardness. This effect is diminished only slightly by the increase in surface energy. The ratio of surface-energy/hardness shows definite correlation with coefficient of adhesion for metals of a given crystal structure.

The effect of crystal structure on adhesion characteristics has been related to the difference in mechanical properties. Since cubic metals have more degrees of freedom as far as plastic deformation is concerned, they can increase their area of contact more easily. Hence, cubic metals are characterized by higher adhesion coefficients than hexagonal metals. There is also a correlation between adhesion and atomic radius. The smaller the atom, the greater the cohesive forces, and thus the lower the tendency for plastic deformation. Certain rare-earth elements (La, Sm, Gd, Dy, Ho, Er, and Yb), most of which have a hexagonal close-packed structure, have been used to demonstrate these correlations. As a group, these metals exhibit low adhesion coefficients due to their hexagonal structure. Within the group, the adhesion coefficient tends to increase with increasing atomic radius, when tested against iron.

A physico-chemical aspect which may well be the most important factor affecting adhesion, is the solid miscibility of the metal pair. The bond strength of a pair of clean metals in contact is related to their mutual solutibility. This effect may provide an explanation for the galling phenomenon. At the high local temperatures that exist at the asperities of sliding metals, there is an opportunity for diffusion to take place across the interface of mutually soluble metals. With relatively pure metals the diffusion would cause an increase in hardness and strength at the interface owing to the distortion of the lattices, and the bond would be stronger than either of the two base metals. Under these conditions, shearing will occur in the weaker of the two base metals resulting in metal transfer. Conversely, if the metal pair are immiscible, little diffusion takes place and the bond does not tend to be strengthened. If the metals differ sufficiently in electro-chemical properties, they may react to form well defined compounds. These compounds are usually brittle and their formation at the interface would again tend to give a junction weaker than either of the base metals. Shearing of this type of junction would probably occur at the interface with little or no metal transfer.

Experiments were performed with slider bearings of about forty elemental metals against rotating flat discs of copper, aluminum, silver, and steel. Kerosene was applied as a boundary lubricant and the slider load was increased until seizure took place, or 1200 lb was reached. The test results are shown in Table II-6.2a. In almost all cases where miscible metal pairs were used, the resistance to seizure was poor. The exceptions were the steel-copper, aluminum-zinc, and copper-antimony couples which showed fair resistance.

When the immiscible metal pairs were run together the results were somewhat less conclusive, as several metals performed poorly against steel. A correlation was noticed between performance and relative position of the elements on the periodic table. For example, the B-subgroup metals (Ag, Cd, In, Tl, and Rp) which are immiscible with iron, showed good resistance to seizure when run against steel; whereas the alkali and alkali-earth metals (Li, Mg, Ca, and Ba), which are also immiscible with iron, performed poorly. This difference has been attributed to the different types of atomic bonding represented by the two groups. The alkali metals have pronounced metallic bonding as do the transition metals such as iron, while the B-subgroups have varying amounts of covalent bonding. The conclusion is that similar bond types tend to promote adhesion, and dissimilar types tend to prevent it.

6.3 Surface Films and Friction

The forces of cohesion decrease as the sixth power of the particle separation, and when the distance becomes greater than a millionth of an inch the force is essentially negligible. Thus, the thinnest film between the surfaces can maintain separation beyond the critical distance and thereby prevent galling.

The effect of surface films on the friction and surface damage of sliding metals is very great. In fact, with most solids the behavior is governed more by the type and extent of the film than by the nature of the solid itself. The coefficient of friction of most metals which have been thoroughly cleaned, but which are exposed to air, is approximately one. If the surfaces are heated to induce outgassing of the chemisorbed and adsorbed gases, and

allowed to cool in a high vacuum, the coefficient of friction becomes indeterminantly high and any attempt to slide the surfaces results in complete seizure. The admission of a trace of oxygen reduces the friction significantly. Most gases and vapors produce a similar effect.

The influence of surface films on friction between non-metallic solids is also marked, but considerably less dramatic than with clean metals. The difference may be attributed to the nature of the deformation in the regions of contact. With metals the deformation is largely plastic; thus when sliding is attempted the area of contact increases rapidly and seizure occurs. With a non-metallic solid such as diamond, the deformation is mainly elastic and therefore the increase in contact area is slight.

The removal of surface films leads to an increase in the surface deformation and wear which may be very great. Experiments with graphite, for example, have shown that the wear in a vacuum may be many thousand times as great as that observed in air.

Metals which are exposed to the air rapidly acquire a thin oxide film. Similarly, metals exposed to fluorine rapidly acquire a thin fluoride film. The extent to which this film can protect the metal depends primarily upon the relative mechanical properties of the film and metal. If the film is much harder than the substrate (as with aluminum oxide), it may be unable to provide protection. The brittle film will fracture easily as the substrate yields and metal to metal contact will occur at light loads. If, on the other hand, the metal and the film have similar properties, as with copper and steel, then both will deform together and the protective film may remain unbroken. In general, the frictional behavior of the surface depends on the extent to which the film is supported by the substrate material.

The rate at which the surface film is formed can affect the frictional behavior significantly. If the film is replenished as quickly as it is removed, a steady state, low friction condition may be established under moderate loading. The rate of film formation is dependent upon the oxidizing (or fluoridizing) potential of the environment. The oxidation rate of most metals increases

with increasing temperature. Correspondingly, the coefficient of sliding friction between metal surfaces generally exhibits a rapid decrease at some elevated temperature where the oxidation rate equals the rate of film removal. At still higher temperatures, however, friction often begins to increase again. This is not fully understood, but it may be due to dissociation, evaporation, or spalling of the oxide film; or it may be connected with a change in the mechanical properties of the oxide.

A friction reducing oxide film is formed by frictional heating at high rubbing velocity. This may be, in part, responsible for the well known decrease in friction coefficient with increasing rubbing speed for unlubricated metals. Some attribute this effect to insufficient time to form a full strength weld between asperities before their separation.

6.4 Friction and Wear

The coefficient of friction of oxide-on-oxide may well be as high as that of metal-on-metal, but this does not conflict with the theory that oxides will reduce wear. When oxide is sliding on oxide the junctions formed may be very strong but they will shear in the oxide layer and material transfer will be small. When metallic junctions are formed, however, galling occurs and the amount of transfer is considerable. Therefore, it is evident that, although the coefficient of friction is often a good indication of wear resistance, it alone is not a sufficient criterion.

Although the presence of an oxide film will generally reduce the wear rate, in some cases wear may be accelerated, even when friction is reduced. The mild wear of steel, for example, is more rapid in air than in nitrogen. The mechanism is not fully understood, but an explanation for wear by oxidation can be visualized. If the oxide film is nonadherent to both rubbing surfaces, and its molecular bonding is weak, it may be removed readily as loose particles. If the environment is favorable for rapid oxidation, this process will be continuous and the wear rate will approach the rate of initial oxidation. Additional acceleration of wear by abrasive action can result if the oxide is

harder than the substrate and the geometry is such as to entrap the wear debris. This type of wear is more predictable than galling, however, and less likely to be catastrophic.

6.5 Behavior of Polished Surfaces

When a metal surface is mechanically polished, it becomes covered with a thin layer, known as the "Beilby layer", which flows over the surface filling up the irregularities in it. This layer has lost its obvious crystal-line properties and is essentially amorphous. It is postulated that this layer is formed by the localized melting or softening of the metal at the points of rubbing contact. The softened metal is then smeared over the surface and is rapidly cooled to form the Beilby layer. Experiments have shown that this layer acts as a protective film with a hardness nearly three times that of the annealed metal, comparable to the hardness of heavily work-hardened metal.

When sliding occurs on these surfaces an abrupt change in the frictional characteristics occurs as the load is increased. Under light loads the friction is low and the surface damage relatively light. As the load is increased a point is reached where both the friction and wear increase rapidly. It is evident that at low loads the load is borne by, and the sliding occurs within the hard Beilby layer, whereas at higher loads the deformation extends into the bulk of the underlying softer metal. This phenomenon is not observed in polished work-hardened specimens where the film receives greater support.

6.6 Design Considerations

It is evident from the foregoing discussion that the wear process can be quite complex, involving a number of interacting factors. The nature of the environment, the chemical and mechanical properties of the surfaces, the applied load, and the rubbing speed all affect the frictional and wear behavior in a manner which defies complete analysis. However, certain criteria can be established for minimizing wear and/or preventing seizure of unlubricated surfaces.

When conventional lubrication is not feasible, as in fluorine applications, particular attention must be paid to surface properties of the contacting material; for assured reliability will generally be governed by the severity of the operating conditions.

Surfaces which will experience only light loading and will be exposed to a sufficiently oxidizing or fluoridizing environment, can in most cases rely upon conventional metals. Metals should be selected which display the following properties: (1) high yield strength or surface hardness, (2) rapid flim formation, and (3) tenacious film with low shear strength.

A high surface finish is recommended to reduce the metal-to-metal contact of asperities projecting above the film. Dissimilar metals should be used whenever possible to reduce cold welding potential in the event of metal-to-metal contact. Further protection may be provided by surface treatments such as nitriding or sulfurizing. The metallic nitrides and sulfides left in the surface by these processes act much like the oxides to prevent welding, however these are not recommended for fluorine service. Sulphate in fluorine reacts with Monel.

Another important consideration in the selection of wear resisting metals and alloys is the metal structure. As previously mentioned, metals and alloys having hexagonal crystal structures, generally exhibit lower friction and wear and less tendency to weld in vacuum, than cubic lattice metals. During tests for the face-centered cubic metals, nickel and copper, complete welding was observed in a vacuum; for the hexagonal metals, titanium, zirconium, beryllium and cobalt much lower coefficients of friction were observed. Pure titanium displays notoriously poor friction characteristics, even in air; however, selective alloying with oxygen, tin, and aluminum can greatly improve these characteristics.

6.7 Non-Metallic Surfaces

Under more severe conditions where the loading may be greater or the presence of a proper atmosphere cannot be assured, it may be necessary to provide at least one "ceramic" surface. Aluminum oxide, titanium carbide,

and tungsten carbide exhibit excellent wear resistance against themselves or against stainless steel. These materials are available in solid form; however, they are expensive and difficult to machine. A similar surface may be obtained by flame plating these materials on a suitable base metal such as a nickel alloy. For the flame plating process, particles of power are suspended in an oxygen-acetylene gas mixture in a specially designed gun. When the mixture is ignited a detonation occurs. The particles are heated to plasticity and hurled at supersonic velocity onto the receiving surface where a microscopic welding action takes place. Flame-plated coatings have an as-coated smoothness of 125 microinch rms and can be finished down to better than one microinch rms. In spite of the 6000°F flame temperature, the part being plated seldom exceeds 500°F. Thus, there is little chance of affecting the properties of the base metal. Coating thicknesses up to 0.010 inch can be built up by successive applications.

Alternate surface coatings which are very effective in reducing friction and wear, are "chromizing", and hard-facing. Chromizing is a high temperature diffusion process. The chromium penetrates into the steel part, alloying with the iron and combining with the carbon. If a high carbon or carburized steel is used the result is a hard, wear resistant chromium carbide case. In the hard facing process a powdered alloy is sprayed onto the surface as in ordinary metal spraying. The overlay is then fused to the base metal with an oxy-acetylene torch. The result is a stable chromium boride compound which is just below diamond on the hardness scale. Chromium, silver, and electroless nickel platings have also been effective in reducing wear under certain conditions.

6.8 Self-Lubricating Surfaces

Under very severe operating conditions where the loading is high and the environment is essentially vacuum, "self-lubricating" surfaces will probably be required. The most common class of metals which exhibit some degree of self lubrication are those which rely upon inclusion compounds in their structure. Since the protective surface oxides will not form in an extreme vacuum, the necessary oxygen can be included directly in the alloy structure

in the form of metal oxides. These inclusions are then smeared over the contacting interface, thereby preventing metal-to-metal contact and cold-welding. Other compounds may be added to metals and alloys to obtain a similar effect. Sulfur present as inclusion compounds may replace surface oxides as a protective agent and in most instances be more effective. For example, 440-C stainless steel and M-2 tool steel have been prepared with inclusions of iron and chrome sulfides with a marked reduction in wear.

It can be shown that the coefficient of friction between sliding surfaces is proportional to the ratio of the shear strength, of the welds formed, to the plastic flow pressure of the "softer" material. The significance of this relationship is that the lowest friction will only be achieved with a structure consisting of a hard substrate covered by a thin layer of material which forms a very weak bond with the mating surface. This concept forms the theory behind the "duplex" structured bearing materials, which provide maximum protection against seizure under severe operating conditions.

The duplex structured materials consist of two phases, one hard and one soft, which on running provide a hard substrate covered with a thin, soft, easily sheared layer. The soft material is the more critical of the two phases. If the surface layer is thicker than the surface asperities and the substrate material is not greatly deformed, the substrate material may be completely protected. Under these conditions the shearing action occurs only in the surface layer where the shear strength is low. Thus the friction force is low and the metal transfer is slight. The major requirements of the hard phase are that it be of sufficient hardness to maintain minimum true contact area, and that it does not interfere with the lubricant action of the soft phase.

After repeated sliding, the surface layer will be worn away and the substrate material becomes exposed. With proper dispersion, however, this surface will contain both hard and soft phases and the soft phase will be sheared, and smeared over the surface. This continuous process provides an effective, protective surface layer until the dimension tolerances have been exceeded. Silver, tin, and silicon have each been alloyed with nickel and have been effectively used in vacuum to reduce friction and wear.

Recent advances in powder metallurgy have introduced new techniques for producing the self-lubricating duplex structures. Through hot pressing processes the new "solid-lubricants" can be evenly dispersed within matrices of hard metal to form a class of materials commonly known as "cermets." The lubricants presently include the sulfides, selenides, and tellurides of the heavy metals; silver, gold, nickel, and palladium. Boron nitride and aluminum-oxide also show great potential. It should be mentioned that the compatibility of these solid lubricants with fluorine has not been adequately established. If stable fluorine compounds were proven to provide the same lubricanting function, any compatibility problem should be eliminated.

6.9 Summary

A summary of the main points of interest is as follows:

1. Clean metal surfaces possess an attraction for each other and will adhere when brought into intimate contact.
2. The degree of adhesion is directly proportional to the atomic attraction of the surfaces and their real area of contact.
3. These surfaces rapidly acquire protective films, from reaction with the atmosphere, which tend to prevent adhesion.
4. Relative motion between surfaces increases the real area of contact, and hence adhesion, by removing the protective film and by deformation of the contact regions.
5. The increase in real contact area due to deformation is directly proportional to the surface loading and inversely proportional to the surface hardness. Deformation of metals is usually plastic whereas non-metallic deformation is usually elastic.
6. The nature of the crystal structure and the type of atomic bonding are important. Hexagonal structured metals are less prone to deformation and thus, more adhesion resistant than cubic structured metals. Metal pairs with crystals having similar types of atomic bonding have a greater tendency to adhere than those with dissimilar bond types.
7. The tendency of a metal couple to weld and the strength of the weld are directly related to the solid solubility of the metals. If the shear strength of the weld region is greater than either of the base metals, galling will result.
8. Surface reaction films cannot reform under vacuum conditions and conditions for adhesion are greatly enhanced; therefore, an oxidizing environment should be provided whenever possible.

9. Adhesion can often be reduced by mating surfaces which are non-metallic. If metals are used they should be as chemically dissimilar as possible and should possess high yield strength and high surface finish.

10. Under the most severe conditions, a layer of soft low shear strength material should be maintained between the two hard substrates to act as a lubricant.

6.10 Criteria for Wear Resistance in Fluorine

The phenomena which contribute to adhesive wear of surfaces in fluorine are essentially the same as those present in an environment containing oxygen. The intimate contact of unprotected surface molecules results in adhesive bonding and subsequent transfer of metal from one surface to the other. If the protective fluoride or oxide film can reform on the surfaces as rapidly as it is worn away, the amount of adhesion can be reduced significantly. Unfortunately, too little is known about the relative rates of fluoride and oxide film formation to predict a difference in the protective nature of the media.

The selection of wear resistant materials for fluorine service, however, is severly limited by the materials compatibility problem, which limits the use of plastics and precludes conventional lubricants. Therefore, it is necessary to establish combinations of compatible metals and/or ceramics which will provide adequate wear resistance under various operating conditions. Paragraph II-2.0 should form the basis for this selection. This information should be supplemented, based on adhesion theory as discussed previously, in paragraph II-6-1 through II-6.4. This will be necessary in these cases where insufficient data are available.

Conventional metals are generally acceptable for surfaces designed for light loads, such as a guide bushing for a poppet value stem. A surface finish of ten microinches rms or better should be provided, and the surfaces should be hardened to the maximum consistent with structural integrity. Table II-6.10a lists the maximum attainable hardness for some of the more common alloys. It is advantageous if at least one of the surfaces will produce a tenacious fluoride film as discussed in paragraph II-6.3. Mating materials should be as

chemically incompatible as possible. The solubilities of elemental metal pairs are presented in Table II-6.10b (see also paragraph II-6.2). Some acceptable combinations which are recommended for fluorine applications are as follows:

SS vs Ag	SS vs Cu
Ni vs Ag	SS vs Al
Al vs Ag	Cd vs SS
Al vs Ni	Cd vs Al
Al vs Cu	Cd vs Ag

The dividing line between lightly and heavily loaded surfaces is not easily defined. In order to establish some guidelines for the designer, the actual stress level as felt by the surface asperities was chosen as the primary criterion. If the actual stress is within the elastic range of the material with the lower yield strength, the loading is considered to be light. If the actual stress exceeds the elastic limit the asperities will begin to deform plastically and the actual contact area will increase rapidly, leading to severe adhesion. Thus, the loading is considered to be heavy.

The actual contact stress of the asperities is determined by the actual surface contact area, which is in turn a function of the material properties and the apparent compressive stress level (load/apparent contact area). In order to determine the relationship between actual and apparent contact areas, a model surface was first established. Sinusoidal asperities with an average slope of two degrees were assumed, and the contour of the contacting peaks were approximated by spheres. The asperity heights for both surfaces were assumed to be equal. Using the expression for the deformation of spheres under direct bearing, the relation between real and apparent stresses was derived. Using a limiting actual stress of 0.9 times the material yield strength, the expression for maximum design stress (for light-duty surfaces) was found to be;

$$\sigma_{Design} = 2.95 \times 10^3 \frac{(k\sigma y)^3}{E^2}$$

$k = 0.9$
σy - psi
E - psi

The results of this equation are plotted in Figures II-6.10a and b. By substituting the material ultimate strength for yield strength the maximum design stress for heavy loading can be found. Design stresses for actual stresses other than 0.9 σy can be found by using the appropriate "k" value. The correction factor is plotted as a function of k in Figure II-6.10c, and the product (C.F. s σ_{Des}) yield the corrected design stress (σ_D').

Heavily loaded surfaces will require more exotic materials to prevent excessive adhesion. Ceramic surfaces appear to be an effective means of reducing wear under moderately heavy loading. The ceramics exhibit good compressive strength but their shear strength is low. Thus, if welding should occur between the ceramic and the mating surface, separation will take place in the ceramic with little effect on the frictional characteristics. Materials such as; aluminum-oxide, titanium-carbide, tungsten-carbide, and calcium-fluoride provide excellent wear resistance when run against stainless steel and other high yield-strength surfaces. These ceramics can be applied to conventional metals through the flame-plating process and surface finishes of one microinch rms can be obtained by lapping. The base material should be a relatively high yield strength alloy to give support to the thin ceramic layer.

For applications where the movement between surfaces is limited or occasional, other types of surface treatments may provide adequate protection. Such treatments include; hard-facing, chromizing, chrome plating, and electroless nickel plating. The cold-welding of threaded joints and fasteners becomes a problem when the mating surfaces are similar metals and are clean, that is, free from contaminants. As the load is applied to the threads, the passivation film is abraded away and the clean metal surfaces come into intimate contact. Gross adhesion then takes place and the threads become frozen. Seizure can be prevented by applying a thin plating of gold, or copper to one or both of the threaded surfaces. Replating may be required each time the threads are separated.

Under the most severe conditions where the surface loading is high, relative motion is frequent, and fluoride film formation is unlikely, "self-lubricating" materials will be required. Two basic types of self-lubricating materials

are currently available; the "duplex" structured metals and the ceramic-metal composites or "cermets." The duplex materials are mixtures of metals which result in two distinct phases; one hard and one soft. Alloys of nickel with silver or tin are typical duplex materials which have proven to be effective in reducing wear. The cermets are an outgrowth of powder metallurgy technology. Through hot pressing techniques, ceramic "lubricants" can be evenly dispersed throughout a matrix of hard metal such as nickel. Aluminum-oxide and titanium-carbide are typical ceramics being employed in these materials. Cermets employing stable fluoride compounds such as barium-fluoride and calcium-fluoride are under development and should be available soon. They may prove useful for fluorine service.

Both the cermets and the duplex materials rely on basically the same principle (see paragraph II-6.8). The low shear-strength material is smeared between the mating surfaces providing a lubricant film, while the hard material provides structural integrity for the compound. These self-lubricating materials provide maximum protection against seizure for applications where conventional lubricants are not feasible.

A self-lubricating composite material employing fluoride lubricants has been developed and tested at the NASA-Lewis Research Center. A eutectric mixture of 62% BaF_2 and 38% CaF_2, by weight, was selected as the lubricant. Porous, sintered metal structures of about 60% density were prepared using both pure nickel and a nickel-chromium alloy. Both metals were then infiltrated with the molten eutectic by means of vacuum impregnation at 2000°F. As a precautionary measure, argon or nitrogen was introduced at a pressure to ten psig in order to force the molten fluorides into any remaining voids. The specimens were cooled under inert gas pressure and then wet sanded to remove any excess fluoride. Composites prepared in this manner have the advantage of increased mechanical strength. When metal and lubricant powders are mixed prior to sintering, particles of lubricant will occupy some of the potential sites for bonding between metal particles, thereby weakening the metallic matrix.

As a result of a series of friction and wear tests, several significant factors were determined:

1. Low wear rates were obtained with both types of fluoride-metal composites, however, friction coefficients were higher than those obtained against dense substrate metals lubricated with a thin sintered film of the fluoride eutectic. The advantages of coatings (lower friction) and of composites (longer life) were combined by coating the composites with a 0.001 inch sintered film of the same composition as the fluoride impregnant.
2. The load carrying-capacity of the nickel composites was severely limited by the low yield strength of the matrix. The stronger nickel-chromium alloy composites were greatly superior in resisting plastic deformation of the load bearing surfaces.
3. The fluoride-coated alloy composites exhibited low wear rates at room temperature as well as high temperature.
4. The alloy composites, because of their high strength, should be useful as a bearing retainer material in ball bearings, as a self-lubricating sleeve bearing material, or possible as a sliding contact seal material. The nickel composites are probably too soft for retainer materials, but this same property provides a degree of conformability at the contacting surfaces that may be desirable in some sliding contact applications.

The wear rates and coefficients of friction observed during the tests are presented in Figures II-6.10d and II-6.10e.

As a part of the same program the physical and compressive stress-strain properties of the composite materials were determined. These data are presented in Table II-6.10c.

6.10.1 Conclusions

The conclusions reached are as follows:

1. Adhesive wear phenomena of surface in fluorine are the same as these in an oxygen environment.
2. Material selection for bearing surfaces must be made first on the basis of material compatibility per the requirements specified in paragraph II-2.0 and then upon conventional wear design techniques.
3. The major problems associated with antiwear design for fluorine service is due to the problem of providing lubrication between moving parts. This is compounded two ways: 1) the conventional lubricants are not generally compatible with fluorine, and 2) the cleanliness level required of fluorine systems results in the removal of many materials which conventionally provide the required lubrication.

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Table II-6.2a (page 1 of 2)

SEIZURE RESISTANCE OF PURE METALS
(After Goodzeit)

Slider Material	Crystal Structure	Disk Material			
		Steel	Aluminum	Copper	Silver
Li	bcc	P*			
Be	cph	P	P	P	P
C	hex		P*	P*	P*
Mg	cph	P*	P	P	P
Al	fcc	P	P	P	
Si	diamd.	P	P	P	P ?
Ca	fcc	P*	P	P	
Ti	cph	P	P	P	F ?
Cr	bcc	P	P	F*	F*
Mn	cub	P			
Fe	bcc	P	P	P ?	F*
Co	cph	P	P	P	F*
Ni	fcc	P	P	P	P* (Plated)
Cu	fcc	F ?	P	P	
Zn	cph	P	F	P	
Zr	cph	P	P	P	P ?
Cb		P	P ?	P ?	F*
Mo	bcc	P	P ?	P ?	P ?
Rh	fcc	P	P	P	
Pd	fcc	P			
Ag	fcc	G*	P	P	
Cd	cph	G*	G*	P	P
In	fct	G*	G*	P	P
Sn	bct			P	
Sb	rhom.			F	
Ba	bcc	P*			
Ce	fcc	P	P	P	
Ta	bcc	P	P	P	
W	bcc	P	P	P	
Ir	fcc	P			
Pt	fcc	P	P	P	

Table II-6.2a (page 2 of 2)

SEIZURE RESISTANCE OF PURE METALS
(After Goodzeit)

Slider Material	Crystal Structure	Disk Material			
		Steel	Aluminum	Copper	Silver
Au	fcc	P	P	P	P
Tl	cph	G*	G*	G*	
Pb	fcc	G*	F*	G*	
Bi	rhom.		F*	F*	
Th	fcc	P	P	P	P ?

G--Good
F--Fair
P--Poor
*--Immiscible with disk material
?--Doubtful Miscibility

bcc	body centered cubic
fcc	face centered cubic
cph	close packed hexagonal
bct	body centered tetragonal
fct	face centered tetragonal
hex	hexagonal
rhom.	rhomboid
diamd.	diamond cubic

Table II-6.10a (page 1 of 2)

MAXIMUM HARDNESS OF COMMON METALS AND ALLOYS
(Reference 200)

Material	Condition	Treatment	BHN	Rockwell
Stainless Steels				
304		cold drawn	240	
304L		cold drawn	240	
308				
309S				
310S		cold worked		C 0-25
316				
316L		cold worked		B 90-105
317				
321				
347				
17-4 PH	H 900 F	precip. hard.	420	C 44
17-7 PH	RH 950 F	precip. hard		C 48
A286				
ARMCo 21-6-9				
440C	hard	heat treat	590	C 58
Nickel Alloys				
Monel	full hard strip	cold rolled		B 98
K Monel	full hard strip	cold rolled		C 40
S Monel	cast	aged	375	
H Monel	cast	none	290	
Inconel	full hard strip	cold rolled		B 96
"A" Nickel	full hard strip	cold rolled		B 96
Copper				
ETP Copper	spring	cold rolled		B 60
OF Copper	hard	drawn		B 50
FRHC Copper				
FRTP Copper				
Brasses				
Red	spring	cold rolled		B 86
Low	spring	cold rolled		B 91
Cartridge	extra spring	cold rolled		B 93
Yellow	extra spring	cold rolled		B 91
Admiralty (inhib)	hard	cold rolled		F 109
Aluminum (inhib)				
Commercial Bronze	spring	cold rolled		B 78

Table II-6.10a (page 2 of 2)

MAXIMUM HARDNESS OF COMMON METALS AND ALLOYS
(Reference 200)

Material	Condition	Treatment	BHN	Rockwell
Bronzes				
Phosphor A	extra spring	cold rolled		B 99
Phosphor C	extra spring	cold rolled		B 102
Phosphor D	extra spring	cold rolled		B 104
Phosphor E	extra spring	cold rolled		B 80
Aluminum 5%		cold rolled		B 93
Aluminum 7%	hard	cold rolled		B 84
Aluminum 10%	cast			B 73
Cupro-Nickel 10%	light-drawn	drawn		B 100
Cupro-Nickel 30%		cold rolled		B 86
Aluminum				
1100	H 18	strain hard	44	H 90
2014	T 6	heat treated	135	B 86
2017	T 4	heat treated	105	
2024	T 36	heat treated	130	B 83
6061	T 6	heat treated	95	E 97
A356	T 7	as cast	75	
Silver (coin)		cold worked	150	
Silver (Eutectic)		cold worked		
Gold		cold worked	58	
Cadmium	Electro deposited		35-50	

	Re	W	Mo	Be	Rh	Cr	Co	Ni	Fe	Pt	Cu	Ti	Nb	Zr	Zn	Au	Ag	Al	Cd	Mg	Sn	La	Pb	
In				G			F	P			P	F		O	P	O	O	G	O	O	O		O	In
Pb		P	F			G	G	G	G	O	G	O	G		G	F	P	G	P	P	O		Pb	
La						G		F	F	O			G	G					O			La		
Sn	F	P		G	O	G	P	P	F	O	P	O	F	P	P	O	O	F	O	F	Sn			
Mg				F				F	F		F	F		O	P	O	O	O	O	Mg				
Cd				P		P	P	F	F	O	P			O	O	O	O	G	Cd					
Al	P	O	P	F	O	O	P	O	O	P	O	O	O	P	O	O	O	Ai						
Ag	F	G		O	F	G	G	G	G	O	P	O		P	O	O	Ag							
Au	F		P	O	F	O	P	O	O	O	O	P			O	Au								
Zn			P			O	O	O	O	O	O	P	F	F	Zn									
Zr		P	O		O	P	O	P	F	P	O	O	O	Zr										
Nb	O	O	O			O		O	F	O	O	O	Nb											
Ti	O	O	O	O		O	P	O	O	O	P	Ti												
Cu	P	F	G	O	O	G	O	O	P	O	Cu													
Pt	O	O	O	O	O	O	O	O	O	Pt														
Fe	O	O	O	O	O	O	O	O	Fe															
Ni	O	O	O	O		O	O	Ni																
Co	O	O	O	O	O	O	Co																	
Cr	O	O	O	O	O	Cr																		
Rh	O	O	O		Rh																			
Be	O		P	Be																				
Mo	O	O	Mo																					
W	O	W																						
	Re																							

NOTE:

GOOD (G)	TWO LIQUID PHASES, SOLID SOLUTION LESS THAN 0.1%
FAIR (F)	TWO LIQUID PHASES, SOLID SOLUTION GREATER THAN 0.1%, OR ONE LIQUID PHASE, SOLID SOLUTION LESS THAN 0.1%
POOR (P)	ONE LIQUID PHASE, SOLID SOLUTION BETWEEN 0.1% AND 1%
VERY POOR (O)	ONE LIQUID PHASE, SOLID SOLUTION OVER 1%

BLANK BOXES INDICATE INSUFFICIENT INFORMATION

THE LESS SOLUBLE THE COMBINATION THE MORE SUITABLE THAT COMBINATION IS FOR SLIDING APPLICATIONS

Table II-6.10b. Solubilities of Metal Pairs

Table II-6.10c

PROPERTIES OF SELF-LUBRICATING, FLUORIDE-METAL COMPOSITES

Property	Nickel Composite*	Nickel-Chromium Composite**
Density (g/cc)	6.57	6.90
Yield Strength (psi) (0.2% Offset)	29×10^3	79×10^3
Ultimate Strength (psi)	50×10^3	83×10^3
Elastic Modulus (psi)	13×10^6	20×10^6
Hardness (Rockwell)	B 54	B 82

All stress-strain properties are compressive.
*53.5 vol% Nickel; balance BaF_2-CaF_2 eutectic
**66.5 vol% Nickel-Chromium Alloy; balance BaF_2-CaF_2 eutectic.

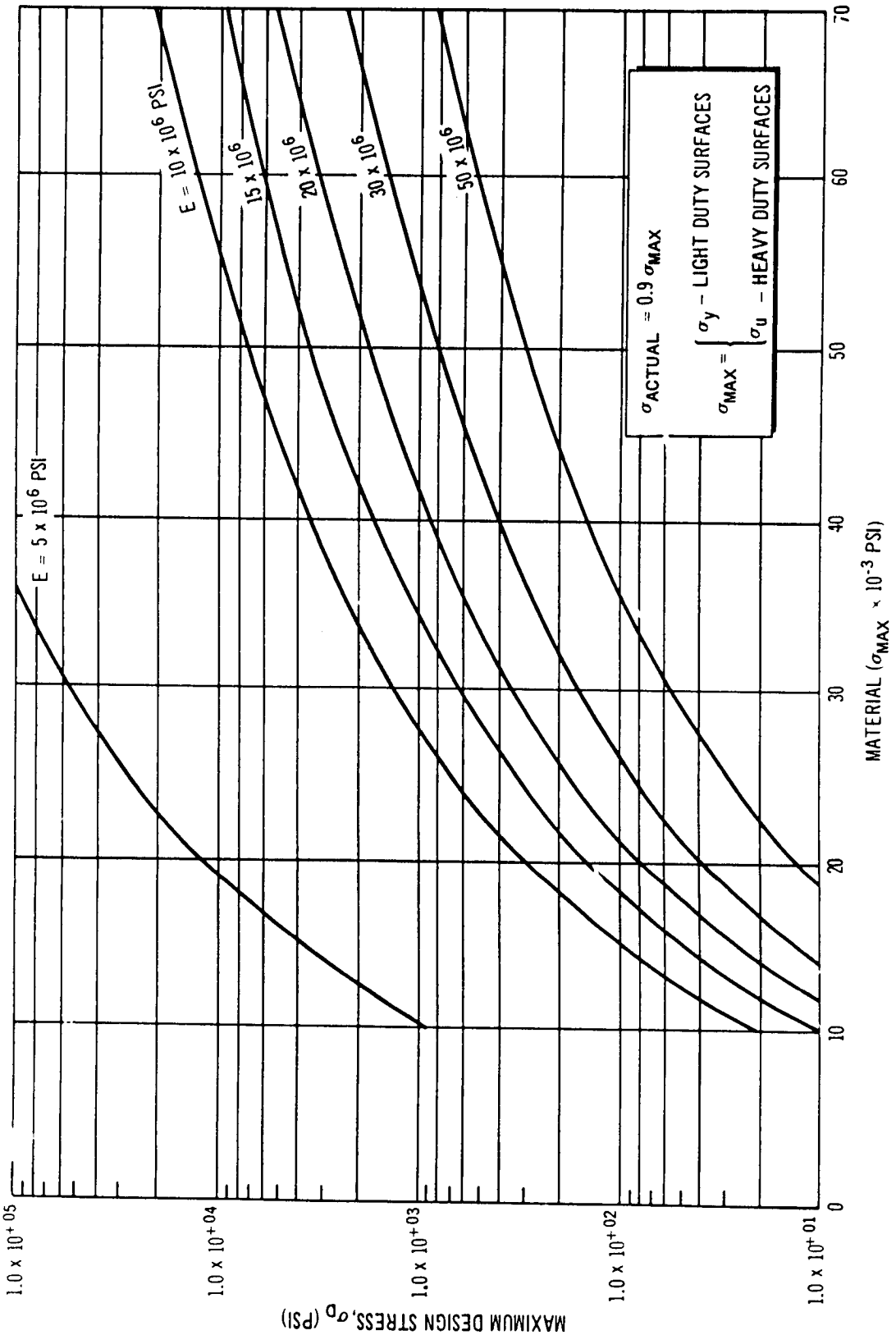

Figure II-6.10a. Design Compressive Stress for Sliding Surfaces (Reference 97)

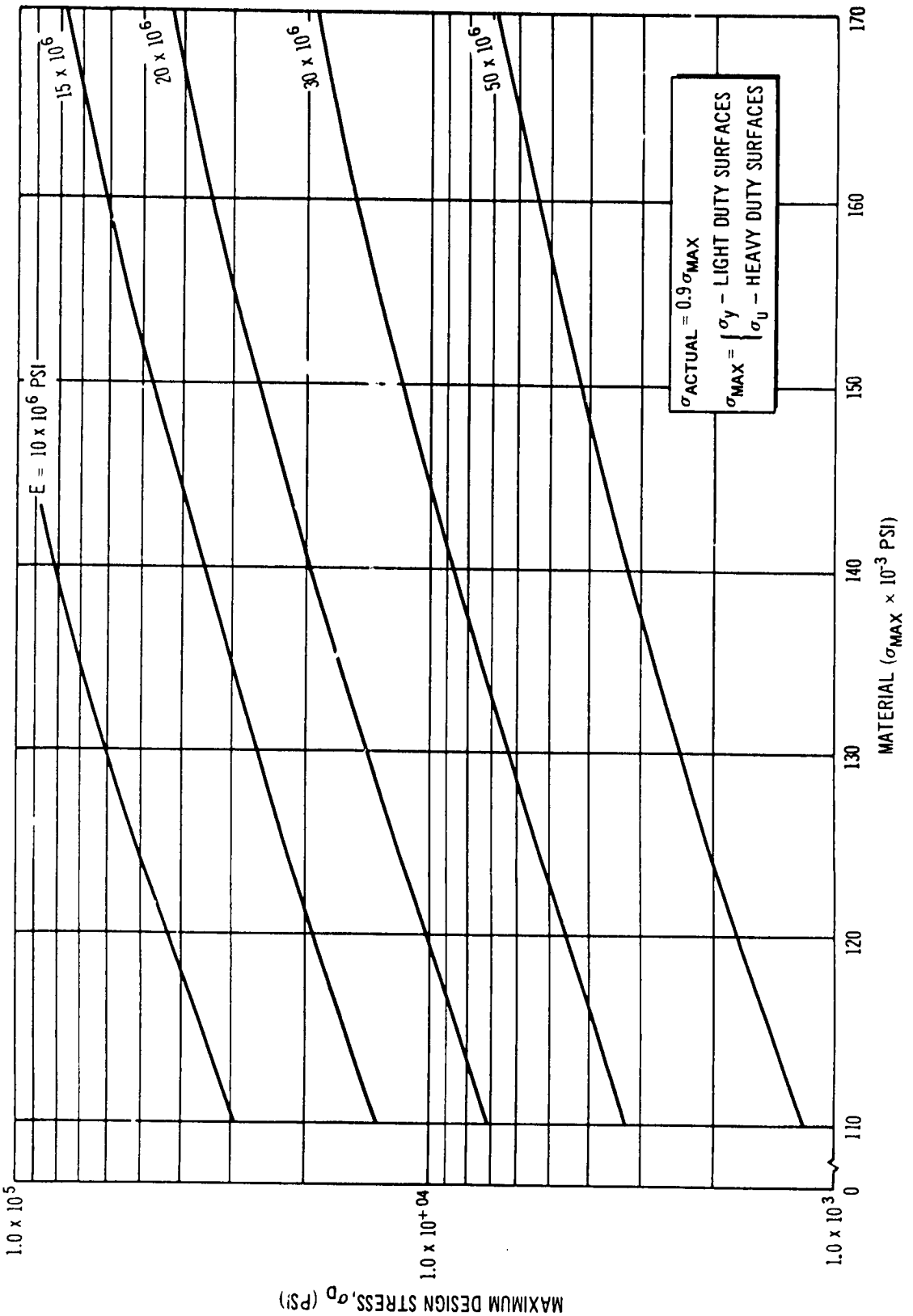

Figure II-6.10b. Design Compressive Stress for Sliding Surfaces (Reference 97)

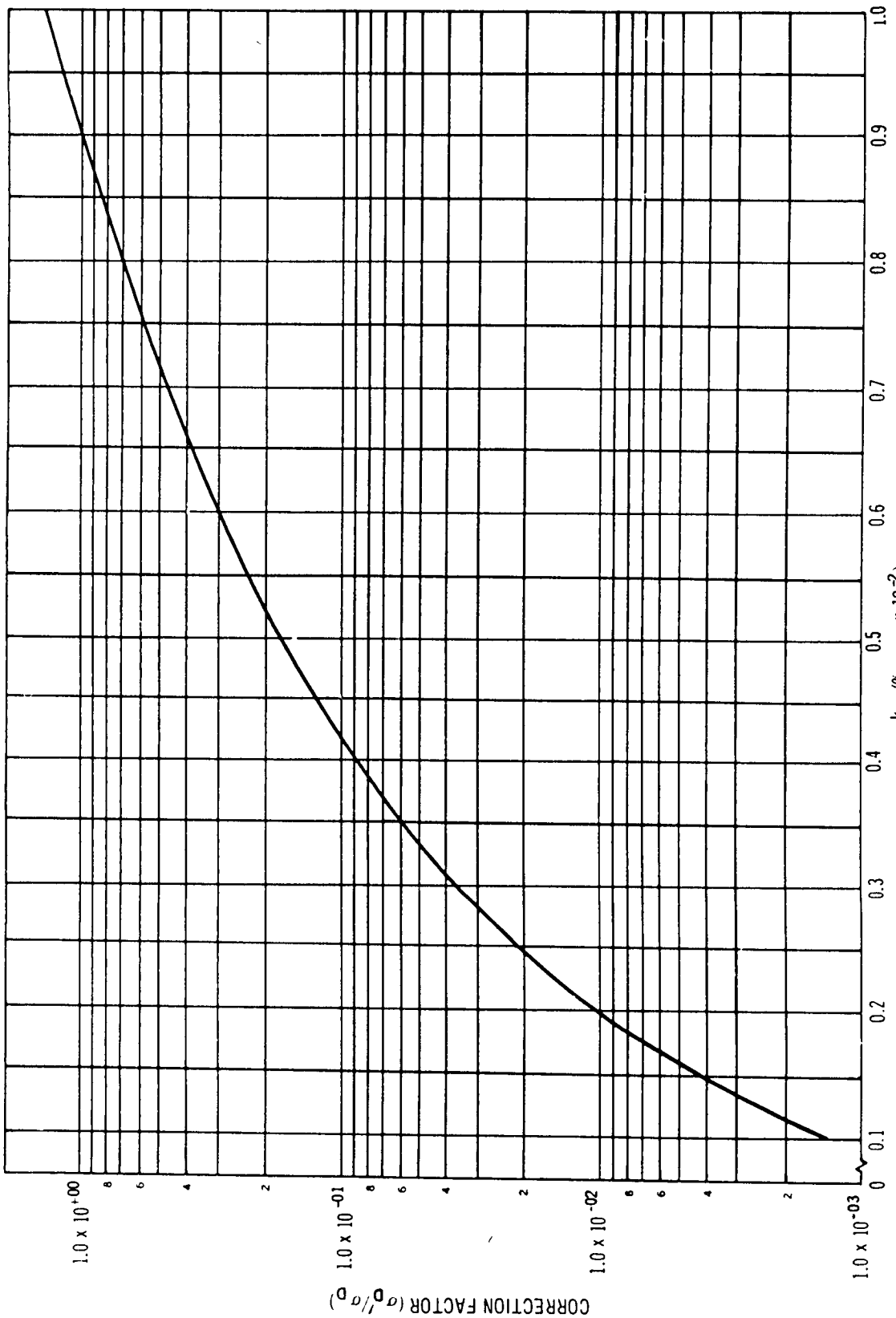

Figure II-6.10c. Correction Factor for Figures 7.10a and b (Reference 97)

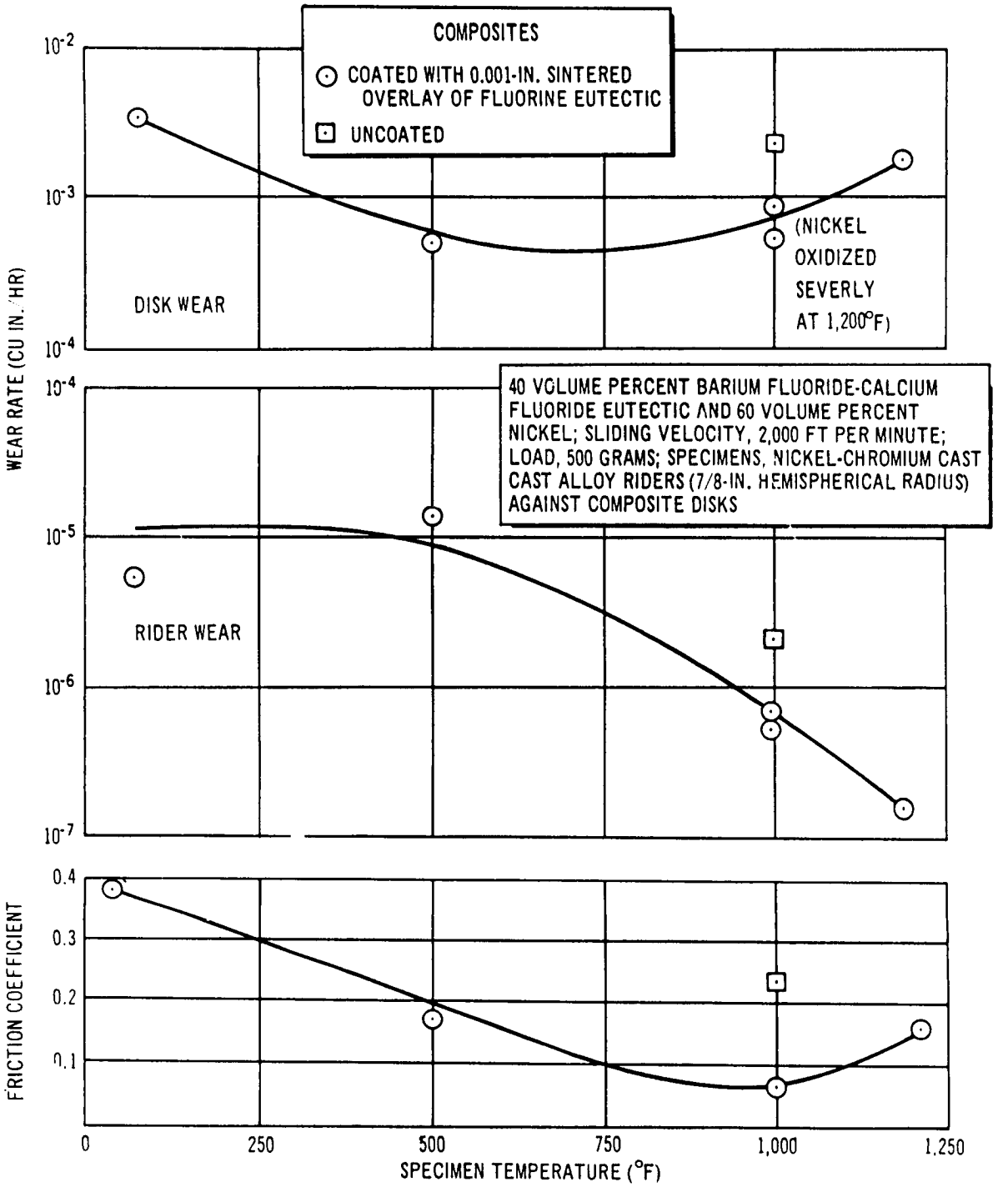

Figure II-6.10d. Lubricating Properties in Air of Eutectic Fluoride and Nickel Composites. (References 26 and 27)

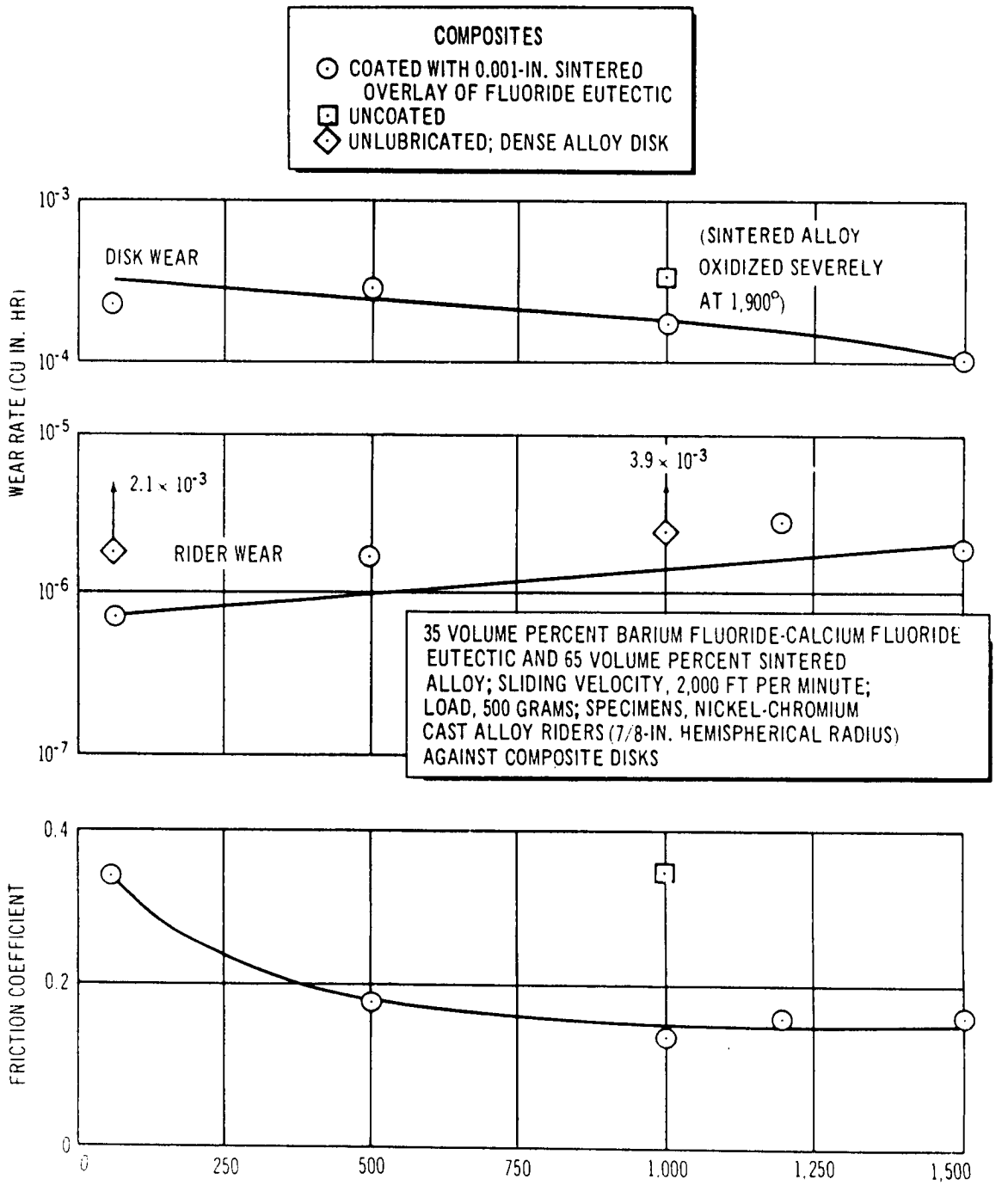

Figure II-6.10e. Lubricating Properties in Air of Eutectic Fluoride and Nickel-Chromium Alloy Composites.

APPENDIX II-1
PROPELLANT, FLUORINE, GASEOUS AND LIQUID

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Appendix II-1

PROPELLANT, FLUORINE, GASEOUS AND LIQUID

1.0 Scope

This specification covers the minimum requirements for gaseous and liquid fluorine for use in propellant systems.

2.0 Applicable Documents

2.1 The following documents (and subsidiaries thereof) of issue in effect on date of invitation for bid, except as otherwise noted or controlled on an individual basis, form a part of this specification to the extent specified herein.

STANDARDS

MILITARY

MIL-STD 105D	Sampling Procedures and Tables For Inspection by Attributes.
MIL-STD 129	Marking For Shipment and Storage.

PUBLICATIONS

Title 49, Part 71-90	Code of Federal Regulations.
AFM 160-39	Handling of Liquid Propellants, United States Air Force.
AFM 127-100	Explosive Safety Manual
AFTO 11c-1-6	General Safety Precautions for Missile Liquid Propellants, United States Air Force.
ICC Tariff No. 15, Regulations	T. C. Geoge's Interstate Commerce Commission Regulation.

The following statement is applicable only for direct Government contracts: Copies of specifications, standards, drawings and publications required by contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting activity.

2.2 Other Publications--The following publications form a part of this specification. Unless otherwise specified, the issue in effect on date of invitation for bid shall apply.

Director of Defense Research and Engineering	The Handling and Storage of Liquid Propellants

(Applications for copies should be addressed to the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.)

3.0 Requirements

3.1 Materials--Type I gaseous and Type II liquid fluorine supplied to this specification shall meet the requirements of both Table 1 and 2.

3.2 Configuration--Type I fluorine gas shall be furnished in single cylinder configuration. At no time shall any cylinders be manifolded together for the purpose of analysis or shipment. Type II liquid fluorine shall be furnished from special vendor carriers to approved and cleaned storage tanks.

3.3 Processing Returned Gas Cylinders

3.3.1 Cleaning--Tanks and returned cylinders shall be emptied and evacuated before charging. The minimum standard of cleanliness maintained prior to charging shall meet the fluorine cleanliness requirements of Table 1.

3.3.2 Chlorinated solvents shall not be used for cleaning cylinders or related hardware. Aqueous ammonia shall not be used for leak detection. Gaseous ammonia is acceptable.

3.4 Product Marking--Each cylinder or tank of Type I or Type II fluorine shall be labeled, tagged or otherwise permanently identified with the title, number and change letter of this specification, date of analysis, manufacturer's name and designation.

Table 1
FLUORINE REQUIREMENTS

Components (helium free basis)	Limit (Weight %)
Fluorine	99.0% min.
Total Non-Condensables	0.9% max.
Nitrogen, Oxygen, Unspecified inert gases	
Total Condensables as:	0.1% max.
Carbon Dioxide, Carbon Tetrafluoride, Carbonyl Fluoride, Hydrogen Fluoride, Silicone Tetrafluoride, Sulphur Hexafluoride, Sulphur Oxyfluorides	
Oxygen Difluoride	0.05% max.
Particulate Matter	1 mg/liter max.
Delivered gas pressure Type I	400 psig at 70°F max. 360 psig at 70°F min.

Table 2
HELIUM CONTENT

Material	Limit (Weight %)
Fluorine Gas (Type I)	0.1% max.
Fluorine Liquid (Type II)	0.5% max.

4.0 Quality Assurance Provisions

4.1 Inspection Responsibility--The supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier may utilize his own or any other inspection facilities and services acceptable to the procuring activity. Inspection records of the examination and tests shall be complete and available to the procuring activity as specified in the contract or order. The procuring activity reserves the right to perform any of the inspections set forth in the specifications where such inspections are deemed necessary to assure that the materials and services conform to the requirements specified herein.

4.2 Lot--For the purposes of sampling, inspection and tests a maximum of 20 cylinders of Type I gaseous fluorine containing a maximum of six pounds of gas per cylinder pressurized to 400 psig at 70°F, produced in one continuous operation or batch, and submitted for acceptance at one time, shall constitute a lot. Each single container of Type II liquid fluorine shall constitute a lot.

4.3 Acceptance Criteria--Failure of individual or composite specimen taken for test to meet the requirements of this specification shall constitute the basis for rejection of the lot. Corroded or damaged containers, valves, or assemblies are unacceptable.

4.4 Sampling--Samples representative of each lot of material shall be selected per MIL-STD 105D for inspection and tested to the requirements of this specification.

4.5 Classification of Tests

4.5.1 Quality Conformance Tests--Quality conformance tests are those selected tests which shall be conducted by the supplier to assure continuing compliance with the requirements of this specification and enable the supplier to certify the conformance of his products to the procuring activity.

4.5.1.1 Tests--The quality conformance tests shall consist of all the tests and examinations outlined in 4.6 and 4.7 of this appendix.

4.6 Test Methods and Procedures

4.6.1 Test Methods--Test methods are given in Tables 3 and 4. The chemical assay method for fluorine, consisting of absorption of hydrogen fluoride by sodium fluoride, conversion of fluorine to chlorine and determination of the chlorine by an Orsat apparatus, shall be considered the referee method for the determination of fluorine.

4.6.2 Calibration--Instrument and certified chemical calibrations shall be performed as frequently as required for accuracy to a maximum interval of 7 days.

4.7 Examination

4.7.1 Inspection of Product--A representative sample from each lot shall be visually examined to determine conformance with 3.4

4.7.2 Inspection of Packaging--The supplier shall make such inspections as are necessary to assure that the requirements for preservation, packaging, packing and marking are met.

5.0 Preparation For Delivery

5.1 Preservation and Packaging

5.1.1 Fluorine Gas (Type I) shall be packaged in approved steel cylinders with valve protection as specified in Code of Federal Regulations. Fluorine, Pressurized, Liquid (Type II) shall be packaged in containers covered by special Interstate Commerce Commission permits.

Table 3

TEST METHODS

Components	Determination Method	Accuracy Level
Fluorine	1. Wet Chemical assay 2. By difference	±0.3%
Total Non-Condensables		
Nitrogen,	Gas chromatography, mass spectrometry or infrared spectrophotometry	±0.01%
Oxygen,	Gas chromatography, mass spectrometry	±0.02%
Unspecified inert gases	Gas chromatography, mass spectrometry	±0.01%
Total Condensables as:	Partial Pressure	±0.02%
Carbon Dioxide,	Gas chromatography, mass spectrometry or infrared spectrophotometry	±0.01%
Carbon Tetrafluoride,	Infrared spectrophotometry	±0.01%
Carbonyl Fluoride,	Infrared spectrophotometry	±0.01%
Hydrogen Fluoride,	Infrared spectrophotometry	±0.01%
Silicon Tetrafluoride,	Infrared spectrophotometry	±0.01%
Sulphur Hexafluoride	Infrared spectrophotometry	±0.01%
Sulphur Oxyfluorides	Infrared spectrophotometry	±0.01%
Oxygen Difluoride	Gas chromatography or infrared spectrophotometry	±0.02%
Particulate Matter	Filtration	±0.01%
Delivered gas pressure Type I	Pressure Gage	±2%

Table 4
HELIUM CONTENT TEST METHODS

Material	Determination Method	Accuracy Level
Fluorine Gas (Type I)	Gas chromatography or mass spectrometry	±0.01%
Fluorine Liquid (Type II)	Gas chromatography or mass spectrometry	±0.01%

5.2 Packing--All Type I fluorine cylinders in multiples shall be properly secured to pallets or appropriate handling racks for shipping and handling by standard handling equipment.

5.3 Marking for Shipment

5.3.1 Shipping name--The proper shipping name shall be shown on the outside shipping container.

a. Type I product--FLUORINE
b. Type II product--FLUORINE, PRESSURIZED, LIQUID.

5.3.2 Container Marking--All containers shall be marked "For Fluorine Service only." The marking shall be stenciled in letters not less than 7/16 inch or more than 1 inch in height. The tare weight shall be stamped on all containers. In addition to any special marking required by the contract or order, unit packages and shipping containers for shipment to the government shall be marked in accordance with the requirements of MIL-STD-129.

6.0 Notes

6.1 Intended Use--The propellant covered by this specification is primarily intended for use as an oxidizer and for purging, passivating and pressurizing of propellant systems and facilities.

6.2 Ordering Data--Contracts or orders shall specify the following:

a. Title, number and change letter of this specification.
b. Amount and type of material
c. Options offered, if required (see 4.1).

6.3 Unit of Purchase--The material shall be purchased by weight.

6.4 Definitions

6.4.1 Condensables--Substances (exclusive of oxygen difluoride, xenon and krypton) with a boiling point above -170°C ± 2° (-274°F).

6.4.2 Particulate Matter--Solid non-volatile matter below +74°C ± 2° (+165°F).

6.5 Precautionary Information--Fluorine is toxic. For safety information consult Air Force Manual AFM 160-39, Handling of Liquid Propellants and Air Force Technical Order AFTO 11C-1-6, General Safety Precautions for Missile Liquid Propellants.

SECTION III
MANUFACTURING AND MATERIAL PROCESSES

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Section III
MANUFACTURING AND MATERIAL PROCESSES FOR AIRBORNE FLUORINE FEED SYSTEMS

1.0 Material Handling and Process Control

The major consideration in the manufacture of fluorine components and/or systems, is a higher level of cleanliness than has been required for the less energetic oxidizer systems. Fluorine is one of the most active chemical elements, which reacts with almost all matter. In general, most fluorine reactions with contaminants are very energetic, and result in a high instantaneous release of energy. If the released energy is of sufficient magnitude it will cause partial or total reaction of the base material and/or container. It cannot be over stressed that it is this high potential reaction that makes fluorine systems unique. The degree of cleanliness necessary to maintain contamination reactions at a nondestructive level, and to obtain high systems reliability, exceeds the present liquid oxygen system requirements. This fact cannot be impressed too strongly upon potential producers or users of fluorine systems.

In order to obtain the required level of cleanliness it is important that complete process control and documentation be established and maintained throughout production. This includes the raw material as well as all intermediate operations as well as the final assembly. Material handling and process control must start with the unfabricated raw product to assure that minimum contaminants are present within, as well as on the surface of, the finished hardware. Contamination below the material surface can be just as detrimental to mission success as surface contamination, if it becomes exposed to the oxidizer. This exposure can result from breaks in the surface due to fatigue, scouring, etc. In general the exercise of reasonable raw product process control is essential to minimize cleaning costs while still assuring a product meeting the requirements of the final usage. This control must include protection during storage as well as during fabrication.

It cannot be overstressed that it is important that all personnel handling fluorine systems material be aware of the absolute necessity for final cleanliness. A single note or precautionary statement on an engineering drawing is not sufficient to assure an adequate quality end product. Fluorine hardware production cleanliness requirements should be included in the manufacturing phase of production by suitable planning and routing paper. At any point during manufacture, as well as after completion of fabrication, the exposure of material to contamination and fabrication processes must be documented sufficiently to allow determination of the suitability of the product for fluorine service.

2.0 Fabrication Techniques

No unique fabrication process requirements exist for the production of fluorine feed system components. However, sufficient controls must be applied to all processes to insure a minimum degree of contamination of the material being fabricated. This contamination can occur by the transfer of material from cutting and forming tools, absorption of coolants and preservants, and the dissolving or the inclusion of foreign material in the raw material which can subsequently be exposed during the manufacturing process, for example, inclusions in castings and moldings.

Contamination of raw material during its production phase is more difficult to control than at any other time during the life of the material. The material can be contaminated internally as well as on the surface, from: containers; chips; impurity additions, both from the surrounding environment, and contained within the primary ingredients; and numerous other means. There is no practical means to predict the degree of contamination prior to production of the raw material. In lieu of this contamination predictability, the necessary fabrication controls to obtain the minimum level of contamination based on past experience, should be established and rigidly adhered to. No firm recommendations can be made in this, but it should be kept firmly in mind that these controls can be extended to unnecessary and costly limits. The limit of control should be closely correlated with the capability of the cleaning methods to be used, to provide a finished product with the necessary purity for fluorine service. As experience is gained, a dollar savings may be effected by judicious passivation in lieu of surface contamination control.

2.1 Coolants and Preservatives

Material surfaces, which are exposed to coolants and preservatives commonly used during the fabrication of a component, can acquire surface contamination. Any coolant or preservative which contains petroleum base materials cannot be completely removed from the component surface unless a laborious and costly cleaning procedure is employed. Further, no convenient nondestructive means of inspecting for this type of surface contamination is known. It

is therefore recommended that an "amine nitrite synthetic coolant" be used in all cutting and forming operations where a coolant is required on porous materials; for example, cast material. This coolant is a polyethyleneglycol with amine nitrite additives and is completely soluble in water, therefore easily removed with the recommended cleaning procedures outlined in Appendix III-4. In addition to being easily removed during cleaning, the amine nitrite additives perform the function of an oxygen scavenger, commonly called a rust inhibitor. This preservation characteristic can only be considered as short term, and not relied upon as a true preservative for long term or outdoor storage of components, due to the high solubility of this solution in water. Table III-2.1a presents a summary of recommended and nonrecommended coolants commonly used in production processes. Caution should be used when machining aluminum since the amine nitrite cleaners may promote galvanic corrosion.

Inks used for material or component identification (ink stamping of part numbers) and dye penetrants used in various inspection methods are very similar in contamination characteristics to the petroleum base coolants and preservatives discussed above, and therefore are not recommended for use. The limitations of these materials are discussed in detail in paragraphs III-5.0 and 7.0.

2.2 Cutting and Forming Tools

Another form of contamination is the transfer of materials from the cutting and forming tools to the surface of the component being fabricated. This contamination is not of sufficient quantity to be of any major consequence and therefore can be ignored.

2.3 Welding

2.3.1 Techniques

All fluorine service welding, of the metals recommended in Section II-2.0, should use inert gas shielding or electron beam techniques. These techniques include: metal inert gas (MIG), gas metal arc (GMA) tungsten inert gas (TIG), or electron beam welded. TIG and MIG welding processes are widely used in building cryogenic tanks, and either of these, as well as electron beam techniques, are recommended for fluorine service tankage, and components.

2.3.2 Inspection

Welds should be inspected visually, ultrasonically, and radiographically. Dye penetrants, even those recommended for liquid oxygen tank inspection, must not be used. Section III-7, Inspection, should be consulted for appropriate inspection methods.

2.4 Polytetrafluoroethylene

Plastic or silastic materials are often required to effect low leakage seals. Very few of the traditional materials meet the compatibility requirements for use with fluorine. The most promising material is polytetrafluoroethylene (TFE Teflon or TFE Halon). This material is available in sheets, rods, tubes, and billets, fabricated by extrusion or molding processes, from powdered raw material. Three other fabrication processes are available, which allow spraying the material, in thin layers, directly onto a substrate material.

Investigations to date, throughout the industry, have resulted in very erratic compatibility data for polytetrafluoroethylene in fluorine. This has resulted in limited use of this material. It is felt that these erratic data are the result of variations in the polymeric material which have not been documented. Section II-2.7.1.2, Polymeric Material Compatibility and Section II-2.0, Material Selection Considerations should be consulted for specific recommendations and limitations in the use of this material.

2.4.1 Sheet, Rod, Tube, Billet

Two specifications for polytetrafluoroethylene, TFE, are presented in Appendix III-1, Polytetrafluoroethylene, Molded, Energetic Propellant Service; and Appendix III-2, Polytetrafluoroethylene, Molded, Cryogenic, Ultra Pure for Fluorine Service. In most cases the material produced within the confines of the former specification will meet the compatibility requirements of flourine systems. The second specification, for ultra pure material, is intended as a guide for procurement of laboratory grade, and quantities, of material, to be used in experimental investigations. Material procured to modifications of this specification may be applicable to production processes after evaluation, by individual users, of the material and use.

2.4.2 Sprayed

Several methods exist for the thin overcoating of material with TFE. One of these polmerizes (forms) the TFE directly on the substrate, from the basic chemical constituents, and the second applies the previously formed polymer

by flame-spraying techniques. Both of these processes make use of presently experimental or proprietary methods, and therefore will not be discussed further. The third process utilizes fully polymerized powder which is sprayed as an emulsion on to the substrate where it is heat cured in place. A recommended spray procedure is included in Appendix III-3. Section II-2.7.1.2 should be consulted for a discussion of the application of this technique to specific hardware.

2.5 Electroplating

Standard commercial electroplating techniques, which yield dense, uniform coatings, are suitable for fluorine service. Particular attention should be given to assure that a strong bond exists between the substrate and the plated material by suitable surface preparation, uncontaminated solutions and the correct electrical potential.

Table III-2.1a
CUTTING AND FORMING COOLANTS (TYPICAL)

Trade Name	Base Material	Recommended
Hocut SS	Polyethyleneglycol	Yes
Cincool T-10	Polyethyleneglycol	Yes
Pems 1755	Polyethyleneglycol	Yes
D. O. Soluble Oil	Petroleum	No
Microcut 5863	Petroleum	No
Vautrol 545	Petroleum	No
Trimsol	Petroleum	No
Tikut	Petroleum	No

3.0 Cleaning and Passivation

3.1 Cleaning

One of the primary factors influencing the reliability of fluorine systems is the level of cleanliness of each component at the time of exposure to fluorine. Fluorine will react with almost all matter, since it is one of the most active oxidizing elements known. A measure of the rate of reaction with any material is the magnitude of released energy, per unit of time. It would be impossible to list the reaction rates of all materials with fluorine, suffice to say that most contaminants are organic, and generally react very rapidly with fluorine. A more complete discussion will be found under the design Sections II-2.0 and II-5.0. It is theoretically possible to remove all contaminants which might be present from any material, however, this removal would require a long, laborious, and costly cleaning process which does not insure against additional contamination from residual products resulting from the reactions of the cleaning solutions and the contaminants being removed. In addition there are no known inspection methods by which the type or degree of surface contamination can be effectively evaluated. It is therefore apparent that the awareness and concern for a high level of product cleanliness must be a continuing one, and extend from the production of the raw material through the component production and installation, to its final operation in the flight vehicle.

Based upon comprehensive review, and evaluation of the cleaning procedures that have been used for liquid oxygen and fluorine service, a recommended fluorine cleaning procedural outline, (specification), is presented in Appendix III-4, Fluorine Service Cleaning Procedure. The major materials in a fluorine system are metals, while Teflon and ceramics or cermets play a minor role. All of these materials are capable of withstanding highly reactive cleaning agents, for short periods of time, without degradation. Assuming that reasonable contamination controls are utilized, as discussed in paragraphs III-1.0 and 2.0, experience has indicated that adherence to this cleaning outline, Appendix III-4, will provide the high level of cleanliness required for fluorine service. This adherence includes subjecting all components to both a "precleaning" and "final cleaning" process. Elimination

of all or part of the "precleaning" procedures may be effected, but only after sufficient experience with the specific contamination controls and products being produced, indicates that no compromise will result in the reliability of the end product.

Metals should be precleaned by vapor degreasing followed by immersion in an appropriate alkaline cleaning solution, followed in turn, by an acid "neutralizing" solution, water rinsed and then dried. Although not rigorously correct the phenomena may be explained as follows: the vapor degreasing removes most of the organic surface contaminants, while the alkalin solution removes the inorganics. The exposure of the metals to the alkaline cleaner leaves the surfaces basic, and therefore, susceptible to recontamination, from chemical salt formations, by reaction of acidic compounds for example, moisture in the air, etc. and the basic metal surface. The acid neutralizing solution eliminates this problem by converting the metal surface from a base to an acid. This acid solution also assists in removing inorganic contaminants and oxides. Copper alloys should not be treated with nitric acid, sulfuric acid should be substituted. Stainless steels should not be rinsed in sulfuric acid since this causes depassivation. "Precleaning" is followed by a "final cleaning" by flushing the component with trichlorotrifluoroethane, or methylene chloride to remove any traces of dust, lint, etc. All traces of the solvent are then removed by baking, as specified in Appendix III-4.

Teflon and ceramics (including cermets) or ceramic coated metals do not generally require "precleaning", if adequate process controls are employed throughout their manufacture. By virtue of the physical and chemical structure of these materials, they possess molecular-voids and/or micro-voids in which contaminants may be trapped, therefore, the best and most effective procedure is to prevent contamination rather than to rely upon cleaning. Experience to date indicates that a thorough flushing of these materials with a solution of water, and a detergent rinse in distilled water, and then baking to evaporate any trapped water, is sufficient to provide the required cleanliness. It must be realized that this process is predicated

upon use of material which meets the physical and chemical properties as specified in Appendix III-1; Polytetrafluorethylene, Molded, Energetic Propellant Service.

3.2 Passivation

Fluorine passivation is recommended for all systems and components prior to subjecting them to fluorine service. This procedure is outlined in detail in Appendix III-5, Fluorine Passivation Procedure. A detailed discussion of the phenomena is contained in Section II-1.2.3.

4.0 Assembly and Functional Testing

All final assembly of components should be done within a "clean room" using only certified, "Cleaned For Fluorine Service" parts, refer to Appendix, III-4, Fluorine Service Cleaning Procedure. No lubricants of any kind should be used to facilitate assembly, since those lubricants normally used to facilitate assembly are not compatible with fluorine. After completion of the required assembly operations, leak and functional tests should be performed, as applicable, on each component as described below.

Each system component which will be subjected to a pressure environment, during its normal functional operation, should be leak checked to the pressure value specified on the applicable drawing, using gaseous nitrogen or helium, per paragraphs 2.2.1 and 2.2.2, respectively, of Appendix III-5. The leak check methods and procedures should be similar to those currently used in the leak checking of airborne feed system components.

A complete functional test must be performed on all components, whose normal function in service, requires the movement of one or more parts after successful completion of the leak test. The test media, performance requirements, etc., should be as defined on the applicable drawing, and must include movement of all parts to the limit of their normal travel. All materials and techniques used should be of a type that will maintain the cleanliness level defined in Appendix III-4.

5.0 Identification

The current methods used in the aerospace industry to provide component identification may be used on fluorine service components with some general exceptions. No markings of any kind should be placed on any component surface that will contact fluorine, except those provided by the electro-etch method. Extreme care must be exercised to insure that no etched markings are placed on any component surface which would impair the performance of the component being marked. Raw material which has organic identification markings such as, inks and paints, etc., may be used, provided they are removed during manufacture. Inks which are commonly used for component identification are highly undesirable, ref. paragraph III-2.0. These materials are not capable of being completely removed during cleaning due to their absorption into the surface of the base material. Therefore, subsequent exposure to fluorine results in "fluorine energy sensitive" products being produced, which could contribute to component failure.

In the event that placement of identification marking is not possible on the non-fluorine contacted surfaces, the parts shall be tagged, using a metal tag, and tie wire made of material within the same electrochemical group as the part. See Table III-5.0a, for appropriate materials. Teflon parts shall be bagged in a polychlorotrifluoroethylene, KEL-F, bag with the necessary tag attached to the bag. Identification of fluorine cleaned parts is discussed in Appendix III-4.

Table III-5.0a

MATERIAL GROUPINGS FOR IDENTIFICATION PURPOSES*

Magnesium, Magnesium Alloys
Zinc, Galvanized Irons
Aluminum, Alclad, Cadmium
Mild Steel, Wrought Iron, Cast Iron
Lead, Tin
Muntz Metal, Maganese Bronze, Naval Brass
Copper, Copper Alloys, Nickel, Inconel, Monel, 300 series stainless steel
Silver, Gold, Platinum

*Identification tags should be made of a material in the same group as the identified material. Inclusion in this table does not imply recommendation for fluorine service. Material recommendations should be obtained from applicable section of Section II.

6.0 Packaging

Components are packaged to provide physical protection, and to reduce contamination. Contamination protection is provided "fluorine clean" components by the container (sealed bag) in which it is stored after cleaning. The recommended methods are described in Appendix III-4, paragraphs 4.3.1 and 4.3.2. Physical protection is a necessity to preclude damage to the component during storage and shipment. The recommended methods to accomplish this protection is described in Appendix III-4, paragraph 4.3.4.

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7.0 Inspection

The nondestructive inspection of materials and subcomponents is, a tool of prime importance in obtaining reliable components. When airborne components are to be used with fluorine, the successful utilization of inspection techniques to prevent the use of materials and/or subcomponents containing detrimental defects and contaminents becomes paramount. Two basic forms of nondestructive inspection are: (1) surface and internal inspection, and (2) dimensional inspection.

Surface inspection is used for detecting surface defects and discontinuities. Of the various methods currently employed in this mode of inspection, such as, dye penetrants, magnetic particles, etc.; few, if any, are compatible with fluorine. Attempts to remove the inspection materials from the surface of the material being inspected, using various stringent cleaning methods, have not been successful. The use of these materials, followed by conventional cleaning, has resulted in material ignition when impacted with 72 ft. lb. of energy, Reference 296, when the material sample was immersed in liquid fluorine. Two methods which do not require the use of any foreign material in the inspection process, are visual and eddy current. Presently these two methods are the only recommended ones for fluorine service components. Visual inspection may be either direct, or indirect with optical means; such as a boroscope. The eddy current inspection should be by the methods appropriate to the equipment being used.

Ultrasonic (through transmission, pulse-echo) and radiographic (X-ray, isotope) inspection are the two primary methods currently used for the detection of internal discontinuities in parts and materials. The choice of methods for a given application depend primarily on part geometry and the defect orientation. In some instances, more than one method may be required to adequately inspect a part. In general, ultrasonic inspection is most effective for detecting linear or essentially two-dimensional defects, such as cracks. Radiography is most effective for detecting essentially three-dimensional defects such as porosity or inclusions in castings and weldments. However, radiographic sensitivity decreases with increasing part thickness, whereas ultrasonic sensitivity is not significantly affected

by thickness variations. Conversely, part geometry can restrict or materially complicate the use of ultrasonic inspection. Also radiography can be used for detection of two-dimensional type defects when the radiation beam can be aligned in the plane of the defect.

Other possible internal inspection methods, such as thermal, microwave, and infrared, are relatively new to the nondestructive inspection field and require special techniques.

Dimensional inspection provides the verification of the component geometric conformance to dimensional requirements as specified on the application engineering drawing. This is important in fluorine service to assure that clearances are maintained to prevent galling or other surface failure when temperature cycled or corroded in service. The current high standard procedures and methods in use in the aerospace industry are appropriate and can be used with confidence.

Additional inspection requirements, which would entail destructive testing of material coupons, in the determination of chemical composition and physical properties of the raw material. These coupons are generally obtained from the supplied material, or provided separately from the same heat, batch, etc., from which the raw material was produced. The chemical composition of the material should be determined, in accordance with ASTM standard procedures, and may be determined at any time between the material formation phase and the material receipt at the user's receiving and inspection station. The physical properties of the material should be determined in accordance with ASTM standard procedures whenever specified on the applicable drawing or material purchase order. The inspection that is performed at the user's "receiving and inspection" station is, in general, the most important quality assurance operation throughout the life of the material or component. At this station, the most thorough inspection of the material or component is accomplished and establishes a firm basis of high reliability of the end item.

At no time during the manufacturing phase should any repair of material and/or component defects be performed without the written authorization of the

cognizant engineer. Any authorized repair shall be followed by all of the necessary inspections which will assure that the integrity and cleanliness of the item being repaired has not been compromised in any way.

Table III 7.0a, Inspection Requirements, lists the inspections requirements which should be accomplished using the applicable techniques described above.

Table III-7.0a

INSPECTION REQUIREMENTS

Application	Dimensional Inspection	Physical Properties	Chemical Properties	Surface Inspection	Internal Inspection
Wrought Metals	1	1	1	1	1
Raw Castings	1	1	1	1	1
Forgings	1	1	1	1	1
Teflon	1, 2, 3	1		1, 2, 3, 4	
Tubing	1, 2, 3	1	1	1, 2, 3, 4	1
Weldments	1, 2, 3	1	1	1, 2, 3	1, 2, 3
Brazed and Soldered Joints	1, 2, 3			1, 2, 3, 4	1, 2, 3
Machined Surfaces	1, 2, 3			1, 2, 3, 4	
Formed Parts	1, 2, 3	1	1	1, 2, 3, 4	1
Coatings	1, 2, 3			1, 2, 3, 4	1, 2, 3
Internal Bonding					1, 2, 3

Note:
1. Receiving and Inspection
2. In Process Inspection
3. Final Inspection
4. Clean Room Inspection

8.0 Documentation and Traceability

8.1 Documentation

All materials used in the manufacture of "fluorine service" components should be documented to provide a complete, itemized history of the individual materials. This should include, but not be limited to, the requirements listed in the following paragraphs, and in sufficient detail to provide a concise background for analysis and evaluation.

8.1.1 Raw Material (Including Weldments and Castings)

a. Lot number
b. Heat number (where applicable)
c. Batch number (where applicable)
d. Rough forming processes
e. Heat treatment (where applicable)
f. Chemical analysis (where applicable)
g. Mechanical properties, such as, tensile strength, etc., (where applicable)
h. Cleaning procedures (where applicable)
i. Repair methods (when approved and where applicable)
j. Date of manufacture
k. Name of manufacturer.

8.1.2 Receiving and Inspection

a. Chemical analysis
b. Mechanical properties
c. Physical inspection, such as, method and materials used, results, including the following:
   1. dimensional
   2. porosity
   3. inclusions
   4. cracks.

8.1.3 Manufacturing

a. Manufacturing process or processes used; such as, saw, lathe, mold, etc.

b. In process inspection methods, materials, and results

c. Cutting oils (where applicable)

d. Coolants (where applicable)

e. Mold release materials used (where applicable)

f. Cutting and/or forming tool materials; such as, high speed steel, carbide tipped, etc.

g. Heat treatment (where applicable), including stress relieving, and normalizing

h. Mechanical properties (where applicable)

i. Repair methods (when approved and where applicable)

j. Date of manufacture

k. Precleaning methods and materials (where applicable)

l. Name of manufacturer.

8.1.4 Post Manufacture

a. Precleaning methods and materials

b. Fluorine level cleaning methods and materials

c. Fluorine clean inspection methods and materials

d. Assembly procedure and materials (where applicable)

e. Leak check procedure, materials, and results

f. Functional checkout procedure, materials, and results (where applicable)

g. Preservation and/or packaging

h. Shipping and handling procedure

i. Fluorine clean certification date

j. Leak check certification date

k. Functional checkout certification date.

8.1.5 System

a. System assembly procedure and materials

b. Assembly working environment; such as, moisture, contamination, etc.

c. Passivation procedure and materials
   1. Component passivation (where applicable)
   2. System passivation
d. System functional checkout and results
e. Certification.

8.2 Traceability

The documentation information, listed in paragraph III-8.1, shall be maintained in a step by step sequence paralleling the documentation outline presented above. This information should be assembled and maintained in a manner to permit concise traceability of a component, from the raw material production phase through the finish form or any intermediate portion therein. Further, this information should indicate all foreign materials, such as, solvents, cutting tools, etc., which contact the component being documented, and the methods by which the contact was made.

The documentation should also indicate component operational cycles, such as leak and/or functional tests, performed during manufacture, to allow evaluation or prediction of operational life. This information should be in sufficient detail to record the operating regime and environment.

APPENDIX III-1
POLYTETRAFLUOROETHYLENE, MOLDED ENERGETIC PROPELLANT SERVICE

Appendix III-1

POLYTETRAFLUOROETHYLENE, MOLDED ENERGETIC PROPELLANT SERVICE

1.0 Scope

This specification establishes the minimum requirements for premium quality polytetrafluoroethylene molded and sintered sheets, billets, rods, parts and tubing.

2.0 Applicable Documents

2.1 Applicable Documents--The following specifications and standards, drawings, and publications of issue in effect on date of invitation for bid, except as otherwise noted or controlled on an individual basis, form a part of this drawing to the extent specified herein.

SPECIFICATIONS

MIL-F-22191	Films, Transparent, Flexible, Heat Sealable, for Packaging Applications.
MIL-STD-129D	Marking for Shipment and Storage.
MIL-STD-105D	Sampling Procedures and Tables for Inspection by Attributes.
ASTM-D149-64	Method of Test for Dielectric Breakdown Voltage and Dielectric Strength of Electrical Insulating Materials.
ASTM-D256-56	Methods of Test for Impact Resistance of Plastics and Electrical Insulating Materials.
ASTM-D792-64T	Methods of Test for Specific Gravity and Density of Plastics by Displacement.
ASTM-D1457-62T	Specification for TFE-Fluorocarbon Resin Molding and Extrusion Materials.
ASTM-E132-61	Method for Determination of Poisson's Ratio at Room Temperature.

Application for copies of ASTM standards should be addressed to the American Society for Testing and Materials, 1916 Race Street Philadelphia 3, Pennsylvania.

The following statement is applicable only for direct military contracts: Copies of specifications, drawings, and publications required by contractors in connection with specific procurement functions, should be obtained from the procuring activity, or as directed by the contracting officer.

3.0 Requirements

3.1 Qualification--The processed material and parts furnished shall be a product that has been tested and has passed the qualification tests specified herein. The qualification testing need not be accomplished for repeat orders, provided the process material and process have not been changed, and a certified statement to this effect is furnished to the procuring activity.

3.2 Material

3.2.1 Quality--Pure, virgin, unpigmented polymer shall be used to produce processed material and parts. Color may vary from white to off-white; mottling is permissible.

3.2.2 Conditions--Unless otherwise specified, processed material and parts shall be furnished in the stress-relieved condition.

3.2.3 Voids--All processed material and parts shall contain no visible voids, fissures, or bubbles.

3.2.4 Contamination--Processed material and parts shall contain minimum contamination consistent with the fabrication process employed, certified by the supplier, and approved by the procuring activity.

3.3 Physical and Mechanical Properties--The mechanical and physical properties shall conform to Table 1 and 2.

Table 1 PHYSICAL PROPERTIES	
Specific Gravity	2.18 - 2.25
Dielectric Strength Minimum Volts per Mil	1,000
Dimensional Stability in/in. max.	0.003

Table 2 MECHANICAL PROPERTIES	
Tensile Strength at 25°C±1°C(77°F±2°F), psi min	3,500
Elongation at 25°C±1°C (77°F±2°F) percent, min	250
Tensile Strength at -196°C±1°C(-320°F±2°F),psi, min	12,000
Elongation at -196°C±1°C(-320°F±2°F), percent min	2
Impact Strength at 25°C±1°C(77°F±2°F) FT-lb per in. of Notch, Min (izod)	2
Poisson's Ratio at 25°C±1°C(77°F±2°F) Min	0.45

3.4 Tolerances--Unless otherwise specified, the following tolerances apply. The processed material and parts shall be measured at 25°C ± 1° C (77°F ± 2°F).

3.4.1 Sheet

Thickness--

Nominal Thickness Inches	Thickness Tolerance, Inch Plus	Minus
0.010 and under	0.0005	0.0005
Over 0.010 to 0.032,	0.001	0.001
Over 0.031 to 0.062,	0.002	0.002
Over 0.062 to 0.157,	0.003	0.003
Over 0.157 to 0.350,	0.005	0.005
Over 0.350	0.010	0.005

Lateral Bow--As specified on the drawing or purchase order.

Width--Minus, zero; plus, as specified on drawing or purchase order.

3.4.2 Rod--

Nominal Diameter Inches	Tolerance, Inch Plus Only
0.750 and under	0.016
Over 0.750 to 2.000,	0.062
Over 2.000 to 3.000,	0.125
Over 3.000 to 5.000,	0.187
Over 5.000 to 12.000,	0.250

3.4.3 Billet--As specified on the drawing or purchase order.

3.4.4 Tubing

Nominal OD or ID Inches	ID Tolerance Inch Minus Only	OD Tolerance Inch Plus Only
2 and under	0.062	0.062
Over 2 to 3,	0.125	0.125
Over 3 to 5,	0.187	0.187
Over 5 to 12,	0.250	0.250

3.4.5 Parts--As specified on the drawing or purchase order.

3.5 Product Marking

3.5.1 Product Marking--No identifying markings of any kind shall be applied to the processed material or parts.

3.5.2 Marking of Package--Processed material or parts shall be enclosed in a package that has been non-destructively, durably, and legibly marked with the manufacturer's name, designation, lot number, date of manufacture, size, serial number, and number of specification.

This marking shall appear only on the outside edge of an air-tight, sealed polytrifluorochlorethylene bag, at least 1/4 inch away from the heat-seal.

3.5.3 Tagging of Package--Any tag affixed to the rim beyond the heat-sealed edge, shall be identified in accordance with 5.1.

3.6 Workmanship--The processed material shall be molded and sintered from clean virgin polytetrafluoroethylene polymer. The processed material or parts shall be unfilled polytetrafluoroethylene uniform in quality and conforming to this specification.

4.0 Quality Assurance Provisions

4.1 Inspection Responsibility--The supplier is responsible for the performance of all inspection requirements, as specified herein. Except as otherwise specified, the supplier may utilize his own or any other inspection facilities and services, acceptable to the procuring activity. Inspection records of the examination and tests shall be complete and available to the procuring activity, as specified in the contract or order. The procuring activity reserves the right to perform any of the inspections set forth in the specifications, where such inspections are deemed necessary to assure that materials and processes conform to prescribed requirements.

4.2 Lot--For purposes of sampling, inspection, and tests, a lot shall consist of all the processed material manufactured at one time from one batch under the same conditions.

4.3 Sampling

4.3.1 Tests--Sampling plans for visual inspection and testing shall conform to MIL-STD-105D, AGL 10.0, Inspection Level I, Double Normal Sampling.

4.4 Classification of Tests

4.4.1 Qualification Tests--Qualification tests are those tests which enable the procuring activity to determine that the processed material complies with this specification. The qualification tests consist of all inspections and tests included in Section 3, except the inspection of packaging.

4.4.2 Quality Conformance Tests

a. Material specifications:

Quality conformance tests are those selected tests which shall be conducted by the supplier to assure continuing compliance with the requirements of this specification and enable the supplier to certify the conformance of his product to the procurring activity. These tests are all considered destructive in nature; therefore, only non-delivered material shall be tested.

	Test	Paragraph
a.	Tensile Strength at Ambient Temperature	4.5.3
b.	Elongation at Ambient Temperature	4.5.3
c.	Specific Gravity	3.3
d.	Dielectric Strength	3.3

4.5 Test Methods and Procedures

4.5.1 Standard Conditions--Unless otherwise specified, standard conditions shall be 25°C ± 1°C (77°F ± 2°F) and a relative humidity of 50 ± 5%.

4.5.2 Physical Properties

a. Specific Gravity:

The specific gravity of the material shall be determined in accordance with ASTM D792, Method A. Results shall conform to paragraph 3.3.

b. Dielectric Strength:

The dielectric strength shall be determined in accordance with ASTM D149-61. The results shall conform to paragraph 3.3.

c. Dimensional Stability:

The material shall be heated at 79°C ± 3°C (175°F ± 5°F) and maintained for 24 hours, then cooled slowly to room temperature. The material shall not change dimensionally more than 0.003 inch/inch, when measured at 25°C ± 1° C (77°F ± 2°F) after the above cycle.

4.5.3 Mechanical Properties

a. Tensile Strength and Elongation:

The tensile strength and elongation of the material shall be determined in accordance with ASTM D 1457. Cross head speed shall be 0.10 inch/minute at both 25°C ± 1°C (77°F ± 2°F), and -196°C ± 1°C (-320°F ± 2°F). Results shall conform to paragraph 3.3.

b. Impact Strength:

The impact strength of the material shall be determined in accordance with ASTM D. Izod Method A. Results shall conform to paragraph 3.3.

c. Poisson's Ratio:

Poisson's ratio shall be determined in accordance with ASTM E 132-61. The results shall conform to paragraph 3.3.

4.5.4 Visual Properties--All processed material and parts shall be examined visually to determine conformance to 3.2.1, 3.2.3 and 3.2.4.

4.6 Examination

4.6.1 Inspection of Product--Inspect to verify, as appropriate, conformance with this specification.

4.6.2 Inspection of Packaging--The supplier shall make such inspections as are necessary to assure that the requirements for preservation, packaging, packing, and marking are met.

5.0 Preparation for Delivery

5.1 Preservation and Packaging--Processed materials or part shall be packaged individually in an environment sufficiently clean to maintain the requirements of 3.2.1, 3.2.2, 3.2.3, and 3.2.4. Package shall consist of a 0.002 minimum thickness bag or tube of polychlorotrifluoroethylene conforming to MIL-F-22191, Type 1, and heat-seal closed, leaving a minimum of 1/4 inch of material beyond heat-seal edge to allow affixing of an identification tag, in accorance with paragraph 3.5.2.

5.2 Marking for Shipment--MIL-STD-129.

5.2.1 Special Marking

POLYTETRAFLUOROETHYLENE
SPECIFICATION _____
MANUFACTURER'S CODE NUMBER _____
LOT NUMBER _____
DATE OF MANUFACTURE _____
PURCHASE ORDER NUMBER _____

6.0 Notes

6.1 Intended Use--The material is primarily intended for seals, gaskets, poppets, etc., in propellant systems for missiles, space and allied systems from -320°F to +165°F.

6.2 Ordering Data--Orders or contracts should specify the following information:

a. Title, part number
b. Quantity _____ Size _____
c. Options 3.1, 4.1
d. Certified vendor test reports shall be included in duplicate.

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APPENDIX III - 2
POLYTETRAFLUOROETHYLENE, MOLDED, CRYOGENIC, ULTRA-PURE FOR FLUORINE SERVICE

APPENDIX III-2
POLYTETRAFLUOROETHYLENE
MOLDED, CRYOGENIC

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Appendix III-2
POLYTETRAFLUOROETHYLENE, MOLDED, CRYOGENIC, ULTRA-PURE FOR FLUORINE SERVICE

1.0 Scope

This specification establishes the minimum requirements for ultra-pure, clean, completely fluorinated polytetrafluoroethylene molded and sintered sheets, billets, rods, parts, and tubing.

2.0 Applicable Documents

2.1 Applicable Documents--The following specifications and standards (and subsidaries thereof), drawings, and publications of issue in effect on date of invitation for bids, except as otherwise noted or controlled on an individual basis, form a part of this drawing to the extent specified herein.

SPECIFICATIONS

a.	MIL-STD-105D	Sampling Procedure and Tables for Inspection by Attributes
b.	MIL-STD-129D	Marking for Shipment and Storage
c.	MIL-F-22191	Films, Transparent, Flexible, Heat Sealable, for Packaging Applications
d.	FED-STD-209	Clean Room and Work Station Requirements, Controlled Environment
e.	FED-STD-595	Federal Specification Colors

2.2 Other Publications--The following publications (etc.) shall apply.

2.2.1 ASTM Standards

a.	ASTM D149-64	Method of Test for Dielectric Breakdown Voltage and Dielectric Strength of Electrical Insulating Materials

b.	ASTM D256-56	Method of Test for Impact Resistance of Plastics and Electrical Insulating Materials
c.	ASTM D792-64T	Methods of Test for Specific Gravity and Density of Plastics by Displacement
d.	ASTM D1457-62T	Specification for TFE-Fluorocarbon Resin Molding and Extrusion Materials
e.	ASTM-E1-6132	Method for Determination of Poisson's Ratio at Room Temperature
f.	ASTM-D648-56	Method of Test for Deflection Temperature of Plastics Under Load
g.	ASTM-E-94-62T	Recommended Practice for Radiographic Testing
h.	ASTM Special Technical Publication	15C:ASTM Manual on Quality Control of Materials

Application for copies of ASTM standards should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania.

3.0 Requirements

The processed materials and parts furnished shall be a product that has been tested, and has passed the qualification tests specified herein. The qualification testing need not be accomplished for repeat orders, provided the processed materials and process have not been changed, and a certified statement to this effect is furnished to the procurring activity.

3.1 Material--Pure virgin unpigmented polymer having particle diameter between 150-375 μ, and containing under 20 ppm terminal carboxyl groups, shall be used to produce materials and parts. The powder shall have been synthesized under conditions insuring 2-sigma control, with respect to molecular weight, fluorine content, melting point, and percent of organic impurities. Both processed materials and parts shall furnish 99.9% assurance of passing the fluorine impact test, detailed in ASTM D256A.

3.1.1 Color--The color shall be within the color range of Federal Standard Colors 27875-27886 as illustrated in Federal Standard 595.

3.1.2 Conditions--Unless otherwise specified, materials shall be processed without mold release, in chromium-plated molds, and resultant parts be furnished in stress-relieved conditions.

3.1.3 Voids--Processed materials and parts shall contain no more than 0.001% by volume, of voids, pinholes, fissures, and bubbles.

3.1.4 Contamination--Processed materials and parts shall contain no contamination such as foreign particles or inclusions. The virgin powder and processed materials and parts shall be processed in clean rooms conforming to FED-STD-209, Class 100,000.

3.2 Physical and Mechanical Properties--The following mechanical and physical properties shall conform to values shown in Tables I and II.

Table I
MECHANICAL PROPERTIES

Tensile Strength at 25°C±1°C (77°F±2°F) psi, min	4,500
Elongation at 25°C±1°C (77°F±2°F) percent, min	250
Tensile Strength, at -196°C±1°C (-320°F±2°F), psi, min	13,000
Elongation at -196°C±1°C (1320°F±2°F), percent min	4
Impact Strength at 25°C±1°C (77°F±2°F), ft-lb per in. of notch, min	2.6
Poisson's Ratio at 25°C±1°C (77°F±2°F), min	0.55

Table II PHYSICAL PROPERTIES	
Specific Gravity	2.19-2.20
Dielectric Strength, min. volts/mil	1,000
Heat Distortion Point, @ 66 psi fiber stress, min	255
Dimensional Stability, in./in., max	0.002
Macroscopic Flaws, % by volume, max	0.001

3.3 Tolerances--Unless otherwise specified, the following tolerances apply; the processed material part shall be measured at 25°C ± 1° C (77°F ± 2°F).

3.3.1 Sheet

Thickness

Nominal Thickness Inches	Thickness Tolerance, Inch Plus	Minus
0.010 and under	0.005	0.0005
Over 0.010 to 0.031	0.001	0.001
Over 0.031 to 0.062	0.002	0.002
Over 0.062 to 0.157	0.003	0.003
Over 0.157 to 0.360	0.005	0.005
Over 0.350	0.010	0.005

Lateral Bow--As specified on the drawing or purchase order.

Width--Minus, zero; plus, as specified on drawing or purchase order.

3.3.2 Rod

Nominal Diameter Inches	Tolerance, Inch Plus Only
0.750 and under	0.016
Over 0.750 to 2.000	0.062
Over 2.000 to 3.000	0.125
Over 3.000 to 5.000	0.187
Over 5.000 to 12.000	0.250

3.3.3 Billet--As specified on the drawing or purchase order.

3.3.4 Tubing

Nominal OD or ID Inches	ID Tolerance Inch Minus Only	OD Tolerance Inch Plus Only
2 and under	0.062	0.062
Over 2 to 3,	0.125	0.125
Over 3 to 5,	0.187	0.187
Over 5 to 12,	0.250	0.250

3.3.5 Parts--As specified on the drawing or purchase order.

3.4 Product Marking

3.4.1 Marking of Package--Processed material or parts shall be enclosed in a package that has been non-destructively, durably, and legibly marked with the manufacturer's name, designation, lot number, date of manufacture, size, serial number, and number of specification.

This marking shall appear only on the outside edges of an air-tight, sealed polytrifluorochloroethylene bag, at least 1/4 inch away from the heat-seal itself.

3.4.2 Tagging of Package--The tag affixed to the rim beyond the heat-sealed edge, shall be identified in accordance with paragraph 5.1.

3.5 Workmanship--The processed material shall be molded and sintered from clean virgin polytetrafluoroethylene polymer. The processed material or parts shall be unfilled polytetrafluoroethylene uniform in quality and condition, free from inclusions, sediment, foreign materials, separation, or other defects detrimental to fabrication or performance.

4.0 Quality Assurance Provisions

4.1 Inspection Responsibility--The supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier may utilize his own or any other inspection facilities and services acceptable to the procurring activity. Inspection records of the examination and tests shall be kept complete, and available to the procuring activity, as specified in the contract or order. The procuring activity reserves the right to perform any of the inspections set forth in specifications, where such inspections are deemed necessary to assure that materials and processes conform to prescribed requirements.

4.2 Lot--For purposes of sampling, inspection, and tests, a lot shall consist of all the processed materials and parts manufactured under 2-sigma control limits about average and standard deviation, from one lot of virgin powder, and submitted to procurement at the same time.

4.3 Sampling--Sampling plans for visual inspection and testing shall conform to MIL-STD-105D-AQL 1.0; LQD 5.0; P_c = 10; failure of an item to conform to the applicable requirements of this specification shall be basis for rejection of the entire lot.

4.4 Classification of Tests

4.4.1 Qualification Tests--Qualification tests are those tests which enable the procuring activity to determine that the processed material complies with the specification requirements. The qualification tests consist of all inspections and tests included in paragraph 4, except for the inspection of packaging.

4.4.2 Quality Conformance Tests

Material specifications:

Quality conformance tests are those selected tests which shall be conducted by the supplier to assure continuing compliance with the requirements of this specification and enable the supplier to certify the conformance of his product to the procuring activity.

	Test	Paragraph
a.	Tensile strength at Room Temperature	3.3
b.	Elongation at Room Temperature	3.3
c.	Specific Gravity	3.3
d.	Dielectric Strength	3.3
e.	Microscopic Flaws	3.3

4.5 Standard Conditions--Unless otherwise specified, standard conditions shall be 25°C ± 1°C (77°F + 2°F) and a relative humidity of 50 ± 5%.

4.5.1 Physical Properties

a. Specific Gravity:

The specific gravity of the material shall be determined in accordance with ASTM D792, Method A. Results shall conform to paragraph 3.3.

b. Dielectric Strength:

The dielectric strength shall be determined in accordance with ASTM D149-64. The results shall conform to 3.3.

c. Dimensional Stability:

The material shall be heated at 79°C ± 3°C (175°F ± 5°F) for 24 hours, and cooled slowly to room temperature. The material shall not change more than 0.003 inch/inch, when measured at 25°C ± 1°C (77°F ± 2°F).

d. Heat Distortion Point:

Heat distortion point shall be determined in accordance with ASTM D648-56. Fiber stress shall be 66 psi.

e. Macroscopic Flaws:

Percent macroscopic flaws shall be determined in accordance with ASTM E-94-62T.

4.5.2 Mechanical Properties

a. Tensile strength and elongation:

The tensile strength and elongation of the material shall be determined in accordance with ASTM D 1457. Cross-head speed shall be 0.01 inch/minute at both 25°C ± 1° C (77°F ± 2°F) and -196°C ± 1°C (-320°F ± 2°F). Results shall conform to paragraph 3.3.

b. Impact strength:

The impact strength of the material shall be determined in accordance with ASTM D 256, Method A. Results shall conform to paragraph 3.3.

c. Poisson's ratio:

Poisson's ratio shall be determined in accordance with ASTM E 132-61. The results shall conform to paragraph 3.3.

4.5.3 Visual Properties--All processed material and parts shall be examined visually to determine conformance to paragraphs 3.2.1, and 3.2.4. A bright electric light source shall be used to aid in the determination of conformance to paragraph 3.2.4.

4.6 Examination

4.6.1 Inspection of Product--Inspect to verify, as appropriate, conformance with this specification.

4.6.2 Inspection of Packaging--The supplier shall make such inspections as are necessary to assure that the requirements for preservation, packaging, packing, and marking are met.

5.0 Preparation for Delivery

5.1 Preservation and Packaging--Processed materials or part shall be packaged individually in an environment sufficiently clean to pass requirements of paragraph 3.2.4. Package shall consist of 0.002 thick minimum bag or tube of polytrifluorochloroethylene conforming to MIL-F-22191, Type 1, and heat-seal closed, leaving a minimum of 1/4 inch of material beyond heat-seal edge to allow affixing of identification tag, in accordance with paragraph 3.5.2.

5.2 Marking for Shipment--MIL-STD-129.

5.2.1 Special Marking

POLYTETRAFLUOROETHYLENE

SPECIFICATION _____

MANUFACTURER'S CODE NUMBER _____

LOT NUMBER _____

DATE OF MANUFACTURE _____

PURCHASE ORDER NUMBER _____

6.0 Notes

6.1 Intended Use--The material is primarily intended for seals, gaskets, poppets, etc., for missiles, space and allied systems, and for service within the temperature range of -320°F to 175°F.

6.2 Testing Procedures for Virgin Powder--The details of all testing procedures and maintenance of statistical control shall be negotiated between the procuring activity and vendor. The testing procedures shall be selected from appropriate documents in paragraph 2.2.1 and from the following references:

a.	Crystallinity, %	"Effects of Fabrication on Properties of TFE Resins." Thomas, Lantz, Sperati, McPherson, SPE Journal, Volume 12, No. 6, June 1956.
b.	Fluorine Content, %	Haslam, J. and S. M. A. Whettum, Journal of Applied Chemistry, 2, 339 (1952).
c.	Organic Impurities, %	"Application of Pyrolysis Gas Chromatography to Polymer Characterization," B. Groten, Analytical Chemistry 36, 1206-1212 (1964).
d.	Organic Impurities, %	"Identification of Polymers in Compounded Cured Rubber Stocks by Pyrolysis/Two Channel Gas Chromatography," Cole, H. M., Pelterson, D. L., Sljaka, V. A., Smith, D. S., Cabot Research Paper 3-28. Paper #25 to A. C. S Division of Rubber Chemistry, Philadelphia, October 1965. Cabot Corporation, 125 High Street, Boston Massachusetts.

e. Fluorine Impact — "Testing Compatibility of Materials for Liquid Oxygen Systems," NASA Specification MSFC-SPEC-106A May 5, 1964.

6.3 Ordering Data--Orders or contracts should specify the following:

a. Title, part number

b. Quantity and Size

c. Inspection requirements

6.4 Certification--Certified test reports shall be included in duplicate with all lots relative to the lot average, lot standard deviation, and upper- and lower-control limits (2-sigma) on virgin powder, processed material and parts.

6.5 Definitions

6.5.1 Lot--A lot shall consist of all the processed materials and parts manufactured under statistically controlled conditions from one batch of virgin powder, synthesized under statistically controlled conditions, and submitted at the same time to procurement.

6.5.2 Statistical Control--Conditions prevailing whenever the average and standard deviation of random samples fall within the 95% confidence limits about the grand average and lot-standard deviation, with respect to prescribed tests.

6.5.3 Virgin--Material which has not been subjected to any mechanical, physical or chemical treatment after leaving the source of raw material.

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APPENDIX III-3
PROCEDURE FOR SPRAY COATING POLYTETRAFLUOROETHYLENE ON METALS

Appendix III-3

PROCEDURE FOR SPRAY COATING POLYTETRAFLUORETHYLENE ON METALS

1.0 Purpose

This appendix defines the recommended materials and procedures to be used in the application of TFE Teflon coatings upon metals.

2.0 Materials

2.1 Primer Coating--The primer coating shall be an unpigmented aqueous dispersion of 48 ± 5% by weight, of tetrafluoroethylene resin, containing modifiers to promote adhesion to the metal, with the required non-ionic wetting agents. DuPont's TFE premixed primer number 850-201, or equivalent should be used on ferrous, nickel, chromium, and copper metals and alloys thereof, and pre-mixed primer number 850-202, or equivalent, used on aluminum and aluminum alloys.

2.2 Primer Storage--The primer coating material described in 2.1 possesses a shelf life of approximately one month if stored at a temperature between 60 and 80°F, and ten months when stored at a temperature between 38 and 42°F. This material will freeze at approximately 32°F and coagulate within a few days at a temperature of approximately 100°F. Therefore, the material temperature should be maintained above 32°F and at or below 80°F. Some settling will occur during periods of storage, therefore, prior to use, the material temperature should be maintained at 70 to 80°F for a minimum of 15 minutes and then agitated by shaking or rolling the container. The material shall not be agitated if the temperature is below 60°F since coagulation may occur.

2.3 Final Coating--The final coating material shall be an unpigmented aqueous dispersion of 48% ± 5% by weight of tetrafluoroethylene resin with the required non-ionic wetting agents. DuPont's TFE fluorocarbon resin, clear finish, number 852-201, or equivalent should be used.

NOTE: "High build" TFE fluorocarbon resins; i.e., DuPont's number 851-221, 851-224, etc., are not acceptable as a final coating material.

2.4 Final Coating Storage--The final coating material described in paragraph 2.3 possesses a shelf life of approximately 12 months if stored at a temperature between 60 and 70°F. For the same reasons discussed in paragraph 2.2, the material temperature should be maintained above 32°F, and at or below 80°F. Some settling will occur during periods of storage, therefore, the material should be agitated, at a temperature above 60°F, once a month, and just prior to use to assure the proper degree of dispersion.

3.0 Procedures

3.1 Substrate Preparation

The surface upon which the polytetrafluoroethylene will be deposited should be processed as follows:

3.1.1 Preparation

Remove all dirt, rust, scale, paint, etc., using NASA specification MSFC-SPEC - 164 procedures for the applicable substrate material and contamination to be removed.

3.1.2 Vapor Degrease

NOTE: After completion of the vapor degreasing, the substrate material should only be handled using polyethylene gloves, in order to prevent hydrocarbon deposits resulting from fingerprints.

3.1.3 Using one of the following methods, roughen the surface, obtaining a smooth matte finish, upon which the polytetrafluoroethylene will be deposited.

1. Grit blast with aluminum oxide.
2. Chemically etch, with subsequent neutralization of the etching medium.

NOTE: Cast surfaces which possess a smooth matte finish should be used without any further roughening.

3.1.4 Raise the metal temperature to 725 to 750°F and maintain for 5 to 10 minutes.

NOTE: Copper and brass should not be preheated in air due to the resulting oxide formation which readily scales off.

NOTE: Aluminum alloys undergo structural property changes below the substrate heating temperature, and TFE fusing temperature. This effect results in removal of the heat treat properties; viz., the alloy is annealed, therefore, there is no advantage in the use of heat treated aluminum with Teflon spray coatings.

3.2 Primer Coating Application

The primer material coating shall be applied to the substrate material by spraying, using the necessary equipment and techniques to provide a homogeneous nonporous coating. The substrate material shall be maintained at ambient temperature during the spraying operations. The following procedure shall be used:

3.2.1 Apply a coating thickness of 0.0003 ± 0.0001 inch using the material described in paragraph 2.1.

3.2.2 Air dry at or below a temperature of 180°F to remove the volatile constituent of the coating.

3.2.3 Heat to a temperature of 725° to 750°F (metal temperature) and maintain for 5 to 10 minutes.

3.2.4 Cool, by air or water quench, to 70° to 80°F.

3.3 Final Coating Application

The final material coating shall be applied over the primer coating by spraying, using the necessary equipment and techniques to provide a homogeneous nonporous coating. The stubstrate material shall be maintained at ambient temperature during the spraying operations. The following procedure shall be used:

3.3.1 Ensure that the primer coating and substrate are completely dry by oven drying if they have been contaminated with free moisture or saturated vapor.

3.3.2 Apply a coating thickness of 0.0008 ± 0.0002 inch using the material described in paragraph 2.3.

3.3.3 Air dry at or below a temperature of 180°F to remove the volatile constituent of the coating as indicated by appropriate color change.

3.3.4 Heat to a temperature 725° to 750°F (metal temperature) and maintain for 5 to 10 minutes.

3.3.5 Cool, by air or water quench, to 70° to 80°F.

3.3.6 Sequentially repeat steps 3.3.1 through 3.3.5 until the required total coating thickness, as specified on the applicable drawing, is obtained.

4.0 Packaging

4.1 General

After completion of paragraph 3.3, the coated part shall be heat sealed in a Kel-F bag. An identification tag shall be attached either to the part, or inserted in, or attached to the bag with sufficient information to identify the part number, spray coating lot number, and date of coating.

4.2 Packaging for Shipment

The part shall be packaged within a container with sufficient padding so as to provide the minimum degree of scoring, scratching, or other physical damage during normal modes of coast to coast transportation.

APPENDIX III - 4
FLUORINE SERVICE CLEANING PROCEDURE

Appendix III-4
FLUORINE SERVICE CLEANING PROCEDURE

1.0 Purpose

This appendix defines the recommended materials and procedures to be used in cleaning oxidizer system components used in fluorine service.

2.0 Environment Requirements

All final cleaning, inspection, assembly, and preservation of cleaned components shall be performed within a clean room meeting the requirements of specification Federal Standard Number 209, Class 100,000.

3.0 Materials

3.1 Cleaning Solvents

3.1.1 Vapor Degreasing

Solvent used for vapor degreasing cleaning processes shall be per MIL-T-7003, O-T-634, Type 2, except the non-volatile residue shall not be greater than 0.010 gram per 500 milliliters.

3.1.2 Component Cleaner

3.1.2.1 Trichlorotrifluorethane

This solvent when used in the final cleaning processes, shall be per MSFC-SPEC-237.

3.1.2.2 Methylene Chloride

This solvent when used in the final cleaning processes, shall be per MIL-D-6998 Grade A.

3.1.3 Drying or Preservation Gas

3.1.3.1 Air

Air used in the drying and preservation processes shall be pre-filtered to a 100 micron level (absolute), the hydrocarbon content shall not exceed 0.5 parts per million by weight in terms of n-cetane, and the moisture content shall not exceed 26.3 ppm by weight.

3.1.3.2 Nitrogen

Nitrogen gas used in the drying and preservation processes shall be in accordance with MIL-P-27401, Type 1, and in addition, shall adhere to the purity requirements listed in paragraph 3.1.3.1.

4.0 Procedures

The following precleaning procedures shall not be used with assembled components which contain dissimilar metals, plastics, elastomers, or have been certified "fluorine clean" by the supplier provided the suppliers procedure adheres to this specification. In the event a multi-material component has not been certified "fluorine clean" it shall be completely disassembled and the individual subcomponents precleaned and final cleaned per the following applicable procedures.

4.1 Precleaning

Components, except those made of Teflon, requiring precleaning shall be processed outside the clean room, and shall include removal of dirt, grit, chips, grease and other major contaminants by flushing with compressed air, scrubbing with methylene chloride using a bristle brush, and again flushing with compressed air. Repeat any or all of this procedure until the component is visually free of these major contaminants. After removal of major contaminants, the following individual material cleaning procedures shall be used.

4.1.1 Low Alloy Carbon Steel

4.1.1.1 Vapor degrease using solvent, per paragraph 3.1.1.

4.1.1.2 Immerse in an alkaline steel cleaning solution. The solution concentration and temperature, and the component immersion time to be in accordance with the recommendations of the manufacturer of the alkaline cleaner used.

4.1.1.3 Rinse thoroughly with tap water.

4.1.1.4 Immerse in a solution of 10 to 15 percent (by volume) sulfuric acid, 85 to 90 percent water maintained at room temperature for approximately 20 minutes.

4.1.1.5 Rinse thoroughly with tap water.

4.1.1.6 Dry thoroughly with warm air.

4.1.2 Stainless Steel, Monel, Inconel

4.1.2.1 Vapor degrease using solvent per paragraph 3.1.1.

4.1.2.2 Immerse in an alkaline steel cleaning solution. The solution concentration and temperature, and the component immersion time to be in accordance with the recommendations of the manufacturer of the alkaline cleaner used.

4.1.2.3 Rinse thoroughly with tap water.

4.1.2.4 Immerse in a solution of 35 percent (by volume) nitric acid, 65 percent water, maintained at a temperature of 125 ± 5°F for 20 minutes.

4.1.2.5 Rinse thoroughly with tap water.

4.1.2.6 Dry thoroughly with warm air.

NOTE: The above procedure, paragraph 4.1.2, shall not be used with annealed or unhardened 440C.

4.1.3 Aluminum Alloys

4.1.3.1 Vapor degrease using solvent per paragraph 3.1.1.

4.1.3.2 Immerse in an aluminum cleaning solution. The solution concentration and temperature, and the component immersion time to be in accordance with the recommendations of the manufacturer of the alkaline cleaner used.

4.1.3.3 Rinse thoroughly with tap water.

4.1.3.4 Immerse in a solution of 15 percent (by volume) nitric acid, 85 percent water, maintained at 125 ±5°F for 20 minutes.

4.1.3.5 Rinse thoroughly with tap water.

4.1.3.6 Dry thoroughly with warm air.

4.1.4 Magnesium Alloy

4.1.4.1 Degrease using solvent per paragraph 3.1.1.

4.1.4.2 Alkaline clean in a steel type cleaner for one to five minutes.

4.1.4.3 Immerse in a solution of ten percent (by weight) chromic acid, 90 percent water maintained at a temperature of 140 ±10°F for one to five minutes.

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4.1.4.4 Rinse thoroughly with tap water between each of the above steps.

4.1.4.5 Dry thoroughly with warm air.

4.1.5 Copper and Copper Alloys

4.1.5.1 Degrease using solvent per paragraph 3.1.1.

4.1.5.2 Alkaline clean in a steel type cleaner for one to five minutes.

4.1.5.3 Immerse in a solution of ten percent (by volume) sulfuric acid, 90 percent water maintained at a temperature of 145 ± 15°F until the surfaces are free of oxides.

4.1.5.4 Rinse thoroughly with hot water between each of the above steps.

4.1.5.5 Dry thoroughly with warm air.

4.2 Final Cleaning

Clean all component exterior surfaces, except Teflon, by vacuuming and/or air purging, and purge the interior of the part with gas, per paragraph 3.1.3.1 or 3.1.3.2, if possible prior to transferring into the clean room.

4.2.1 Single Material Metallic Components and Subcomponents

4.2.1.1 Flush all significant surfaces (those surfaces which will come in contact with the system fluid) with trichlorotrifluorethane or methylene chloride meeting the requirements of paragraph 3.1.2, for two to five minutes.

4.2.1.2 Place in an oven at a temperature of 240 to 260°F and bake for one hour.

4.2.1.3 Package per paragraph 4.3 if assembly into a component is not forthcoming within a reasonable time.

4.2.2 Filters and Anti-Vortex Devices

4.2.2.1 Disassemble the component per the applicable drawing.

4.2.2.2 Immerse parts in a component cleaner per paragraph 3.1.2 for a minumum of 15 minutes. A nylon brush may be used to remove dirt.

4.2.2.3 Purge the interior of the filter element with a component cleaner per paragraph 3.1.2.

4.2.2.4 Place in an oven at a temperature of 240 to 260°F and bake for one hour.

4.2.2.5 Repeat the above procedures until the component parts are visually clean.

4.2.2.6 Reassemble the components per the applicable drawing.

4.2.2.7 Package per paragraph 4.3.

4.2.3 Teflon Subcomponents

4.2.3.1 Flush all significant surfaces with a solution of water containing one or two percent (by volume) of detergent; i.e., Alconox or equivalent, maintained at room temperature for a minimum of five minutes.

4.2.3.2 Rinse thoroughly with distilled water.

4.2.3.3 Place in an oven at a temperature of 240 to 260°F and bake for one hour.

4.2.3.4 Package per paragraph 4.3 if assembly into a component is not forthcoming within a reasonable time.

4.2.4 Component Assembly

4.2.4.1 All necessary component assembly shall be accomplished per the applicable drawing, after individual subcomponent final cleaning has been completed.

4.2.4.2 Package per paragraph 4.3.

4.3 Packaging

4.3.1 Small Components

Components and/or assemblies which are sufficiently small or possess external significant surfaces shall be packaged as follows:

4.3.1.1 Wrap all significant surfaces and/or openings thereto with a minimum of two layers of aluminum foil. Secure the foil with pressure-sensitive tape, completely covering all loose ends, obtaining as tight a seal as possible. Under no conditions shall the tape contact any significant surface.

4.3.1.2 Place the component in a Kel-F bag.

4.3.1.3 Purge the interior of the bag with gas conforming to paragraph 3.1.3.

4.3.1.4 Exhaust the gas atmosphere from the bag by hand.

4.3.1.5 Heat seal the open bag end.

4.3.1.6 Identify per paragraph 4.3.3.

4.3.2 Large Components

Components and/or assemblies which do not meet the limitations stated in paragraph 4.3.1 shall be packaged as follows:

4.3.2.1 Place a Kel-F tube over all significant surface openings. Secure the tube with pressure-sensitive tape to the external component surface obtaining as tight a seal as possible.

4.3.2.2 Purge the interior of the component and tube with gas conforming to paragraph 3.1.3. Exhaust the gas atmosphere from the tube by hand.

4.3.2.3 Heat seal the open tube end.

4.3.2.4 Identify per paragraph 4.3.3.

4.3.3 Identification

Firmly affix a tag to the outside of the packaged component without penetrating any portion of the protective bag which forms the contaminant barrier for the component. The tag shall contain the following information:

4.3.3.1 Part name.

4.3.3.2 Part number.

4.3.3.3 Manufacturer's serial number, if applicable.

4.3.3.4 Cleaned for fluorine service.

4.3.3.5 Date of cleaning.

4.3.4 Packaging for Shipment

4.3.4.1 Small Components

Small parts shall be protected by wrapping with protective material and placing each part in a container prior to transporting. The parts shall be packed within the container to prevent movement.

4.3.4.2 Large Components

Place large components in compartmented padded box, one part per compartment. Large components may also be placed on a pallet or within an individual container with designed padded covers. These components shall be secured to the pallet or within the container to prevent movement.

APPENDIX III - 5
FLUORINE PASSIVATION SERVICE

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Appendix III-5
FLUORINE PASSIVATION PROCEDURE

1.0 Purpose

This appendix defines the recommended procedures to be used in passivation of fluorine systems and components thereof.

2.0 Requirements

2.1 Cleanliness

2.1.1 Components

All components which are to be passivated using the procedures specified herein shall be certified as having been cleaned, preserved, and packaged for fluorine service as defined in Appendix III-4.

2.1.2 Gases

The gases used in the following procedure shall be prefiltered to a 100-micron level (absolute), the hydrocarbon content shall not exceed 0.5 ppm (parts per million) by weight, in terms of n-cetane, and the moisture content shall not exceed 5 ppm by weight.

2.2 Purging and Passivating Gases

2.2.1 Nitrogen

A source capable of supplying gaseous nitrogen in accordance with MIL-P-27401, type 1, and paragraph 2.1.2, at a pressure of 110% of the maximum operating pressure as specified on the applicable system and/or component drawing, shall be provided.

2.2.2 Helium

A source capable of supplying Bureau of Mines, Grade A (7500-156410) gaseous helium in accordance with paragraph 2.1.2, at a pressure of 110% of the maximum operating pressure as specified on the applicable system and/or component drawing, may be provided, refer to paragraphs 3.1.1 and 3.1.2.

2.2.3 Fluorine

A source capable of supplying gaseous fluorine meeting the following requirements:

F_2	99.0% minimum
O_2, N_2 and other inerts	0.9% maximum
CO_2, HF and other gases	0.1% maximum

at a minimum pressure of 110% of the maximum expected operating pressure, as specified on the applicable system and/or component drawing, shall be provided.

3.0 Procedure

3.1 Passivation

3.1.1 Component

The component shall be mounted in the passivation system using all necessary techniques to maintain the original cleanliness level. The component shall be pressurized with nitrogen, per paragraph 2.2.1, to the pressure limit specified on the applicable component drawing, and completely leak checked. The methods and/or procedures to be utilized shall be commensurate with those currently used in the leak checking of oxidizer feed system components. Helium, per paragraph 2.2.2, may be used in lieu of nitrogen if desired, however, this is not necessary. The component shall then be purged with

nitrogen or helium gas, per paragraphs 2.2.1 and 2.2.2 respectively, for a minimum of 5 minutes. Every effort should be made to effect a thorough flush of all fluorine contact surfaces with this gas. If feasible, the system and component should be evacuated to a maximum level of 5 inches of Mercury for a minimum of 15 minutes after completion of the above operations.

After performance of the above purging and leak check operations, the component shall be statically exposed to fluorine gas, per paragraph 2.2.3 as follows:

3.1.1.1 Fill the system and component with the fluorine gas at a pressurization rate not to exceed 25% of maximum expected operating pressure per minute. The system and component shall be statically maintained at 110% of this maximum expected operating pressure for a minimum of 30 minutes.

3.1.1.2 Vent the fluorine gas from the system.

NOTE: During any venting operation, a minimum system pressure of 0.5 psig shall be maintained, to prevent atmospheric contaminants from entering the system.

3.1.1.3 Purge the system and component with nitrogen gas per paragraph 2.2.1 for a minimum of 15 minutes.

3.1.1.4 While maintaining a minimum system pressure of 0.5 psig, break the components downstream system connection. Cover all significant surface (those surfaces which in service normally contact fluorine) openings with one layer of Alcar (Kel F), using tape to secure the Alcar to the external surfaces of the component. The tape seal shall be as airtight as possible. If, in the event the component has more than one downstream connection, only one connection shall be broken and Alcar covered at any one time.

3.1.1.5 After completion of paragraph 3.1.1.4 above, the component's upstream connection shall be broken and the opening covered in the manner described above in paragraph 3.1.1.4. It should be noted that expediency is of prime importance in this operation to prevent component contamination.

NOTE: If the procedure of protection as described in paragraph 3.1.1.4 and 3.1.1.5 above is impractical, i.e., the component should be covered with one layer of Alcar and the opening heat sealed. A chamber (component containment chamber) purge of nitrogen at a minimum pressure of 0.5 psig shall be maintained through this operation.

3.1.1.6 The passivated component shall immediately be packaged as described in paragraph 4.3.4 of Appendix III-4 and stored in such a manner as to prevent its exposure to moisture. The specific storage method will be dictated by the and use and anticipated storage time.

3.1.2 System

The system passivation procedure is basically the same as that used for component passivation. The passivation supply source shall be connected to the system and the system pressurized with nitrogen, per paragraph 2.2.1, to the pressure limit specified on the applicable system assembly drawing, and completely leak checked. The methods and/or procedures to be utilized shall be commensurate with those currently used in the leak checking of oxidizer feed systems. Helium, per paragraph 2.2.2, may be used in lieu of nitrogen if desired, however this is not necessary.

The system shall then be purged with nitrogen or helium gas, paragraph 2.2.1 and 2.2.2, until the moisture content of the gas exhausting from the system is equal to or less than 5 ppm by weignt.

After performance of the purging and leak check operations, all system valves shall be placed in an "Open" position. The system shall be statically exposed to fluorine gas, per paragraph 2.2.3, as follows:

3.1.2.1 Fill the system with the fluorine gas at a pressurization rate not to exceed 25% of maximum expected operating pressure per minute. The system shall be maintained at 110% of this maximum expected operating pressure for a minimum of 30 minutes.

3.1.2.2 Vent the fluorine gas from the system.

NOTE: During any venting operation, a minimum system pressure of 0.5 psig shall be maintained to prevent atmospheric contaminants from entering the system.

3.1.2.3 Purge the system with nitrogen gas per paragraph 2.2.1 for a minimum of 15 minutes.

3.1.2.4 Vent the nitrogen gas from the system maintaining 0.5 psig minimum system pressure.

3.1.2.5 Disconnect the passivation supply source from the system and secure connection to prevent atmospheric contamination from entering the system.

3.1.2.6 Thoroughly flush the external portion of the system's passivation supply source connection with nitrogen or dry compressed air.

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SECTION IV
OPERATIONAL PROCEDURES AND SAFETY

Section IV

OPERATIONAL PROCEDURES AND SAFETY IN THE TESTING OF AIRBORNE FLUORINE FEED SYSTEMS

1.0 Introduction

The handling of fluorine requires more care than the handling of oxygen. This is brought about not only because of the increased chemical reactivity, but also due to the biological toxicity. Fluorine has been handled over a long period of time in large quantities in ground systems. This emphasizes that this energenic propellant is safe to handle. It must be realized, however, that airborne systems present additional hazards due to the lower safety factors utilized in the design of systems. In general test procedures, utilizing fluorine, will be governed by the toxicity constraints provided the system has been designed, built and cleaned as set forth in Sections II and III. Each test facility and different airborne system will require unique and specialized procedures due to physical variations among the systems, therefore specific procedures are not included in this handbook. A general discussion follows which will assist personnel in establishing specific operational procedures. Sections II and III should also be consulted to establish the background philosophy for handling fluorine. It must be reiterated that procedures established for oxygen testing may be applicable to fluorine systems, however they will need to be enlarged and be made more inclusive before they can be considered adequate for fluorine.

2.0 Procurement and Transportation

2.1 Procurement

Liquid and gaseous fluorine may be purchased from any chemical supply company which is capable of supplying a consistently acceptable grade of fluorine which meets the requirements of the specification presented in Appendix II-1. Corporations currently capable of supplying a suitable grade of fluorine include: Allied Chemical Co., Air Products Corp., Union Carbide (Linde), Callery Chemical Co., and Matheson Co., Inc.

2.2 Transportation

Fluorine gas may be shipped by common carrier in metal containers complying with ICC specification 3A 2000 or 3BN400, Parts 71-90. Cylinders must not be charged to over 400 psig at 70°F and must not contain over 6 pounds of gas.

Liquid fluorine is shipped by tank trucks in quantities of 1,200-5,000 pounds. A special ICC permit is required for this operation. Allied Chemical Corporation has obtained a special permit for transport trailers which utilize a double-jacketed Dewar-type container. The inside vessel contains the liquid fluorine, the first jacket is filled with liquid nitrogen coolant, and the outer jacket is evacuated and filled with insulation to reduce the heat flux into the coolant. A detailed description of the tank assembly and the fluorine transfer procedure is given in Reference 91. At the present time, shipment of liquid fluorine by rail has not been authorized.

3.0 Safety

Prior to activating any fluorine test facility it is essential that all cognizant personnel be apprised of the nature of fluorine. These personnel include security forces, firemen, safety specialists, laboratory and test personnel, etc. It is essential that this information be readily available and abbreviated sufficiently so that all personnel will be familiar with it. The normal instrument to accomplish this is a safety manual. This should be required reading for all personnel who might come in contact with fluorine and should also be readily available for reference.

Recommended operating procedures, safety measures, and other information pertinent to the safe handling of fluorine are presented below. This type of information should be included in the safety manual of any organization involved with handling fluorine. Supplemental safety information may be found in Reference 91 and 146, which should be reviewed by Safety Department and supervisory personnel.

4.0 Toxicology

4.1 General

No accurate data have been presented, to date, which specifically define the toxic nature of fluorine. The toxic effects of liquid fluorine are similar to those of gaseous fluorine, only greater due to the higher concentration of vaporized fluorine. If one can smell fluorine, the concentration can be considered to be excessive for continuous exposure, and one should leave the area within 15 minutes. Douglas found that venting of fluorine in a still atmosphere created heavy pockets of the gas in areas that originally contained no fluorine. Inhalation of a high concentration of fluorine is considered impossible because its stifling effect is so severe that choking and asphyxia would result if relief or escape were delayed beyond a few seconds.

Fluoride dusts are toxic; therefore, any flaky or powdery deposits formed on equipment exposed to fluorine should be handled as toxic material. Exposure to fluorine compounds, such as metallic fluorides can cause nose bleeds and sinus trouble, loss of weight, back stiffness and spinal chord paralysis.

Following the ingestion of fluorine or fluorides, the action of the stomach acids upon fluorides releases potent hydrofluoric acid. It is a moot question whether poisoning is caused by the fluorine itself or by the hydrofluoric acid formed by the hydrolysis of fluorine with water in the body.

4.2 Governmental Regulation of Maximum Allowable Concentration

The levels of the maximum allowable toxic gas concentration and exposure to dosages defined under the "Clean Air Act," Public Law 88-206, Reference 304, must be considered in defining the specific hazard potential of the site for fluorine and fluorine compounds. The threshold limit values (often referred to as the maximum allowable concentrations) for 1964, established by the American Conference of Governmental Industrial Hygienists (Reference 321), are 0.1 ppm for fluorine and 3 ppm for hydrogen fluoride. These values were recommended as a guide in the control of health hazards and

represent conditions to which nearly all workers may be exposed, day after day, without adverse effect. The values refer to time-weighted average concentrations for a normal work day. The amount by which these figures may be exceeded for short periods without injury to health depends upon a number of factors, such as: the nature of the contaminant; whether very high concentrations, even for short periods, produce acute poisoning; whether the effects are cumulative; the frequency with which high concentrations occur; and the duration of such periods.

The above threshold limits were also recommended in June 1964 by the Chief of the Safety Office for NASA rocket launch sites (Reference 320). In addition, the following emergency exposure limits, recommended by the American Conference of Governmental Industrial Hygienists, are being used at the John F. Kennedy Space Center:

Fluorine (F_2)

Emergency Exposure Limits

GROUP I (controlled work force)	GROUP II (uncontrolled community)	Duration
25* ppm	5 ppm	5 min
15* ppm	3 ppm	15 min
10* ppm	2 ppm	30 min
5* ppm	1 ppm	60 min

Hydrogen Fluoride (HF)

Emergency Exposure Limits

GROUP I (controlled work force)	GROUP II (uncontrolled community)	Duration
300 ppm	30 ppm	5 min
150 ppm	15 ppm	15 min
100 ppm	10 ppm	30 min
50 ppm	8 ppm	60 min

*Includes a safety factor of 2X because of incomplete animal data and inadequate analytical methods for determining F_2. Expected values would otherwise read 50, 30, 20, and 10 ppm for 5, 15, 30, and 60-minute exposures respectively.

These emergency exposure limits are designed to give guidance in the control of single, brief exposures to airborne contaminants in the working environment. They are based on the following assumptions:

1. Exposures at these levels will be accidental, not the result of engineering controls designed to hold exposures at these levels.
2. Normally prevailing values of airborne contamination will be below threshold limit values or maximum allowable concentrations.
3. These accidental exposures will be single events, such as, if a man is exposed at these levels further exposure will be prevented until he gains his normal resistance.
4. Men who could be exposed under these conditions are not idiosyncratic, hypersensitive, or otherwise predisposed to disease from the specific contaminant.
5. Persons who could be exposed under such conditions are under medical surveillance.
6. The probable severity of injury due to secondary accidents resulting from impairment of judgment and coordination will be considered in applying these values. A degree of intoxication, even though reversible, that prevents self-rescue is not considered acceptable.
7. "Safety factors" of 10 used in deriving threshold limit values, maximum concentrations, and air-quality guides are not applied to emergency exposure levels except in cases of low confidence in the extrapolation of animal data to man.
8. Mixtures of contaminants that may produce possible interactions such as potentiation or antagonism have not been considered in proposing the E. E. L. values.

The National Research Council Committee of Toxicology in August 1963 recommended the following emergency tolerance levels for fluorine:

Emergency Tolerance Level	Duration
2.0 ppm	5 min
1.5 ppm	15 min
1.0 ppm	30 min
0.5 ppm	60 min

These recommendations were based on the assumption that exposures are rare in the life of any individual. If repeated exposures are anticipated, the values for 5, 15, and 30 minutes were recommended to be reduced to 0.5 ppm.

The ETL values discussed at the November 19, 1964, NRC Committee of Toxicology Meeting (Reference 325) are the following:

Emergency Exposure Limits

Fluorine	Hydrogen Fluoride	Duration
5 ppm	30 ppm	5 min
3 ppm	20 ppm	15 min
2 ppm	10 ppm	30 min
1 ppm	8 ppm	60 min

Mr. H. Schmidt (Reference 323) of the NASA Lewis Research Center stated in March 1965 that the following toxicity limit changes for fluorine were suggested to the NRC Committee on Toxicology:

Emergency Tolerance Level	Duration
From 2.0 ppm to 5 ppm	5 min
From 1.5 ppm to 3 ppm	15 min
From 1.0 ppm to 2 ppm	30 min
From 0.5 ppm to 1 ppm	60 min

The emergency tolerances levels supposedly will produce only mild temporary toxic effects. However, the toxicity effect varies with the individual.

The Hygienic Guide Series on Fluorine published by the American Industrial Hygienic Assn. (Reference 308) presents a complete summation of hygienic standards, toxic properties, industrial hygiene properties, and medical information relating to the handling of fluorine.

5.0 Leak Detection and Measurement

5.1 Gross Detection

The human nose is one of the best and most sensitive detectors of fluorine. Tests at Lewis Research Center indicate that the threshold concentration for detection by smell is one ppm or lower. Allied Chemical Corp. claims that quantities as low as a few parts per billion (possibly 3-17) might be the minimum concentration detectable by odor.

For the detection and location of small gas leaks, anhydrous ammonium hydroxide in plastic squirt bottles can be used as a rapid qualitative test. If fluorine is present, the reaction produces a smoke which is easily visible. This test must be performed with caution, however, since a larger leak may produce a flame jet. Potassium iodide paper provides another rapid detection method. This paper will react by discoloration on exposure to fluorine concentrations as low as 25 ppm.

Leak-indicating paints that undergo vivid color changes when exposed to halogens, have been investigated and may be applicable. However, their reported low sensitivity to vapor exposure and their weathering characteristics indicate that additional development is required and therefore are not recommended for fluorine service.

5.2 Trace Detection and Measurement

5.2.1 General

The checkout, tests, and qualification of components designed for use with fluorine oxidizers require sensitive and reliable instrumental physicochemical methods to detect concentrations, ideally, in the range of 0.1 ppm to several percent in air or purge gas.

A variety of chemical reactions known to give traceable reaction products has been tested in the laboratory and has been used to detect leaks. In most cases the chemicals and sampling equipment are awkward to handle and require a

highly trained engineer or chemist to use them successfully. Some development of specialized instrumentation has taken place and several types are now available. Others are in the laboratory developmental stage or have been constructed only for in-house use. The operational criteria for a satisfactory detector for use in the field are as follows:

1. Sensitivity - The minimum concentration of a substance that can be detected and indicated by an analytical instrument or method. At least 0.1 ppm full scale.
2. Specificity for fluorine, CTF, FLOX, and Compound A - The ability of an instrument to detect one substance without interference from impurities or other foreign substances. Less than 1% interference from other oxidizers.
3. Precision and accuracy - Precision - the degree to which the analytical instruments or method repeatedly indicates the concentration of a substance. Accuracy - the measure of the difference between the indicated concentration and the true concentration, assumed or accepted on the basis of a standard independent method. ±10% or better in ppm range; ±2% or better in percent range.
4. Response - (Response Time) - The time interval required for an instrument or device to detect and measure the concentration of a substance. Automatic gas sampling rates permitting the following:
   A. Dynamic response - 80% of final reading in 10 sec or better.
   B. Integrated Data (Total Dose) - Direct readout in ppm-minutes or ppm-hours.
5. Range of concentration detected - 0.1 ppm to 100,000 ppm full scale.
6. Read out
   A. Alarm - Visual and sound.
   B. Remote - Recording in blockhouse.
7. Maintainability
   A. Corrosion Resistance - Against weather and acid gases.
   B. Detector Life - Maximum possible or paralleled units.
   C. Ease of Calibration - Internal or simple standard source.
8. Portability - Not over 75 lb with batteries and amplifier.
9. Cost - $5,000 or less.

5.2.2 Commercially Available Instruments

Four instruments are commercially available for leak detection and on-site monitoring. The salient features of these instruments are compared in Table IV-5.2a.

Table IV-5.2a

COMMERCIALLY AVAILABLE INSTRUMENTS FOR F_2 DETECTION

Manufacturer	Tracerlab	Mine Safety Appliances Company	Teledyne Systems Company	Davis Instruments
Detection Principle	Dry Krypton-85 Clathrate	Ionization Chamber Detects on Aerosol	Transducer operated on the principle of a micro fuel cell 200 L/min	Measurement of conductivity after gas sample ionizes in water 0.2 to 5 L/min
Sample Flow Rate	0.5 L/min	4 to 10 L/min	200 L/min	0.2 - 5 L/min
Ranges	0 to 10, 0 to 30, 0 to 100 ppm full scale	0 to 5, 0-200 ppm	0 to 5, 0 to 50, 1-2000 ppm	0 to 10, 1 to 100 ppm
Sensitivity	0.1 ppm	0.05 ppm at 5-ppm range, 2 ppm at 200-ppm range	0.1 ppm	1 ppm as HF
Precision & Accuracy	±10% full scale	±2% of full scale	±2% of full scale	±2% of full scale
Selectivity	Selective to F_2 and F_2 compounds	Not selective	Not selective	Not selective
Interferences	Humidity, HF	Other acid gasses--HF, HCl, N_2, O_4, etc.	All oxidizers	Any ionizable gas, such as NH_3, CO_2, SO_2, HCl, N_2H_2, etc.
Portability	Small (19 in. x 14 in. x 16 in.), compact, rugged	15 lb	Weight < 15 lb	Portable, 50 lb with batteries
Maintainability	Clathrate cell life limited	Fill reagent container and charge batteries every 24 hours	Maintenance required every 3 to 6 months	After 8 hours continuous use, batteries must be charged
Operational Period	Calibration good for 3 months with continuous operation at 5 ppm	1% change in calibration every 30 days	Calibration required every 2 to 4 weeks	Must be calibrated for specific gas; seldom need to change ion exchange resin
Warning System	Adjustable alarm set at all ranges	Alarm--audio and visual	Audio and visual alarms	Alarms available
Effect of Overdose	Shuts off	Recovers after overdose	Has presetable high-concentration cutoff	Will saturate
Cost	$3,000	$1,250 to $4,000	$3,500 + accessories	$3,000 to $6,000
Remarks	AEC license for 50 mc of Kr-85 required	Remote recorder readout possible; need radioactive source license	Remote read out, probe mode, multiple sampling systems all available	Cannot determine F_2 accurately because of F_2 hydrolysis to HF

5.2.3 Noncommercial Methods for Detection of F_2 and F_2 Compounds

5.2.3.1 Methods Based on Direct F_2 Measurement

5.2.3.1.1 Spectrophotometric (Ultraviolet Absorption)

The F_2 concentration in F_2-O_2 mixtures has been determined by completely vaporizing a liquid sample, allowing it to expand into a special 10-cm-long spectrophotometer cell, and measuring the intensity of the broad absorption band for fluorine in a spectrophotometer. Because of the corrosive properties of fluorine, the cell was constructed of stainless steel and coated with polytetrafluoroethylene, which served to minimize the absorptive effects of the metal. Sapphire windows were used because of their adequate ultraviolet transmission characteristics and resistance to attack by fluorine. A Beckman Model DK-1 recording spectrophotometer was used for the intensity measurements. The intensity of the absorption at a wave-length of 278.0μ, which is a function of the fluorine concentration, was measured. Unknown concentrations can be determined immediately by reading the intensity and comparing it with calibration curves prepared from known concentrations. The liquid fluorine mixtures were sampled with a cosmodyne sampler and transferred to the spectrophotometer cell through a system containing a vacuum pump and manometer.

Concentrations of F_2 that can be analyzed range from 0.5% to 100%. The precision and accuracy claimed for the method are 0.3% and ±0.6%, respectively. This method is not applicable to CTF and Compound A analyses since they will not absorb at the same wavelength of the ultraviolet spectrum. This technique could possibly be adapted to in-line monitoring of F_2 concentrations.

5.2.3.1.2 Radiochemical Exchange by Use of Kryptonates

Radioactive Krypton (Kr-85) is incorporated in the surface of solid silver iodide (AgI) and is released when F_2 reacts with the AgI. The proportionate amount of Kr-85 is detected by a Geiger tube.

A kryptonate differs from a clathrate in that a kryptonate consists of any solid material into which Kr-85 has been incorporated, while a clathrate

consists of a three-dimensional organic crystalline cage in which a second component such as the inert gas, krypton, has been trapped. The most commonly used clathrate is hydroquinone krypton 85. In this clathrate, the element or compound to be detected must oxidize the hydroquinone to release Kr-85, which in turn is radiochemically counted. It can be used to detect F_2, O_3, ClO_2, and other oxidizers. One of its severest shortcomings is its sensitivity to relative humidity, which must be compensated for in calibration.

In the kryptonates, the Kr-85 is entrapped in a lattice of solid. To release the Kr-85, the kryptonated solid must undergo a chemical reaction to destroy the surface layers. Presumably the kryptonates can be made to have greater specificity for detecting gases, because a solid can be used that will only react with the gas to be detected. Parametrics, Inc., have developed a kryptonate in which the F_2 reacts with AgI to form AgF and release I_2, which in turn releases the Kr-85, which is radiochemically counted. This company has developed one instrument for use at Wright Field. It is superior to the clathrate because it is selective for F_2 and is not sensitive to relative humidity, HF, or O_3. The kryptonated cell has a life of several weeks at the 1-ppm level but will only last 1 hour if used at the 1 to 5% F_2 level. From the weight of the kryptonate, and knowing flow rate and F_2 concentration, cell life can be calculated. FLOX, CTF and Compound A should also be detectable by this instrument, because they will react with the AgI.

5.2.3.1.3 Electrochemical

This oxidation-reduction instrument was designed and assembled at General Dynamics/Astronautics. The cell consists of a glass tube in which a platinum gauze electrode and a silver wire electrode are immersed in a lithium choride solution. When an atmospheric sample is bubbled through the lithium chloride solution, any fluorine present will oxidize an equivalent amount of chloride to chlorine. The electromotive force (EMF) developed by the cell is a function of the partial pressure of chlorine and, therefore, of the partial

pressure of fluorine in the atmospheric sample. The EMF developed in the cell produces a proportional electric current in the external circuit, the value of which is continuously recorded on a strip-chart recorder. In the absence of fluorine, the cell still produces a small EMF as a result of the difference in electrochemical potential of the silver and platinum electrodes, but this is nulled by a bucking voltage provided by a small battery.

The atmospheric sample is drawn through the cell at nominal flow rate of 220 cc/min.

The instrument is 14-1/2 in. wide by 10-1/2 in. high, 11 in. deep and weighs 32 lb. It is completely portable and powered by batteries. No provision is made for remote readout.

Normal ranges of concentrations of fluorine determined are 0 to 5 ppm and 0 to 10 ppm. It could possibly be adapted, by buffering the electrolyte to 1,000 ppm detection. The response is approximately 90% in 30 sec in the 0 to 5-ppm range.

While the instrument is selective to fluorine, with no HF interference, it should also detect CTF, FLOX and Compound A, individually, since they undergo similar reactions with lithium chloride.

The cost to build the instrument was reported as $1,200.

5.2.3.1.4 Mercury Reaction

Gaseous fluorine oxygen mixtures are introduced into an apparatus and mercury is added to react with the fluorine. As a result of the reaction, the fluorine gas is reduced by the mercury to form mercuric fluoride which reduces the pressure in the apparatus. After completion of the reaction, Kel-F polymer oil is added to restore atmospheric pressure to the apparatus. The volume of oil plus the volume of mercury equals the volume of fluorine in the sample. The apparatus is a simple glass setup operated at near-atmospheric pressures and therefore does not require vacuum-type stopcocks; however, a manometer and vacuum manifold (to 1 mm Hg pressure) is

required as well as a constant temperature bath. This technique was used to analyze fluorine in approximately 30% fluorine oxygen mixtures. A precision of ±0.3% was indicated from 5 tests.

These operations would be limited to laboratory use and to the determination of percentage amounts of fluorine, such as in FLOX. CTF and Compound A could be analyzed in the same manner, since they will also react with mercury.

5.2.3.1.5 Chemical Fluorine and Fluoride Dosimeter

General Dynamics Corporation has also packaged this instrument, which operates as an absorber of atmospheric contamination and, as such, gives only the total integrated dose for the test run. In operation, an atmospheric sample is purged through a cylinder containing an absorber solution of 1% potassium iodide and then is expelled through the outlet tubing. The potassium iodide solution absorbs both fluoride (from any hydrogen fluoride formed from hydrolysis of fluorine) and fluorine and further reduces the absorbed fluorine to fluoride, and equivalent amount of iodide being oxidized to iodine in the process.

At the conclusion of a test run, the absorber solution is removed to the laboratory and analyzed for total fluoride and iodine. The iodine is probably titrated with sodium thiosulfate. One of a number of methods could be used to determine total fluoride. The amount of iodine present is proportional to the amount of fluorine absorbed and the total fluoride present minus the fluorine absorbed is proportional to the amount of hydrogen fluoride absorbed. Alternately, the fluorine and hydrogen fluoride content could be determined, as Levy and Copeland did, by titrating the liberated iodine with sodium thiosulfate to determine the fluorine content, and then, by adding potassium iodate solution, further iodine is formed from the hydrogen fluoride present and is then titrated with sodium thiosulfate.

The packaged instrument, prepared by General Dynamics, is 14 in. wide by 12-1/2 in. high by 9-1/2 in. deep and weighs 24 lb.

The nominal instrument sampling rate is 220 cc/min.
Power to operate the pump is supplied by batteries.
The approximate cost of the instrument is $1,000.

The range of concentration determined is 20 to 200 ppm for fluorine and 0 to 550 ppm for hydrogen fluoride.

This type of detection should also determine FLOX, CTF, and Compound A since they will oxidize iodide to iodine.

5.2.3.1.6 Gas Titration Analyzer (Continuous Monitor)

An automatic fluorine analyzer was developed at Oak Ridge National Laboratory by C. W. Weber for monitoring on-stream gas systems. It is based upon a gas titration of fluorine with sulfur dioxide and the detection of the subsequent reduction in molar flow. A gas titration consists of transferring two gases, each from a chamber called a buret, into a reactor, where chemical combination is reduced. The volumes of all chambers, or at least the relative volumes, have been predetermined. The titration is followed by plotting the pressure changes in the reactor after each incremental addition of the titrant gas. The method is applicable to most gaseous reactions that bring about a change in molar volumes. The change in molar flow is apparent in the reaction

$$SO_2(g) + F_2(g) \rightarrow SO_2F_2(g).$$

The greater the fluorine content of the sample gas, the greater the flow change. Adapting the gas titration to a continuous analyzer involved the continuous introduction of the reactants and removal of the products, proper reaction conditions, and appropriate means of detecting the molar flow changes, which indicate the concentration of the unknown. This was accomplished by use of metering capillaries, pressure control valves, and pressure transmitters, which converted the gas pressure signals to air pressure signals, various pressure gages, and so on. The resultant gas flow product, which varies with the fluorine concentration, was reflected in the forepressure-signal changes at an exit constriction. The exhaust gases from the analyzer

were removed and disposed of with chemical traps and a mechanical vacuum pump. With the reactor maintained at 200°C, reaction was complete for 0.1 to 90% fluorine. The residence time in the reactor was 2.5 to 5.0 sec. The flow rate for sample and reagent was 25 standard cc min. Seventy samples analyzed in the range from 5 to 60% fluorine matched a calibration curve within ±2.5% fluorine at the 95% confidence level. Precision is ±1% fluorine. Neither oxygen nor hydrogen fluoride interfere; therefore, it would be possible to analyze FLOX by this method. Materials similar to CTF and Compound A were not tested but UF_6 did not react.

5.2.3.1.7 Thin Film Sensor

This method is based on the detection of toxic vapors by their reaction with thin metal films to reduce the mass of the metal. The rate of metal removal is dependent on the concentration of the vapor. Because the electrical resistance of a conductor is inversely dependent on its cross-sectional area, a reduction in metal mass results in a reduction of cross-sectional area and thus an increase in electrical resistance. The amount and rate of reaction of the thin film under controlled conditions, therefore, is proportional to the amount and rate of change of electrical resistance and can be measured with proper instrumentation.

Thin film sensors for the detection of low concentrations of nitrogen tetroxide and fluorine were developed by the Magna Corporation. They found that silver films deposited on plastic substrates and sensitized with potassium chloride had the highest sensitivity for both nitrogen tetroxide and fluorine. The effects of temperature and humidity were studied and found to be significant in some cases, but not large enough to prevent use of the sensors over a wide range of atmospheric conditions. The sensors can be used to provide an indication of exposure to toxic vapors of nitrogen tetroxide and fluorine. A portable instrument was devised that could be carried in a pocket or worn on a belt. The instrument will respond to nitrogen tetroxide in concentrations of 0.05 ppm and to fluorine in concentrations of 1 ppm, in air, within ±30% of the true value. The effects of other toxic vapors were not studied. The

instruments were developed as a study for the Air Force, hence the company has not pursued further development or manufacture.

5.2.3.2 Methods Based on Replacement of Fluorine with Chlorine and Its Subsequent Detection

Fluorine quantitatively displaces an equivalent amount of chlorine by reaction with sodium chloride and, in turn, the quantity of liberated chlorine is determined by various methods, which could not readily be applied to fluorine directly.

5.2.3.2.1 Thermoconductivity Measurement

This technique has been applied to analysis of fluorine in fluorine-oxygen mixtures, where the measurement of fluorine is too similar to oxygen to be detected but where chlorine can be readily detected. These detectors work on the principle that gases differ in their heat conduction properties. The sample gas is passed over a heated wire in an analysis cell. The resulting change of temperatures of the wire will change its resistance. This results in unbalancing a bridge circuit that has been calibrated in terms of concentration of the gas to be detected. While the detector is portable, the sodium chloride reactor may restrict the method to the laboratory. Concentrations of fluorine from 0 to 20% in oxygen were analyzed by this method. It should be applicable to the determination of CTF and Compound A, because these also will displace chlorine from sodium chloride.

5.2.3.2.2 Photometric

The concentration of chlorine, liberated from the reaction of fluorine with sodium chloride, is measured by passing the gas through a chlorine-sensitive colorimeter, which generates an electrical signal directly related to the concentration of fluorine in the samples. The analyzer consists of the heated sodium chloride reactor flow colorimeter, pressure-control system, flow limiter, a vacuum pump for drawing a continuous sample through the analyzer, and a recorder. The colorimeter used was a Beckman Model 3700 flow colorimeter, fitted with spectral filters to measure the

chlorine absorption at the wavelength of 360μ. A 10-cm-long nickel cell with calcium fluoride windows was used for the optical cell. The range for the instrument with the 10 cm cell length and 500 mm of Hg pressure was 0.05 to 15% fluorine. With a shorter cell or a lower pressure, up to 100% fluorine could be determined.

Hydrogen fluoride has no effect on the analyzer, but while bromine and certain oxides of nitrogen cause optical interferences, ozone would probably interfere by liberating chlorine. CTF, Compound A, and FLOX could be determined by the analyzer because they also liberate chlorine.

The analyzer requires intermittent renewal of the sodium chloride, the chemical trap, and the recorder chart, occasional replacement of the tungsten source lamp in the colorimeter, and cleaning of the colorimeter cell as indicated by inspection.

The relative standard deviation of the analyzer is about ±1.5% above 0.8% fluorine.

5.2.3.3 Methods

5.2.3.3.1 Gas Chromatography

A gas chromatograph utilizing only Monel and stainless steel parts was designed at Rocketdyne for analyzing fluorinated materials. A gas chromatographic substrate was developed from 50% Kel-F polymer plasticized with 50% Halocarbon oil. This substrate is classified as a monophase gel and is vastly superior to the duophase columns for separating fluorinated materials. A hot-wire thermoconductivity detector, with the hot wires coated with Teflon, was used. Rocketdyne claims analyses of fluorine, CTF, and HF are possible, and from its data it appears that the compounds could be determined even if present in mixtures. Small gas samples were used for analysis, and no attempt was made to use the instrument for in-stream analysis. Gas liquid chromatography was applied to in-line analyses of plant streams containing CTF, Cl_2, HF, and other reactive gases at the United Kingdom Atomic Energy Installation at Capenhurst, England. A Split-column chromatograph was developed and automated.

Clemons and Altshuller used a Micro-Tek dual-column gas chromatograph, equipped with an electron-capture detector mounted in parallel with a flame ionization detector, for studying various halogenated compounds. It is interesting to note that they made sample dilutions of 250, 000, 000 to 1 with nitrogen.

5.2.3.3.2 Radioactive Cl-36

This technique is being developed at Douglas. Radioactive sodium chloride will be prepared from Cl-35. The fluorine to be determined will be passed over the sodium chloride to release radioactive Cl-36. This chlorine, equivalent to the amount of fluorine, will be detected by radiochemical counting techniques.

5.2.3.3.3 Infrared Absorption

Infrared absorption might be used for detecting CTF and Compound A directly or by their reaction with carbon to form CF_4, which, in turn, could be detected by infrared absorption. The conversion to CF_4 could be used for fluorine and FLOX detection. Detectors have been developed using infrared absorption for N_2O_4 and UDMH.

5.2.3.3.4 Microwave Detectors

Microwave (1 mm to 30-cm wavelength) detectors are being developed where positive identification of specific compounds is possible.

The interaction of a unique microwave frequency with a molecule of vapor will result in its partial absorption by the molecule. This energy can be detected and measured by electronic methods.

5.2.4 Summary

None of the instruments available commercially or those known to be for laboratory test satisfactorily fulfill all the requirements for leak test measurement and site monitoring.

A new instrument or an adaptation of a currently available instrument should be used to detect and measure leaks in the oxidizer system, as well as in the site proper.

6.0 Methods of Analysis

The various methods of analyzing fluorine are tabulated in Appendix II-1. These are essentially the instrumental methods and the chemical assay method used by Allied Chemical Company. If liquid fluorine samples are gasified and then analyzed the same techniques are applicable for gaseous and liquid fluorine.

Newer methods of analysis of fluorine are being developed at Edwards Air Force Base by F. Forbes and J. Nakamura. They are attempting to determine the hydrogen fluoride content of fluorine by infrared absorption spectrophotometric measurement. Mr. Nakamura is also developing a gas chromatographic method for hydrogen fluoride which may prove to be better than the infrared absorption method. In Analytical Chemistry, December 1966, p. 1859, J. A. Donahue and F. S. Jones found the oxygen difluoride content of hydrated hydrogen fluoride by a gas-solid chromatography technique. This method may be applicable to the determination of oxygen difluoride in fluorine as well. Allied Chemical Company is developing a special gas chromatograph for the analysis of most of the contaminants in fluorine. The method seems very promising.

J. G. Million, W. S. Pappas and C. W. Weber, of the Oak Ridge, Tenn., gaseous diffusion plant, have developed a specially designed process gas chromatograph which is used to analyze some of the most corrosive gas mixtures known. The instrument (see Chemical and Engineering News, December 5, 1966, p.61) uses a column, which is constructed from various polyhalocarbons. It has been used to analyze mixtures containing hydrogen fluoride as well as uranium hexafluoride and halocarbon coolants. This instrument may be adapted to fluorine analysis.

7.0 Meteorological Factors in Fluorine Handling

In the establishment of guidelines for the operation of facilities where fluorine is used as a fuel agent, three major factors: (1) Meteorological parameters of the toxic hazard and air pollution problem; (2) Government regulation of maximum allowable concentration and exposure dosage of pollutants; and (3) Estimation of downwind atmospheric pollution, will each be discussed in the following paragraphs.

7.1 Meteorological Parameters of the Toxic Hazard and Air Pollution Problem

In order to ensure a proper evaluation of the pollution potential at a toxic propellant facility, a micrometeorological study of the location must be completed. The most important meteorological parameters in this evaluation are: (1) the atmospheric temperature change with altitude, commonly called lapse rate, and (2) the wind speed and direction, and their fluctuations, in the first few hundred feet of the atmosphere. By measurements of these parameters, local circulations such as ; daytime ocean breezes, nighttime land breezes, and mountain-valley wind systems, induced by differential daytime heating and nighttime cooling of surfaces, will be identified. The temperature and wind velocity data for the site should be known for at least 1 year, preferably 5 years, and ideally 20 years, and statistically analyzed by the hour of the day, month, season, and year. In the statistical analysis of the data, the following information should be derived:

1. the percentile levels of temperature lapse rate and its variability for three finite layers up to 200 ft for the purposes of determining (A) the probable thermal stratification of the atmospheric boundary layer, and (B) the probable safe downwind dispersion distance for different wind speeds;
2. the percentile levels of the wind direction and its variability about the prevailing direction, for the purpose of delineating the optimum operable downwind sector;
3. the percentile levels of the wind speed for each wind direction and its variability for the purposes of determining (A) the probability that the wind speed will be above some minimum operational value, and (B) the probable safe downwind dispersion distance for different atmospheric stabilities;

4. the hour-to-hour persistency of the wind speed and direction at various wind speed levels for the purpose of determining the duration of the operable period;
5. the percentile levels of favorable wind speed, wind direction, and temperature lapse rate existing jointly, and the hour-to-hour persistency of the same combination for the purpose of scheduling by defining the operable period for the optimum sector.

Thus, on the basis of the frequency, duration, and intensity of favorable and unfavorable atmospheric conditions, a comprehensive assessment can be made of a location's suitability for intentional pollutant releases as well as the location's potential pollution capability for accidental releases during the most unfavorable microclimatological conditions.

7.2 Estimation of Downwind Atmospheric Pollution

In addition to studying the microclimatology, computations of downwind dispersion of the toxic gases help to estimate the hazard potential in handling fluroine. In order to finalize hazard-potential estimation, diffusion experiments should be designed and conducted at handling sites in order to develop quantitative, reliable definitions of the air pollution hazard. These experiments should be done for all seasons and times of day. Some of the theoretical and empirical methods, which are particularly favored in estimating the downwind exposure levels, will be briefly discussed.

7.2.1 Sutton's Diffusion Equations: Sutton's diffusion equations are the most widely known atmospheric turbulent diffusion prediction equations to meteorologists, as well as to people of many other disciplines interested in air pollution work. In the absence of any obvious alternative Sutton's well-known point source mathematical dispersion model (Ref. 322) has been used in many air pollution hazard analyses far beyond the limits of the assumptions (Ref. 317). The assumptions for which the model can confidently be expected to be reliable are:

1. distances of the order of 1 km.
2. level, unobstructed terrain.
3. near adiabatic (neutral) conditions (see Figure 304 for the explanation of the terminology, Ref. 309).

4. conical expansion of the plume from a point source under the influence of a steady wind (no looping, fumigating, not a volume source, etc., Ref. 302).
5. isotropic turbulence and diffusion,
6. no depletion due to washout, fallout, deposition, or chemical reactions and complete reflection of pollutant back into the atmosphere by ground surface,
7. thermodynamic and aerodynamic equilibria,
8. pollutant follows the air motions strictly.

The dispersion of a point-source pollutant occurs differently depending upon whether the pollutant is introduced into the atmosphere continuously or instantaneously. In the continuous case (>2 minutes) a long line of pollutant, the plume, is produced and mixes rapidly with a large volume of air; in the instantaneous case (about a minute or less, depending upon the meteorological conditions and location) a blob or puff of pollutant is produced and mixes slowly with a limited volume of air as it drifts with the main air current. Sutton's isotropic diffusion equation (Ref. 12) for the continuous point source is

$$X_{(x,\,y)} = \frac{2Q}{C^2\,\bar{u}x^{2-n}} \exp\left(-\frac{y^2 + h^2}{C^2\,x^{2-n}}\right), \qquad \text{(Eq. 1)}$$

and for the instantaneous point source is

$$X_{(x,\,y)} = \frac{2Q}{\pi^{3/2}\,C^3(x)^{3\,\frac{(2-n)}{2}}} \exp\left[-\frac{x^2 + y^2 + h^2}{C^2(x)^{2-n}}\right], \qquad \text{(Eq. 2)}$$

where,

X = concentration (grams per cubic meter),

Q = emission rate (grams per second) for the continuous case, and

Q = source strength (grams) for the instantaneous case,

C = generalized diffusion coefficient $[(\text{meters})^{n/2}]$ for isotropic turbulence.

n = non-dimensional parameter associated with stability,

x, y = downwind and crosswind coordinates measured from the ground point beneath the continuous source and from the center of the moving concentration of gas in the instantaneous case (meters),

h = height of source.

In the different applied forms of Sutton's equations. there are four adjustable parameters to which values must be assigned to adequately describe any given diffusion experiment or accidental release of pollutants. Present experimental evidence shows that the value of these parameters varies over wide ranges. To maintain a consistent degree of prediction accuracy over a wide range of meteorological conditions, requires choosing appropriate values for these parameters, which is far from being a straightforward process (Refs. 315 and 324).

The concentration values computed from Sutton's equations are very sensitive to the "n" and "C" values selected and can be several orders of magnitude different according to the location. Cramer (Refs. 303 and 307) eliminates these parameters and relates the important "Project Prairie Grass" dispersion data (Ref. 17) to the following formula based upon mass continuity and Gaussian concentration distributions:

$$X = \frac{Q}{2\pi\sigma_y\sigma_z u} \exp\left[\left(-\frac{1}{2}\ \frac{y^2}{\sigma_y{}^2} + \frac{z^2}{\sigma_z{}^2}\right)\right] \qquad \text{(Eq. 3)}$$

With this formula the data reflect directly the spatial variability of the dispersion coefficients σ_y and σ_z. Data of Hay and Pasquill (Ref. 306), as well as the discussion in Reference 307, indicate that, as a practical matter, the Gaussian assumption is acceptable; but a careful analysis (Ref. 315) of the Project Prairie Grass data has indicated that significant departures from Gaussian concentration distributions do occur.

7.2.2 Empirical Diffusion Equations: For the reasons indicated above, empirical or statistical methods are now being utilized to develop the diffusion

prediction equation. In principle, such an approach leads to a less complex equation than Sutton's equation. The prediction equation developed in Reference 312 from "Project Prairie Grass" (Ref. 319) and the Projects "Ocean Breeze" and "Dry Gulch" (Ref. 311) diffusion data, is extremely simple and, within the limits of available experimental data, statistically reliable. Extreme downwind distance measurements of concentration varied from 800 m for the "Prairie Grass" data to 9,200 m for the "Dry Gulch" data. The prediction equation for the continuous, ground-level point source is the following:

$$\frac{C_p}{Q} = 0.00211\, x^{-1.96} (\Delta T + 10)^{4.33}\, \sigma(\theta)^{-0.506} \qquad \text{(Eq. 4)}$$

where,

C_p = peak concentration at a given downwind travel distance, X,

X = the downwind travel distance in meters,

Q = source strength,

C_p/Q = normalized peak concentration in sec/m^3,

ΔT = the temperature difference (that is, the temperature at 54 ft minus the temperature at 6 ft in °F. Ten is added to ΔT to avoid raising a negative number to a power), and

$\sigma(\theta)$ = the standard deviation of wind direction in degrees of azimuth.

Experimental evidence indicates that the following three meteorological parameters, two of which appear in Equation 4, should be considered in characterizing the rate of low-level atmospheric diffusion:

1. The mean wind speed, $\bar{u}$, as an indicator of the downwind "stretching" of the cloud emitted from a continuous source.
2. The standard deviation of the wind direction fluctuations, $\sigma(\theta)$, as an indicator of the horizontal rate of mixing.
3. The vertical temperature gradient, ΔT, as an indicator of the vertical rate of mixing.

It was found (Ref. 20) that $\bar{u}$ does not contribute significantly to the accuracy of the diffusion prediction equation after ΔT and $\sigma(\theta)$ have been included and

hence was omitted from Equation 4. This apparent discrepancy is explained by the fact that π is also correlated with ΔT and $\sigma(\theta)$. Since C_p/Q is given in terms of seconds per cubic meter, it may not be meaningful or useful. To obtain ppm/lb/min, C_p/Q (in sec/m^3) is multiplied by a factor over the grammolecular weight of the gaseous contaminant. These factors for fluorine and hydrogen fluoride are respectively 4.47×10^3 and 8.50×10^3. The empirical prediction equations developed in Ref. 311 have gained considerable favor (Refs. 305, 313, and 318) and are used at Cape Kennedy and Vandenberg AFB. Reference 318 contains a useful but approximate nomogram, which relates the toxic vapor emission rate to wind speed for various areas wetted by spills. More empirical verification, however, is needed for such a nomogram for specific toxic contaminants.

The case of the instantaneous point source should also be considered. The laws which govern the diffusion from a quasi-instantaneous, quasi-point source, such as a cloud puff from a short burst of a rocket motor or from a spill on the pad, are not well known. Prior to Project Sand Storm (Ref. 316) there were no more than a few experimental investigations of a limited nature on the behaviors of puffs. Useful results of the data analysis of "Project Sand Storm" are shown in Figures 10 and 11 of Reference 316. The conversion factors previously indicated for fluorine and hydrogen fluoride should also be used for these figures to convert from sec/m^3 to ppm/lb/min. It is recommended that Figures 10 and 11 (Ref. 316) be used as a guideline in the fluorine test site selection and operation and in the potential hazard evaluation of an instantaneous point source release of fluorine into the atmosphere.

A recent effort to solve the fluorine point source diffusion problem based on theoretical and empirical considerations is presented in Ref. 314. A preliminary mathematical model is formulated to describe the transport and growth of a vapor cloud released from a quasi-instantaneous volume source in a low-level shearing wind flow. Figures 12-15 from Ref. 314 can be used as a guideline in estimating the downwind fluorine hazard. Allowance is made for deposition of fluorine at the earth's surface. The dosages are

expressed in units of parts of fluorine gas per million parts of air (by weight) times, time (secs) per gram of fluorine released at the source.

7.3 Conclusions

It should be emphasized that hazard sectors or areas should be constructed for all locations where fluorine is scheduled to be used. The available times for protection or evacuation of personnel after the release of the pollutant should also be determined. Furthermore, the meteorologist should be required to assign probabilities to this wind direction forecast in order that the hazard sector or areas be adequately defined prior to the operation of the facility. Field diffusion tests should be conducted at the site to verify the constructed hazard sectors or areas.

SECTION V
BIBLIOGRAPHY

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BIBLIOGRAPHY

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DYNAMIC COMPATIBILITY OF
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AFRPL-TR-72-119

FLUORINE SYSTEMS HANDBOOK

SECTION VI

DYNAMIC COMPATIBILITY OF FLUORINE WITH METALS

R. E. Anderson

Aerojet Liquid Rocket Company
Sacramento, California

Technical Report AFRPL-TR-72-119
October 1972

Approved for Public Release; Distribution Unlimited

Air Force Rocket Propulsion Laboratory
Director of Science and Technology
Air Force Systems Command
United States Air Force
Edwards Air Force Base, California

FOREWORD

This special technical report is submitted in compliance with and partial fulfillment of the requirement of Contract F04611-72-C-0031, "Dynamic Compatibility of Halogen Propellants," Phase III - Data Publication, Task 4 - Special Technical Reports (B005). The effort under this contract was sponsored by the Air Force Rocket Propulsion Laboratory under Air Force Project 5730 Task 07. The Air Force Project Engineer was Capt Howard M. White.

This program was conducted by the Chemical Processes and Materials Section of Aerojet Liquid Rocket Company with Dr. S. D. Rosenberg serving as Program Manager and Dr. E. M. Vander Wall serving as Project Chemist.

The work reported in this document was performed from 3 January to 31 August 1972.

The following technical personnel contributed to the compilation and analysis of the data and information contained in this report: R. E. Anderson, R. L. Beegle, Jr., and J. A. Cabeal.

This report was submitted by the author on 31 October 1972.

This report has been reviewed and is approved.

Howard M. White, Capt, USAF
Project Engineer

ABSTRACT

This document is a special technical report prepared under Contract F04611-72-C-0031, "Dynamic Compatibility of Halogen Propellants" and is issued as Section VI of the Fluorine Systems Handbook (NASA CR-72064, Douglas Aircraft Co., Inc., Missiles and Space Div., Santa Monica, California, Contract NASw-1351, 1 July 1967). It is a compilation of all pertinent data and design criteria concerning the dynamic compatibility of fluorine with metals. The information was obtained in the course of the contract which involved both literature search and review and original experimental investigations.

TABLE OF CONTENTS

		Page
I.	Introduction	1
II.	Metals Behavior in High Temperature Gaseous Fluorine Flow Systems	3
	A. Effect of Temperature and Velocity on F_2/Metal Reactions	3
	B. Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures	9
III.	Metals Response to Liquid Fluorine Flow and Impact	26
	A. Liquid Impact on Heated Metals	26
	B. Liquid Flow Through and Impact on Metals at Low Temperatures	28
IV.	Metals Behavior in the Presence of Fluorine Adiabatic Compression	35
V.	Effect of a Fluorine Liquid Phase Shock Wave on Metals	42
VI.	Effect of Ultrasonic and Low Frequency Vibration on the Interaction of Metals with Fluorine	45
	A. Ultrasonic Vibration in the Presence of Liquid Fluorine	45
	B. Low Frequency Vibration in the Presence of Gaseous Fluorine	47
VII.	Response of Metals to Flexure in a Fluorine Environment	48
	A. Elastic Flexure in Gaseous and Liquid Fluorine	48
	B. Plastic Flexure in Gaseous and Liquid Fluorine	50
VIII.	Effect of Mechanical Impact on Metals in the Presence of Fluorine	56
IX.	Response of Metals to Friction, Abrasion, and Fracture in a Fluorine Environment	62
	A. Metal/Metal Frict' ı in Gaseous Fluorine	62
	B. Metal Abrasion ı Liquid Fluorine	62
	C. Metal Fracture in Fluorine	63
References		66

TABLE LIST

Table		Page
I	Response of Metals to Gaseous Fluorine at Various Temperatures and Flow States	4
II	Low and High Probability Threshold Temperature for the Failure of Metals in Gaseous Fluorine	6
III	Ignition Temperatures of Metals in Static Gaseous Fluorine	7
IV	Effect of Nozzle Distance on the Corrosion Rate of Tungsten in a Fluorine-Argon Mixture (6.5/93.5 Vol) at 4000°F	12
V	Effect of Fluorine Flow Rate, Velocity, and Concentration on the Corrosion Rate of Tungsten in Fluorine-Argon Mixtures at 4000°F	14
VI	Effect of Nozzle-Specimen Distance and Temperature on the Corrosion Rate of Tungsten in a Fluorine-Argon Mixture (6.5/93.5 Vol.)	18
VII	Corrosion Rate of Tantalum in Flowing Fluorine-Argon Mixtures	20
VIII	Corrosion Rate of Tungsten in Flowing Fluorine-Argon Mixtures	21
IX	Corrosion Rates of Tungsten-Base Alloys in Flowing Fluorine-Argon Mixtures	22
X	Corrosion Rates of Rhenium-Base Alloys in Flowing Fluorine-Argon Mixtures	23
XI	Corrosion Rates of Iridium and Iridium-Base Alloys in Flowing Fluorine-Argon Mixtures	24
XII	Maximum Temperatures of Metal Surfaces on Which Impacting Streams of Liquid Fluorine Do Not Result in Ignition	27
XIII	Compatibility of Metals with Liquid Fluorine under High Velocity Flow and Impact Conditions	29
XIV	Compatibility on an Aluminum-Silicon Alloy with Liquid Fluorine under High Velocity Flow and Impact Conditions	34
XV	Behavior of Various Metals in the Presence of Gaseous Fluorine Subjected to Adiabatic Compression	38
XVI	Terminal Adiabatic Compression Conditions that Result in a 50% Probability of Fluorine/Metal Reaction	40

TABLE LIST (cont.)

Table		Page
XVII	Behavior of Various Metals Subjected to a Shock Wave of Liquid Fluorine	43
XVIII	Effect of Ultrasonic Vibration on "Passive Films" on Various Metals in the Presence of Fluorine	46
XIX	Response of Metals to Elastic Flexure in Liquid Fluorine	48
XX	Fatigue Life of Flexed Metal Bellows in Gaseous and Liquid Fluorine	52
XXI	Early Impact Test Results on Aluminum and Titanium Alloys in Liquid Fluorine at -320°F	58
XXII	Impact Test Results on 2014-T6 Aluminum and Ti-6Al-4V (ELI) Titanium in Liquid Fluorine	60
XXIII	Results of Friction Tests of Silver-316 Stainless Steel in Gaseous Fluorine	62
XXIV	Results of Abrasion Tests of Metals in Liquid Fluorine	64

FIGURE LIST

Figure		Page
1	Schematic Diagram of Refractory Metals/Fluorine Reaction Chamber	10
2	Effect of Nozzle Distance on the Corrosion Rate of Tungsten at 4000°F in Fluorine-Argon Mixture (6.5/93.5 Vol.)	13
3	Effect of Fluorine Flow Rate on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.	15
4	Effect of Nozzle Velocity on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.	16
5	Effect of Fluorine Concentration on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.	17
6	Effect of Temperature and Flow Condition on the Corrosion Rates of Tungsten in a Fluorine-Argon Gas Mixture (6.5/93.5 Vol.)	19
7	Corrosion Rates of Refractory Metals in Flowing Fluorine-Argon Gas Mixtures (6.5/93.5 Vol.)	25
8	Schematic Diagram of U-Tube Adiabatic Compression Apparatus	36
9	Fatigue Strength of Hydroformed 6061-T6 Aluminum Bellows in Fluorine Environments	53
10	Fatigue Strength of Hydroformed Armco 21-6-9 Bellows in Fluorine Environments	54
11	Fatigue Strength of Hydroformed Inconel 625 Bellows in Fluorine Environments	55

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SECTION I

INTRODUCTION

The use of fluorine, F_2, in military systems has attracted considerable attention over a period of years. As a result, a rather large number of basic research, component, and technology programs involving this very reactive oxidizer has been conducted. The inherent reactivity of fluorine is well known and, as a consequence, materials compatibility problems have always figured prominently in such programs. A significant amount of compatibility data has been generated, compiled, and factored into successive programs. In most cases, the application of available compatibility data (and proper cleaning, passivation, and handling procedures) has permitted the use of fluorine in static systems without incident. Unfortunately, practically all real systems employing fluorine are dynamic, while most compatibility data have been established for static conditions. Many incidents, ranging from benign to catastrophic, have occurred. Almost invariably, the origin of an "incident" can be traced to a dynamic fluorine/material interface and has been attributed to some poorly defined, basic dynamic incompatibility problem or to "contamination". Post-incident inspections often cannot discriminate between these two possibilities.

The compatibility data available on fluorine up to 1965 and/or 1967 were compiled in Design Handbook for Liquid Fluorine Ground Handling Equipment*, Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems**, and Fluorine Systems Handbook***. Although these documents are excellent data sources on the compatibility of fluorine with many materials, the data relating to the dynamic compatibility of fluorine with metals were scant. That inadequacy in data and recurring problems in systems employing fluorine, which were in many cases attributed to an inadequate understanding of dynamic compatibility, prompted the Air Force Rocket Propulsion Laboratory to issue Contract F04611-72-C-0031, "Dynamic Compatibility of Halogen Propellants," to Aerojet Liquid Rocket Company. The objective of this program was to establish design criteria on the dynamic compatibility of liquid and gaseous fluorine and chlorine pentafluoride with metallic materials. The program covered both

*Design Handbook for Liquid Fluorine Ground Handling Equipment, 2nd ed., AFRPL-TR-65-133, Aerojet-General Corp., Sacramento, California, Contract AF 04(611)-10541, August 1965.

**Schmidt, H. W., Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems, NASA SP-3037, (Lewis Research Center, Cleveland, Ohio), NASA, Washington, D.C., 1967.

***Fluorine Systems Handbook, NASA CR-72064, Douglas Aircraft Co., Inc., Missiles and Space Div., Santa Monica, California, Contract NASw-1351, 1 July 1967.

I, Introduction (cont.)

literature search and review and experimental evaluation of the effects of gas velocity, adiabatic compression, liquid impact, flexing/film degradation, vibration/film degradation, and liquid phase shock wave ("water hammer") on oxidizer/metal reactions.

This document is a special technical report prepared under Contract F04611-72-C-0031 and is issued as Section VI to the Fluorine Systems Handbook, NASA CR-72064. It is a compilation of all the pertinent data and design criteria which have been obtained in the course of the contract from both the literature search and review and experimental portions of the program.

Users of fluorine and designers of systems employing fluorine are cautioned that although the information contained herein clearly indicate that the metals investigated can withstand significant inputs of energy from various dynamic system effects without dangerous consequences, these levels of compatibility have been obtained under laboratory conditions where test equipment and metal specimens have been scrupulously cleaned and exposed to fluorine of high quality. Failures to follow recommended cleaning and passivation procedures (see Appendices III-4 and III-5 of the Fluorine Systems Handbook) can lead to major failure in spite of the use of the most compatible materials. The information in this section strongly suggests that most instances of burnthrough, explosions, etc., in dynamic systems involving the metals covered here are the result of contaminants that may be undetectable in the relatively complex dynamic systems or are released to the fluorine environment by the action of the fluorine on the system.

SECTION II

METALS BEHAVIOR IN HIGH TEMPERATURE GASEOUS FLUORINE FLOW SYSTEMS

A. EFFECT OF TEMPERATURE AND VELOCITY ON F_2/METAL SYSTEMS

Under Contract F04611-72-C-0031, Dynamic Compatibility of Halogen Propellants, (Reference 1), the Aerojet Liquid Rocket Company conducted flow tests with gaseous, preheated F_2 on heated specimens of nine metals. The metals investigated were:

304-L Stainless Steel	6061-T6 Aluminum
347 Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
A-286 Stainless Steel	Monel K-500
	Nickel 200

The flow specimens consisted of drilled passages 0.020-in. dia by 0.250-in. long in the test materials. The specimens were carefully cleaned (but not passivated) and rigidly mounted in a Nickel 200 tube which was electrically heated. The system was orificed upstream and/or downstream to provide desired flowrates, velocities, and pressure drops through the test specimens. Instrumentation included specimen temperature at a point 0.010-in. from the flow passage, specimen pressure drop, upstream gas temperature, and outside tube wall temperature. In test operation, the system was orificed to produce one of three basic flow conditions in the specimen: (1) static, (2) subsonic flow, or (3) sonic flow. The incoming F_2 and the specimen were then simultaneously electrically heated to produce a nominal temperature rise rate of 10°F/sec. Plots of temperature versus time were used to define both minor and major exotherms and plots of specimen pressure drop versus time or temperature for specimens flowing in the subsonic regime were used to define major changes in film buildup or degradation. In most tests which were initially flowing in a subsonic regime, film buildup during the course of a test was sufficient to cause the flow passage to become sonic prior to a major exotherm or change in geometry. Thus, terminal material effects in the subsonic flow regime could not normally be ascertained. The F_2 gas pressure upstream of the test specimen was nominally 100 psia.

The results of these tests are summarized in Table I wherein threshold temperatures and the corresponding material responses are defined for the various materials and flow regimes. Although some of the materials tested under some of the flow conditions exhibited very little or very gradual geometric and/or thermal responses as temperature increased up to the point a very dramatic change occurred, the most common behavior was for the materials to undergo several "minor or nonfailing" responses prior to a "major or failing-type" response. This latter common behavior makes the definition of a single threshold set of dynamic conditions for incipient failure difficult because a

TABLE I

RESPONSE OF METALS TO GASEOUS FLUORINE AT VARIOUS TEMPERATURES AND FLOW STATES

Material	Static: Threshold Temp., °F	Static: Material Response	Subsonic Flow: Threshold Temp., °F	Subsonic Flow: Material Response	Sonic Flow: Threshold Temp., °F	Sonic Flow: Material Response
6061-T6 Al					~1000 1150	Probable onset of film buildup. Major exotherm and loss of specimen.
OFHC Cu	1090*	Probable onset of film buildup.	1000 σ = 40*	Onset of film buildup.	855	Onset of a series of small exotherms and endotherms.
	1230*	Apparent exothermic reaction (slight).	1190 σ = 25*	Significant change in film buildup/thermal effects.	1150	Significant exotherm.
	1400* 1585*	Apparent endothermal reaction (slight). Significant exotherm, modest specimen attack.	1380 σ = 25* 1525 ± 58*	Moderate exotherms and film changes. Major exotherm and loss of specimen material.	1250 1485	Relative large exotherm. Major exotherm reaching a max. temp. of ~2100°F, specimen suffers modest attack.
321 S.S.	1145 1890	Probable onset of rapid film buildup. Onset of a series of exotherms reaching a max. temp. of 2475°F, significant material loss.			1115 1700	Probable onset of rapid film buildup. Major exotherm with significant loss of specimen material.
304-L S.S.	1285 1930	Probable onset of rapid film buildup. Major exotherm with significant loss of specimen material.			1140 1722	Probable onset of rapid film buildup. Major exotherm with significant loss of specimen material.
347 S.S.	1833	Major exotherm with significant loss of specimen material.	1335	Onset of rapid film buildup.	1315 1723 σ=2	Probable onset of rapid film buildup. Major exotherm with significant loss of specimen material.
A-286 S.S.	~1400 1900	Probable onset of rapid film buildup. Onset of a series of exotherms reaching a max. temp. of 2320°F, significant material loss.	1350	Onset of rapid film buildup.	1350 1704	Probable onset of rapid film buildup. Major exotherm with significant loss of specimen material.
Inconel 718			~1675	Onset of very rapid film buildup.	1675	Onset of a series of exotherms reaching a max. temp. of 2480°F, flow passage corroded closed.
Monel K-500	162[illegible] 1905	Significant exotherm. Major exotherm reaching max. temp. of ~2400°F, flow passage corroded closed.	1575	Onset of very rapid film buildup.	1520 1715	Probable onset of rapid film buildup. Major exotherm reaching max. temp. of 2300°F, flow passage corroded and restricted.
Nickel 200			1785 ≥2300**	Onset of a series of exotherms with max. temp. ≥ 2340°F, no significant change in flow passage. No evidence of melting or ignition.	1755	Onset of a series of exotherms with max. temp. >2360°F, no significant change in flow passage.

* Temperature based on outside wall temperature.
**Information based on Reference 2.

II, A, Effect of Temperature and Velocity on F_2/Metal Systems (cont.)

particular "minor or major" material response in terms of these tests could be accentuated or damped in a related but different flow systems. Inspite of this limitation, the data do provide the firmest set of low and high probability threshold temperature and velocity conditions available for a variety of metals subjected to gaseous F_2 in a variety of flow conditions.

On the basis of the test results presented in Table I, the low and high probability threshold temperatures for the various flow conditions, i.e., static, subsonic, and sonic velocity, are presented in Table II and recommended for the guidance of designers. In the use of Table II, it must be recognized that the high probability threshold should never be used for design purposes without specific independent test verification. Additionally, an analysis of test to test variations in repetitive samples shows standard deviations as high as 40°F, suggesting that the low probability thresholds should be reduced approximately 3σ or 120°F when considering limiting design capabilities.

In a related series of fluorine flow tests reported by Duckering (Reference 2), a 0.050-in. wall Nickel 200 tube was electrically heated to selected temperatures and then exposed to gaseous fluorine at ∿260 psig and a velocity of ∿30 ft/sec for 1-sec periods of time. The tests were conducted at specimen temperatures of 1000 to 2000°F at 200°F increments and from 2000 to 2300°F at 100°F increments. There was no evidence of tube melting or ignition in any of the tests. A sonic orifice located downstream of the tube specimen and exposed to gaseous fluorine at ∿140 psia, 200-250°F, and ∿1000 ft/sec was similarly unaffected.

Goodwin and Lorenzo (Reference 3) determined the ignition temperatures of several metals in essentially static gaseous fluorine using two experimental techniques both of which involved electrical heating of metal wire specimens. Temperatures were calculated from current, voltage, and temperature-resistivity data. In "Technique A" an evacuated bomb was filled with gaseous fluorine at atmospheric pressure and the temperature of the specimen was gradually increased until burnout was achieved. In "Technique B" the test specimen was brought to a predetermined temperature in the evacuated bomb before the introduction of fluorine. Fluorine was admitted and the time for the reaction to go to completion was measured. The data obtained from these tests are summarized in Table III. The ignition temperatures defined by the two techniques are in reasonable agreement; however, both techniques give ignition temperatures of questionable accuracy because the effect of preignition reactions on the current, voltage, temperature-resistivity data used in calculating temperatures are not taken into account. The preignition reaction effect appears less significant in "Technique B" and, therefore, probably yields the more reliable data.

TABLE II

LOW AND HIGH PROBABILITY FAILURE THRESHOLD TEMPERATURES FOR THE FAILURE OF METALS IN GASEOUS FLUORINE

Material	Threshold Temperature for a Low Probability of Failure, °F(1)			Threshold Temperature for a High Probability of Failure, °F(2)		
	Static F_2	Subsonic F_2	Sonic F_2	Static F_2	Subsonic F_2	Sonic F_2
6061-T6 Aluminum			1000			1150
OFHC Copper	∿1090	∿1000	855	1585	1525	1[illegible]85
321 Stainless Steel	1145		1115	189[illegible]		17[illegible]0
304-L Stainless Steel	1285		1140	1930		1720
347 Stainless Steel		1335	1315	1830		1720
A-286 Stainless Steel	∿1400	1350	1350	1900		1700
Inconel 718		∿1675	∿1675			∿1675(3)
Monel K-500	∿1695	1575	1520	1905		1715(3)
Nickel 200		∿1785	∿1755			∿1755(3)

(1) Temperature at which the onset of a discernible but relatively minor material response is observed in a period of a few seconds. These values, when reduced by ∿120°F to account for test-to-test variations, may be used when considering reasonable limiting design capabilities (excluding stress).

(2) Temperature at which the onset of a major material response is observed in a period of a few seconds or less.

(3) These temperatures correspond to the onset of significant to major exotherms which may be accompanied by the buildup of appreciable quantities of corrosion products. Metal ignition is not evident, however.

TABLE III

IGNITION TEMPERATURES OF METALS IN STATIC GASEOUS FLUORINE

Technique A

Material	Average Ignition Temp., °F	Observed Range of Ignition Temp., °F	Standard Deviation, °F
Molybdenum	398	370 - 428	22
Tungsten	540	500 - 630	45
Monel	745	658 - 819	61
Iron	1241	1233 - 1251	9
302 Stainless Steel	1259	1058 - 1465	164
Copper	1277	1193 - 1377	64
Nickel	2123	1983 - 2226	86
Aluminum	>M.P.		

Technique B

Iron	1144 - 1191
Copper	1272 - 1294
Nickel	2287 - 2311

II, A, Effect of Temperature and Velocity on F_2/Metal Systems (cont.)

Inspection of the data presented in Tables I, II, and III for aluminum, shows: (1) the earliest signs of attack have been observed to occur near 1000°F under sonic flow conditions, (2) a major exotherm occurs at ∿1150°F with sonic fluorine and results in a melting- and/or burnout-type failure, and (3) ignition in static fluorine occurs at or above the melting point of aluminum. A similar inspection of the data on copper shows: (1) the earliest signs of copper attack occur in the temperature range of ∿850 to 1100°F, varying within this range more or less inversely with flow velocity, (2) a number of more significant velocity dependent exotherms, endotherms, and film changes are observed in the temperature range of ∿1150 to 1400°F which may result in ignition under certain poorly defined conditions that are not strongly dependent on velocity, and (3) a major reaction is almost certain to occur when the temperature reaches 1485 to 1585°F. The combined data from References 1 and 3 on austenitic stainless steels indicate: (1) significant attack occurs within the temperature range of ∿1100 to 1400°F, varying within this range somewhat inversely with velocity and the particular stainless steel, (2) ignition may occur within this same temperature range under certain poorly defined conditions apparently not related strongly to flow velocity, and (3) a major reaction involving a large heat release and material loss is almost certain to occur upon reaching a temperature of ∿1700°F under sonic conditions and 1830 to 1930°F under static conditions.

The data on Inconel 718 are difficult to interpret but indicate an important threshold temperature near 1675°F that is quite velocity independent. Gradual film buildup appears to be the significant reaction at temperatures up to this threshold at which point the reaction rate increases rapidly. In some cases this condition appears to cause the film to immediately fail and reform resulting in significant exotherms and formation of corrosion products while in other cases, the film is not disrupted until temperatures of up to 1835°F are reached. Although appreciable quantities of corrosion products and pulse temperatures of over 2400°F have been observed following film failures on Inconel 718, true ignition with the loss of substantial base metal has not been observed.

Monel K-500 undergoes a rapid increase in the rate of film buildup in the temperature range of ∿1500 to 1600°F, apparently varying somewhat inversely with velocity. At a temperature near 1700°F the film may fail in either static or sonic fluorine and result in an exotherm as it reforms. This film may remain intact, however, up to temperatures as high as 1850°F and ∿1900°F in sonic and static fluorine, respectively. Although pulse temperatures approaching 2400°F were recorded following film failures, an appreciable loss of base material was observed in only one case, and true ignition was never observed. An ignition temperature of ∿745°F for Monel as reported in Reference 3, cannot be reconciled with the data from Reference 1.

II, A, Effect of Temperature and Velocity on F_2/Metal Reactions (cont.)

Inspection of the data on nickel from Reference 1 shows the earliest signs of reaction with fluorine occur at ∿1750 to 1800°F and are apparently only slightly influenced by velocity. This onset of reaction appears normally as a series of mildly exothermic film-forming reactions. As temperature increases beyond ∿1900°F, the exotherms may become quite large, increasing the specimen film temperature several hundred degrees (°F) in less than a second. In Reference 1, peak temperatures of greater than 2360°F were recorded while the specimens underwent no significant damage other than the formation of a film. This agrees well with the data of Reference 2 wherein temperatures up to 2300°F in low velocity fluorine caused no evidence of melting or ignition. In Reference 3, the "ignition temperature" of nickel in static fluorine is indicated to be in the range of ∿1980 to 2310°F; however, the indirect method of defining temperature decreases the reliability of the data.

From all the data available, it must be concluded that nickel is the best metal known for containing hot, flowing, gaseous fluorine. In descending order of preference the other metals studied are ranked as follows: Inconel 718 and Monel K-500, austenitic stainless steels, copper, and aluminum.

B. DYNAMIC CORROSION RATES OF REFRACTORY METALS IN FLOWING HIGH TEMPERATURE FLUORINE-ARGON GAS MIXTURES

IIT Research Institute (References 4, 5, and 6) has conducted an extensive investigation of the dynamic corrosion rates of various refractory metals in flowing, high-temperature, fluorine-argon gas mixtures. The test facility was capable of producing variable gas flow conditions and maintaining specimens at temperatures up to 5800°F. A schematic diagram of the test chamber is shown in Figure 1.

Test samples 0.5 x 0.5 x 0.125-in. thick are heated by self-inductance in a thick-walled stainless steel chamber using a 2.5 or 5 Kw induction unit. Thus, the maximum temperature limit is defined by the material under test and the input power. Temperature measurements are made optically through a top sight glass which permits visual observation of specimen deterioration during exposure. Argon and the corrosive gases are metered in precision flow meters and premixed before entering the nozzle assembly. Fluorine is passed through a sodium bifluoride trap to remove residual hydrogen fluoride prior to entering the fluorine flow meter. The nozzle assembly consists of thick-walled stainless tubing swaged to obtain a 0.036-in. exit nozzle. During testing, the nozzle exit is maintained at a fixed distance (usually 1 in.) from the test specimen. Test specimens are supported in the induction coil by a 0.125-in. tungsten rod, which is split to minimize the contact area and to stabilize the test specimen. Exiting reaction products are passed through an activated charcoal absorption column prior to exhausting through a laboratory hood.

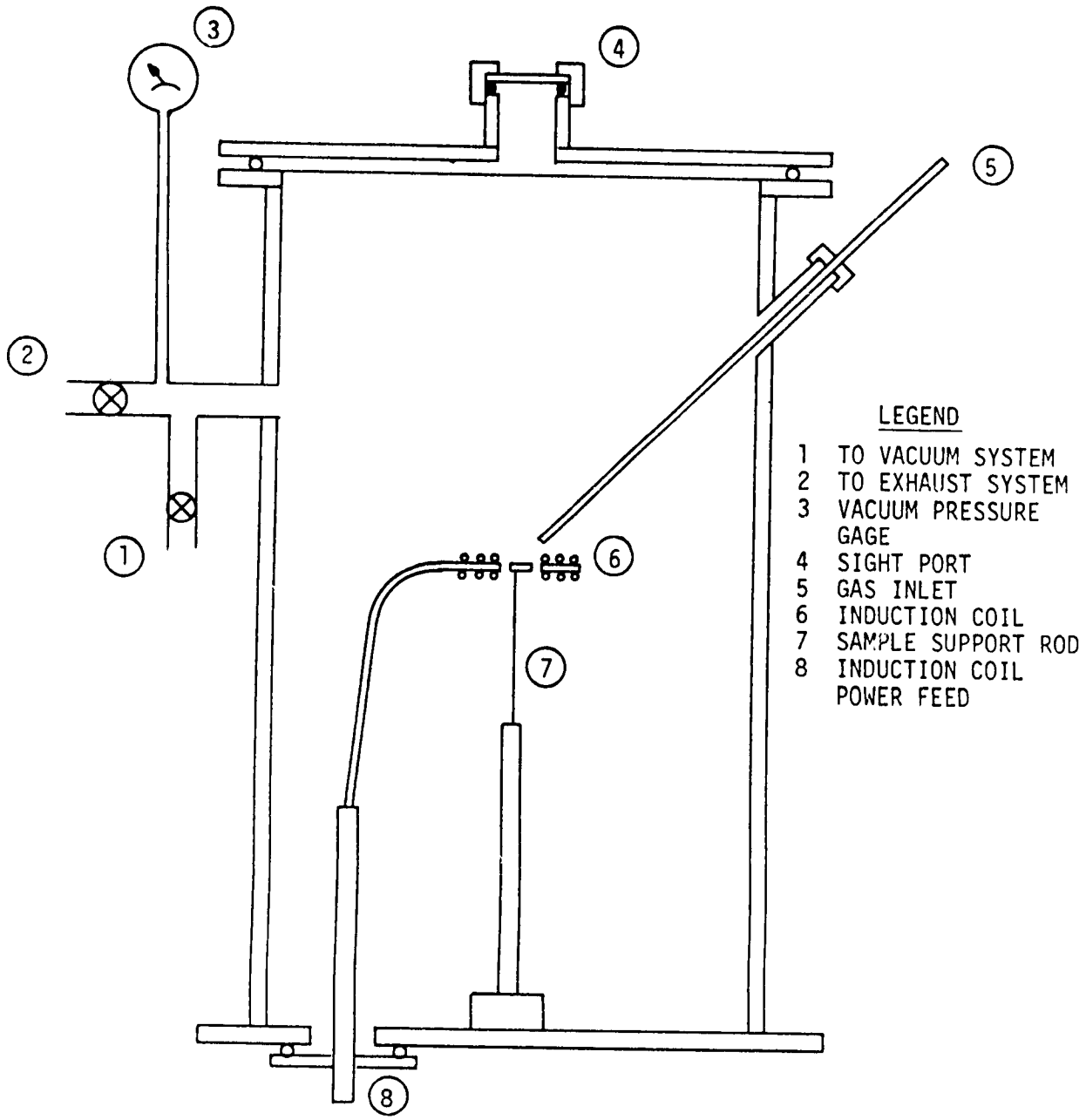

Figure 1. Schematic Diagram of Refractory Metals/Fluorine Reaction Chamber

II, B, Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures (cont.)

The following conditions for corrosion tests were constant during most of the tests: (1) nozzle distance, 1 in.; (2) total gas flow rate, 10 ft^3/hr; (3) exposure time, 5 min; and (4) nozzle exit velocity, 400 ft/sec. Deviations were made only in specific cases where the effects of variations were examined. The test procedure was constant for the various corrosion tests. Test samples were heated to the exposure temperature with only the argon flowing. After stabilization of the sample temperature, the fluorine was introduced. Normally, this did not result in significant variation of the sample temperature as argon represented the major portion of the gas stream. In some cases, it was necessary to reduce the exposure time to 3 min or increase exposure time up to 10 min to obtain total weight losses of an amount required for recession rate calculations.

The surface recession rates were calculated from weight loss of the 0.5 x 0.125-in. (nominal) thick test samples, assuming a linear time dependence of the weight loss. The effective surface area was obtained using one of the 0.5 x 0.5-in. surfaces (location of direct gas impingement) and the four 0.5 x 0.125-in. edges of the test sample. This is consistent with the observed location of attack on all test samples. Attack of the corrodent gases was usually not uniform over the test sample; material removed was maximum at the center of the 0.5 x 0.5-in. surface where direct gas impingement occurred. Thus, test samples tended to have a concave top surface after exposure. This concave top surface is described as "cratering".

The effect or nozzle distance on the surface recession of tungsten in argon-6.5 vol% fluorine at 4000°F is summarized in Table IV and plotted in Figure 2. These data show that corrosion rate increases with decreasing nozzle distance but varies only a minor amount for nozzle distances of around 1 in. At the 1 in. nozzle distance the gas velocity across the sample surface is considered to be only slightly less than the nozzle exit velocity (400 ft/sec). Also plotted in Figure 2 are the maximum recession rates obtained by micrometer measurements of the minimum thickness of the test samples after exposure. Note that the "cratering" increases rapidly at distances less than 1.5 in.

The effects of fluorine flow rate, velocity, and concentration on the corrosion rate of tungsten in fluorine-argon mixtures were determined at 4000°F. The pertinent data are summarized in Table V and plotted in Figures 3, 4, and 5. These data show that the corrosion rate is dominantly dependent upon the fluorine flow rate rather than either velocity or concentration, although the latter effects may not be negligible. This suggests that the corrosion rate is not controlled by reaction rates but rather by mass transport conditions at this high temperature.

TABLE IV

EFFECT OF NOZZLE DISTANCE ON THE CORROSION RATE OF TUNGSTEN IN A FLUORINE-ARGON MIXTURE (6.5/93.5 VOL) AT 4000°F* (Ref. 5)

Nozzle Distance, in.	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min	Maximum Measured Surface Recession, mils/min
0.75	140.0	2.86	9.3
1.0	128.6	2.62	6.8
1.25	130.5	2.66	6.2
1.25	137.0	2.79	6.3
1.5	119.5	2.44	4.6
1.75	109.0	2.22	3.8
1.75	120.5	2.46	4.3
2.5	109.0	2.22	3.0
3.0	90.5	1.83	2.5
3.0	94.5	1.93	2.4

*Total gas flow rate, 10 ft^3/hr; fluorine flow rate, 0.65 ft^3/hr; nozzle exit velocity ∿400 ft/sec. Specimen oriented ∿45° to gas stream.

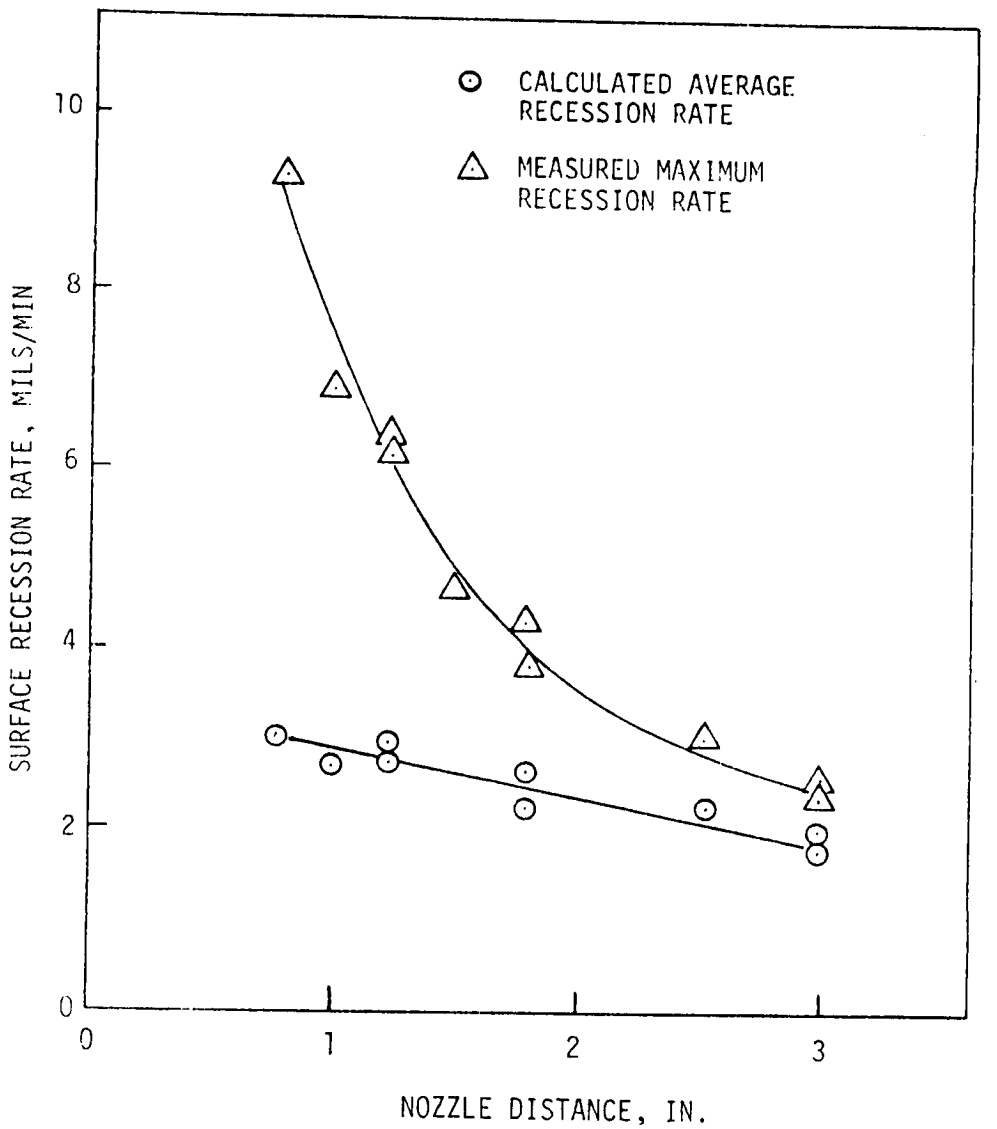

Figure 2. Effect of Nozzle Distance on the Corrosion Rate of Tungsten at 4000°F in Fluorine-Argon Mixture (6.5/93.5 vol)

TABLE V

EFFECT OF FLUORINE FLOW RATE, VELOCITY, AND CONCENTRATION ON THE CORROSION RATE OF TUNGSTEN IN FLUORINE-ARGON MIXTURES AT 4000°F (Ref. 5)

Total Flow Rate, ft^3/hr	Fluorine Flow Rate, ft^3/hr	Fluorine Content, % vol	Nozzle Exit Velocity, ft/sec	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min
2.5	0.65	26	98	115.0	2.34
4	0.26	6.5	157	50.6	1.03
5	0.65	13.0	196	120.0	2.45
8	0.52	6.5	314	101.0	2.06
10	0.25	2.5	393	47.6	0.97
10	0.65	6.5	393	128.6	2.62
10	1.0	10.0	393	186.5	3.80
12.5	0.65	5.2	491	139.0	2.83
12.5	0.25	2.0	491	51.5	1.05
12.5	0.81	6.5	491	152.0	3.10
12.5	1.0	8.0	491	191.0	3.90

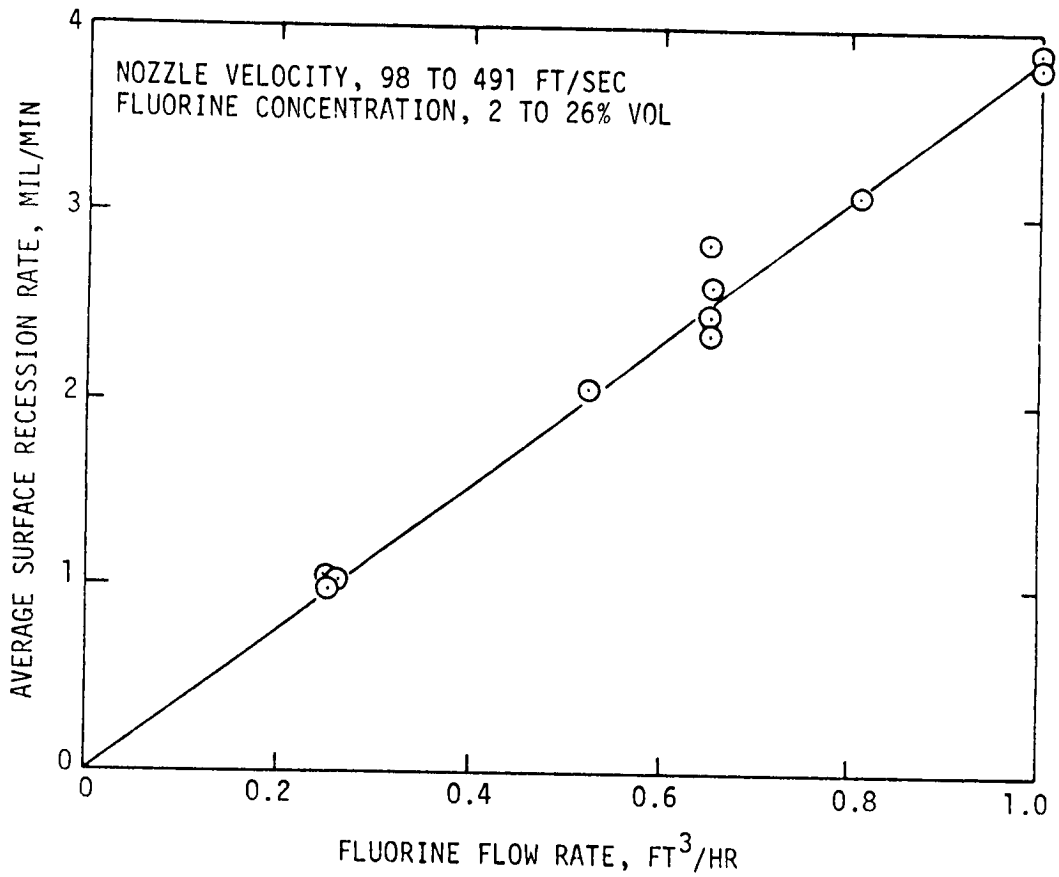

Figure 3. Effect of Fluorine Flow Rate on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.

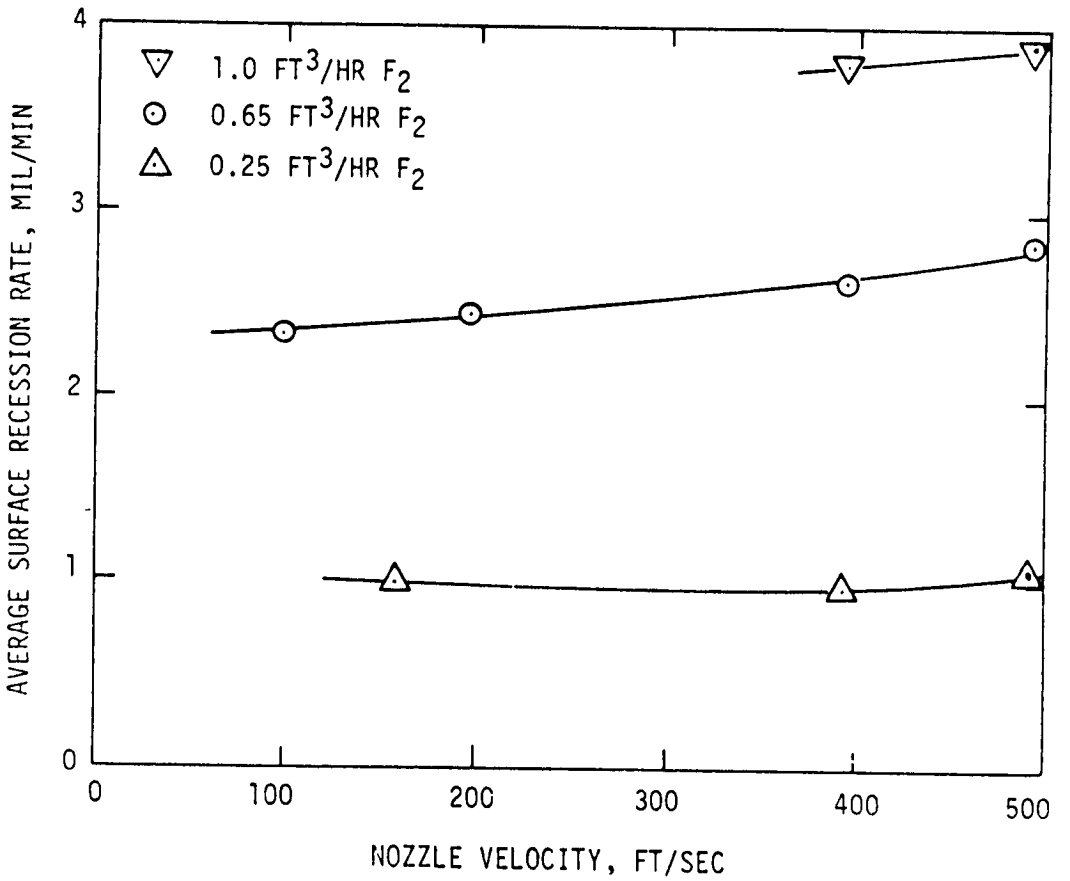

Figure 4. Effect of Nozzle Velocity on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.

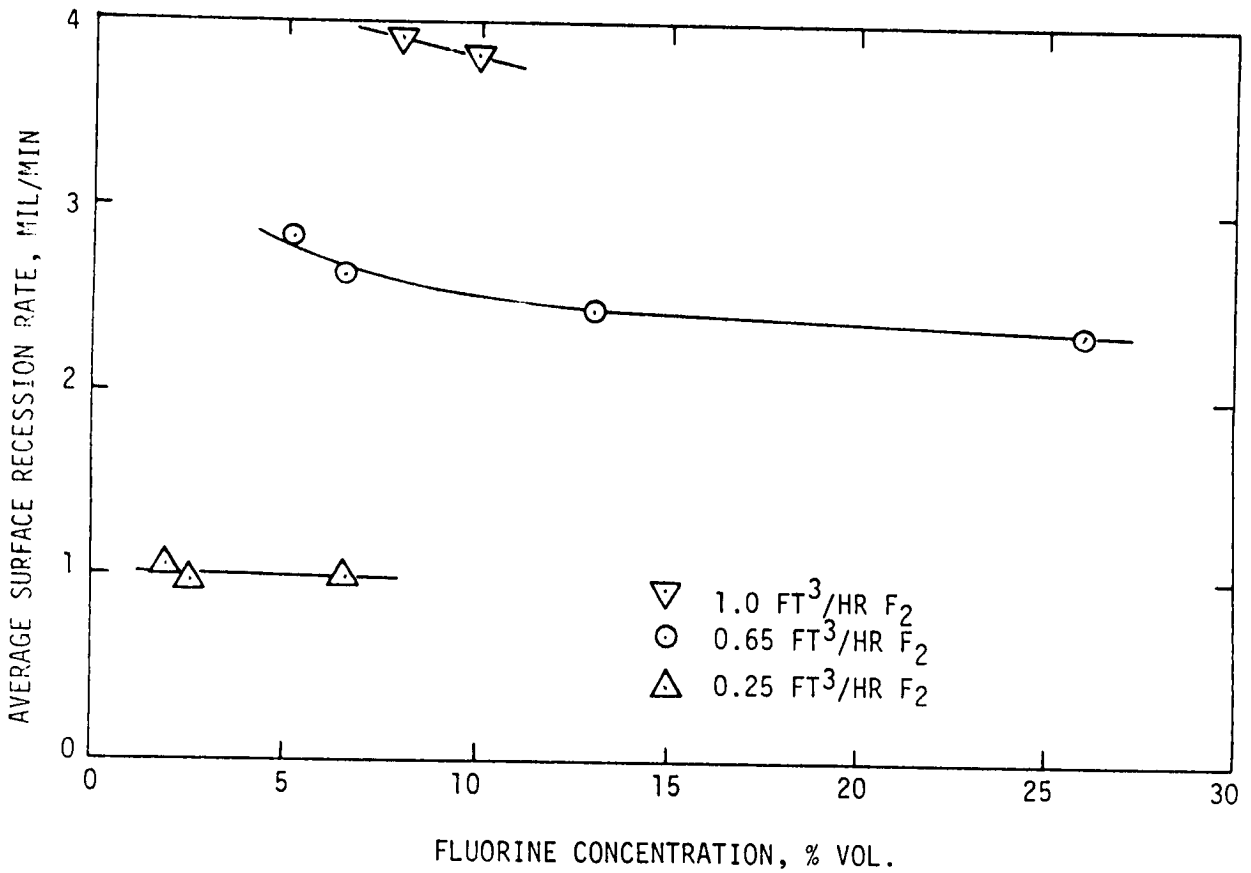

Figure 5. Effect of Fluorine Concentration on the Corrosion Rate of Tungsten at 4000°F and a Nozzle Distance of 1 in.

II, B, Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures (cont.)

The effect of temperature on the corrosion rate of tungsten under various flow conditions was studied to obtain insight into the possible corrosion mechanism. The pertinent data are summarized in Table VI and shown graphically in Figure 6. It can be seen in Figure 6 that the curves all have the same general shape and that corrosion rates decrease quite rapidly at approximately 4700 to 5000°F. This decrease is attributed to the thermal instability of the tungsten/fluorine reaction products at temperatures within that range. That apparent basis for decreased corrosion rates is strengthened by the observation that tungsten hexafluoride, WF_6, in contact with tungsten shows markedly decreasing tungsten surface recession rates at about 4500°F. This is most directly reconciled by the dissociation of WF_6 (or a lower fluoride) to solid tungsten and fluorine.

TABLE VI

EFFECT OF NOZZLE-SPECIMEN DISTANCE AND TEMPERATURE ON THE CORROSION RATE OF TUNGSTEN IN A FLUORINE-ARGON MIXTURE (6.5/93.5 VOL)

Nozzle Distance, in.	Specimen Temperature, °F	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min
1	3000	121.5	2.48
1	3500	126.4	2.58
1	3500	128.6	2.63
1	4000	128.8	2.62
1	4580	124.8	2.54
1	5110	92.0	1.88
1	5500	55.2	1.13
1	5800	30.6	0.62
3	4000	90.3	1.84
3	5000	71.0	1.45
*	4000	16.8	0.34
*	5000	10.8	0.22
*	5280	4.5	0.09

*Nozzle baffled to avoid direct impingement of gas mixture on the sample.

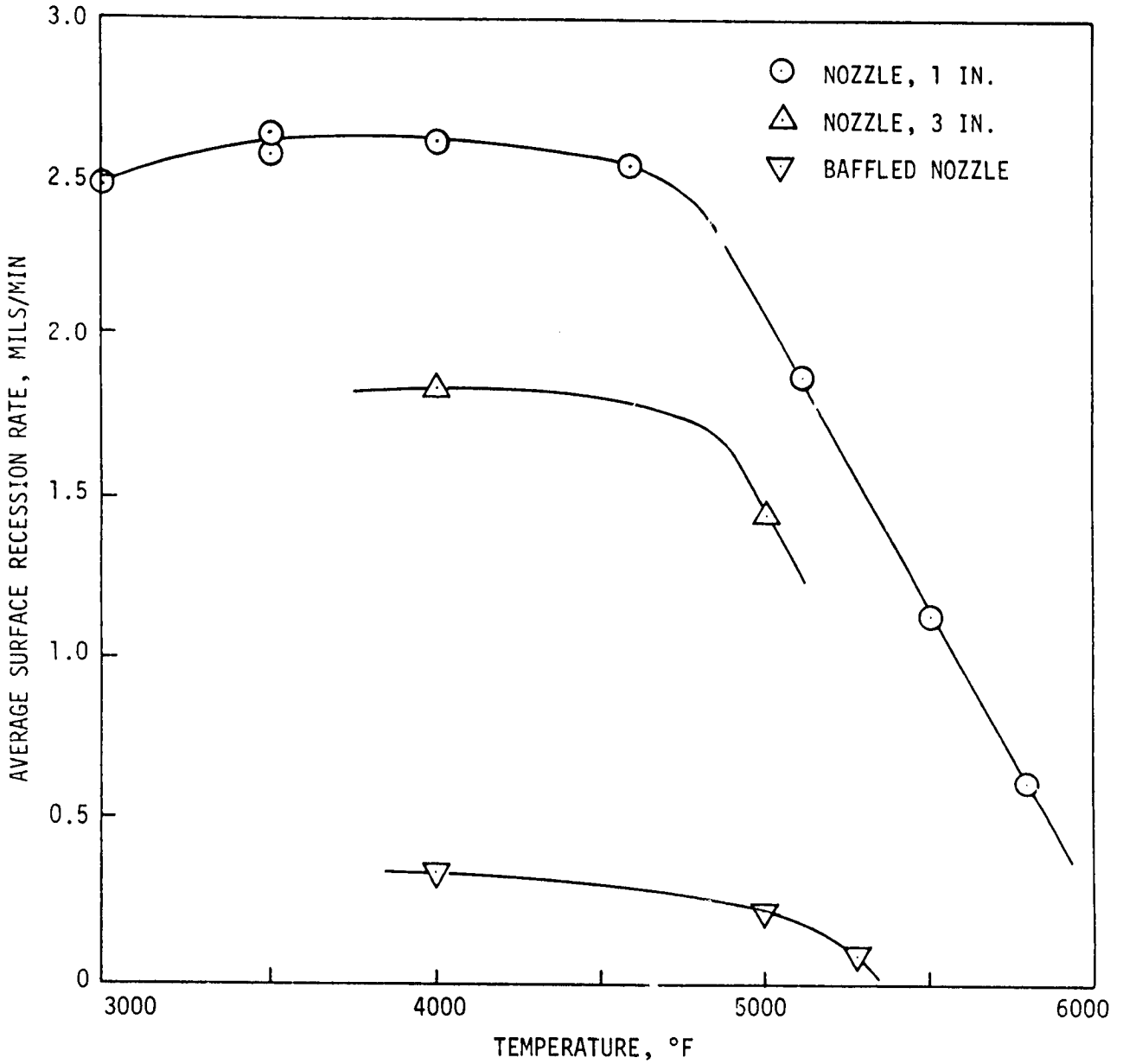

Figure 6. Effect of Temperature and Flow Conditions on the Corrosion Rates of Tungsten in a Fluorine-Argon Gas Mixture (6.5/93.5 vol)

II, B, Dynamic Corrosion Rates of Refractory Metals in Flowing High Temperature Fluorine-Argon Gas Mixtures (cont.)

A summary of the corrosion rate data obtained with fluorine-argon gas mixtures and tantalum, tungsten, tungsten-base alloys, rhenium-base alloys, and iridium and iridium-base alloys is given in Tables 7, 8, 9, 10, and 11, respectively. Representative data from these tables are graphically displayed in Figure 7 for the 6.5/93.5 vol fluorine-argon gas mixture. It is interesting to note that the metals appear to be corroded at about the same rates at 2500°F but differ very substantially at higher temperatures. Each material begins to show a rapidly decreasing corrosion at some high temperature and that temperature would appear to represent the temperature at which the metal fluoride shows an appreciable tendency to dissociate.

TABLE VII

CORROSION RATE OF TANTALUM IN FLOWING FLUORINE-ARGON MIXTURES (*)

Specimen Temp., °F	F_2 Conc., % Vol.	Average Specific Weight Loss, mg/cm^2/min	Average Specific Surface Recession, mils/min	Ref.
4000	2.5	53.2	1.26	4
5000	2.5	58.4	1.38	4
4000	6.5	144.8	3.44	4
5000	6.5	137.0	3.25	4

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ~400 ft/sec. Specimen 1 in from nozzle at ~45° to gas stream.

TABLE VIII

CORROSION RATE OF TUNGSTEN IN FLOWING FLUORINE-ARGON MIXTURES*

Specimen Temp., °F**	F_2 Conc., % vol	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mils/min	Ref.
5110	0.4	5.6	0.12	4
3550	2.5	52.8	1.07	4
4000	2.5	47.6	0.97	4
4580	2.5	42.5	0.87	4
5110	2.5	27.1	0.55	4
5110	2.5	28.8	0.55	4
2225	6.5	106.5	[illegible]	5
2380	6.5	103.2	[illegible]	5
2390	6.5	100.0	[illegible]	5
2830	6.5	121.2	[illegible]	5
3000	6.5	121.5	[illegible]	5,6
3500	6.5	126.4	[illegible]	4,5,6
3500	6.5	128.6	[illegible]	4
4000	6.5	128.8	[illegible]	5,6
4580	6.5	124.8	[illegible]	5,6
4580	6.5	124.8	[illegible]	4
5110	6.5	92.0	[illegible]	4,5
5500	6.5	55.2	[illegible]	6
5800	6.5	30.6	[illegible]	6
3500	10.0	195.0	[illegible]	4
4000	10.0	186.5	[illegible]	5
4580	10.0	169.0	[illegible]	4
5110	10.0	142.4	[illegible]	4

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity 400 ft/sec. Specimen 1 in. from nozzle at 45° to gas stream.

**Emittance of 0.35 used in optical temperature correction.

TABLE IX

CORROSION RATES OF TUNGSTEN-BASE ALLOYS IN FLOWING FLUORINE-ARGON MIXTURES*

I. Tungsten-Rhenium (74/26 wt)

Specimen Temp., °F	F_2 Conc., % vol	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mil/min	Ref.
4000	2.5	47.2	0.94	4
4500	2.5	40.0	0.80	4
5000	2.5	40.2	0.80	4
4000	6.5	113.2	2.25	4
4500	6.5	102.0	2.03	4
5000	6.5	91.0	1.81	4
4000	10.0	163.2	3.25	4
4500	10.0	151.0	3.01	4
5000	10.0	132.6	2.63	4

II. Tungsten-Iridium (95/5 wt)

3500	6.5	104.5	2.12	5
4000	6.5	109.0	2.22	5
4500	6.5	103.5	2.11	5
4660	6.5	110.0	2.23	5
5000	6.5	106.0	2.15	5

III. Tungsten-Iridium (90/10 wt)

3500	6.5	103.8	2.09	5
4000	6.5	98.5	1.98	5
4500	6.5	96.0	1.93	5
4660	6.5	97.5	1.96	5
5000	6.5	89.5	1.80	5

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ~400 ft/sec. Specimen 1 in. from nozzle at ~45° to gas stream.

TABLE X

CORROSION RATES OF RHENIUM AND RHENIUM-BASE ALLOYS IN FLOWING FLUORINE-ARGON MIXTURES*

Specimen Temp., °F	F_2 Conc., % vol	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mil/min	Ref.
I. Rhenium				
5000	2.5	4.0	0.07	4
2500	6.5	119.5	2.24	6
2500	6.5	119.0	2.24	6
3000	6.5	119.0	2.22	5,6
3500	6.5	123.0	2.30	5,6
4000	6.5	87.6	1.64	4,6
4000	6.5	73.2	1.37	4,5,6
4500	6.5	61.9	1.16	4,5,6
4500	6.5	45.2	0.85	4,5,6
5000	6.5	23.0	0.43	4,5,6
5000	6.5	18.0	0.33	5,6
5200	6.5	28.3	0.53	6
4000	10.0	150.0	2.72	4
5000	10.0	42.2	0.79	4
II. Rhenium-Iridium (85/15 wt)				
4000	6.5	90.0	1.67	5
4500	6.5	69.2	1.27	5
4840	6.5	43.3	0.81	5
4500	10.0	75.6	1.4	5
5000	10.0	59.5	1.10	5
III. Rhenium-Iridium (75/25 wt)				
4000	6.5	81.5	1.50	5
4500	6.5	60.6	1.11	5
5000	6.5	30.3	0.56	5
4500	10.0	69.4	1.28	5
5000	10.0	43.8	0.81	5
IV. Rhenium-Iridium (65/35 wt)				
4000	6.5	71.0	1.30	5
4500	6.5	52.9	0.96	5
5000	6.5	26.8	0.47	5
4500	10.0	58.2	1.06	5
5000	10.0	41.5	0.75	5

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ~400 ft/sec. Specimen 1 in. from nozzle at ~45° to gas stream.

TABLE XI

CORROSION RATES OF IRIDIUM AND IRIDIUM BASE ALLOYS IN FLOWING FLUORINE-ARGON MIXTURES*

I. Iridium

Specimen Temp., °F	F_2 Conc., % vol	Average Specific Weight Loss, $mg/cm^2/min$	Average Surface Recession Rate, mil/min	Ref.
2500	6.5	131.0	2.29	5,6
2730	6.5	105.0	1.84	5,6
3000	6.5	78.0	1.36	5,6
3000	6.5	68.0	1.19	6
3000	6.5	65.5	1.15	5,6
3500	6.5	29.4	0.51	4,6
3500	6.5	22.4	0.39	4
3500	6.5	18.7	0.33	5,6
4000	6.5	15.3	0.27	5,6
4000	6.5	11.2	0.20	4
4370	6.5	12.8	0.22	4
4400	6.5	10.2	0.18	4,6
4000	10.0	21.7	0.38	4

II. Iridium-Rhenium (67/33 wt)

4000	2.5	13.1	0.23	4
4425	2.5	11.2	0.20	4
2630	6.5	105.6	1.89	6
3060	6.5	70.6	1.27	6
3500	6.5	47.0	0.84	4
3500	6.5	46.0	0.82	6
3500	6.5	43.0	0.77	5,6
4000	6.5	29.3	0.53	4,6
4000	6.5	18.9	0.34	5,6
4420	6.5	16.0	0.29	6
4425	6.5	16.0	0.29	4
4500	6.5	13.3	0.24	5,6
4700	6.5	13.2	0.23	4
4000	10.0	46.0	0.82	4
4425	10.0	37.0	0.66	4

*Total gas flow rate, 10 ft^3/hr. Nozzle exit velocity ~400 ft/sec. Specimen 1 in. from nozzle at ~45° to gas stream.

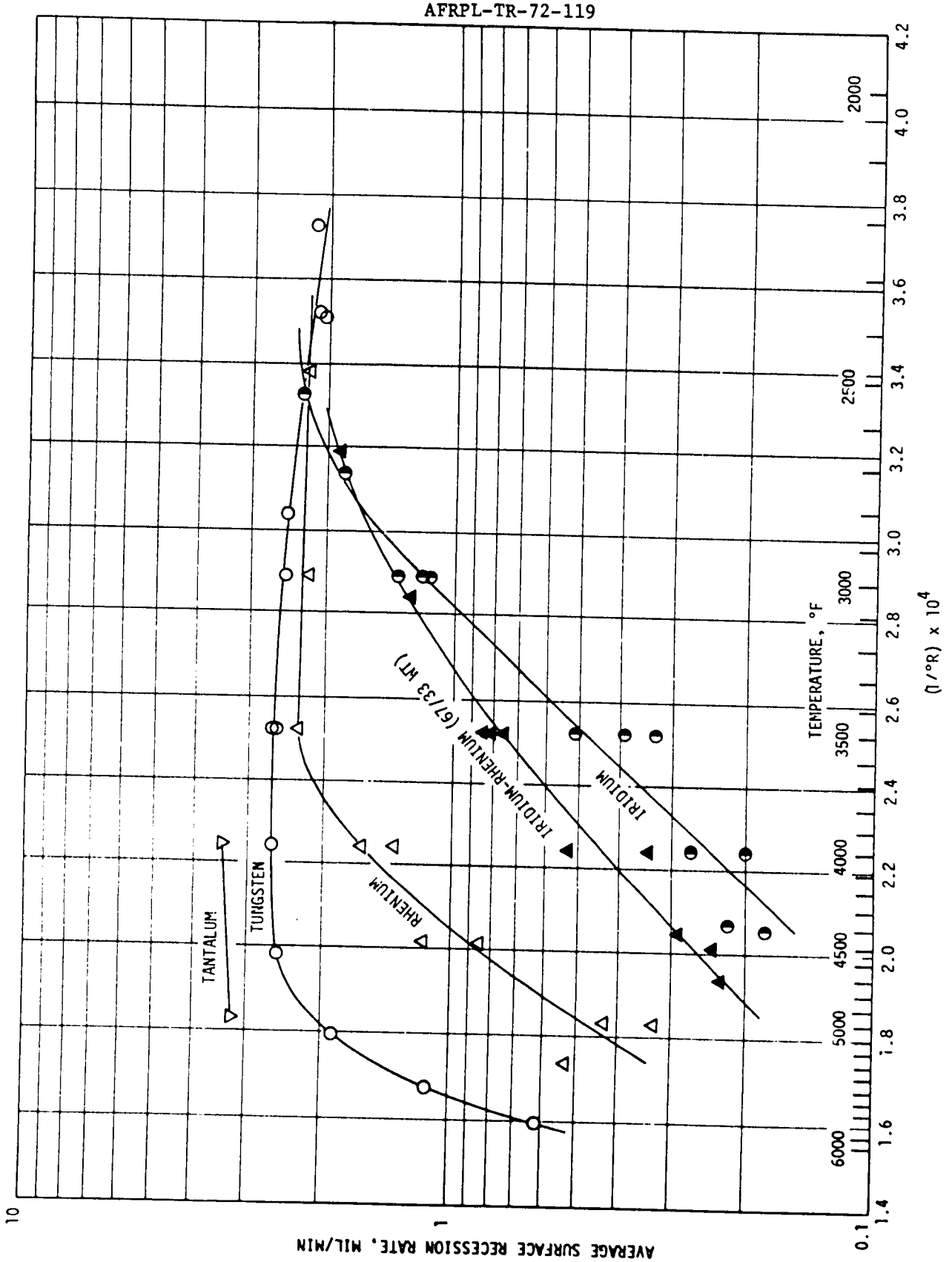

Figure 7. Corrosion Rates of Refractory Metals in Flowing Fluorine-Argon Gas Mixtures (6.5/93.5 Vol.%)

SECTION III

METALS RESPONSE TO LIQUID FLUORINE FLOW AND IMPACT

A. LIQUID IMPACT ON HEATED METALS

Under Contract F04611-72-C-0031, Dynamic Compatibility of Halogen Propellants (Reference 1), the Aerojet Liquid Rocket Company conducted flow tests in which liquid fluorine was impacted on heated specimens of twelve metals. The metal investigated were:

304-L Stainless Steel	6061-T6 Aluminum
301 Stainless Steel	2219 Aluminum
301 Cryo Stainless Steel	OFHC Copper
347 Stainless Steel	Inconel 718
321 Stainless Steel	Monel K-500
A-286 Stainless Steel	Nickel 200

The test apparatus consisted of two major components: (1) a liquid feed system and (2) an electrical-resistance heating system for the metal specimens. The temperature of the metal specimens was measured by means of thermocouples attached to the back of the metal strip which was 0.010-in. thick. The metal specimens were placed within 3/16 in. of the discharge orifice of the liquid feed system. The orifice diameter of the system was 0.015 in. and the entire feed system was temperature conditioned to -320°F. For each test, a fresh, clean, unpassivated metal specimen was used and the temperature level was increased in 100°F increments in the presence of air for each test until the impacting liquid propellant caused the metal specimen to burn. The temperature below which significant attack no longer occurred was determined within ±50°F. Until the ignition temperature was reached, there was only slight evidence of attack on the metal surfaces. The data are presented in Table XII.

Recognizing that the threshold temperatures given in Table XII are accurate to within only about ±50°F, it would appear that the velocity of impingement generally has a weak influence on threshold temperatures with few exceptions. For example, the apparent velocity effect on threshold temperatures is greater than 150°F for more than a two-fold change in velocity on only certain of the stainless steels, i.e., 301, 321, and 304-L.

Comparing the nonignition threshold temperatures in Table XII for liquid impingement with the high-probability-of-failure threshold temperatures in Table II for flowing gas shows that both tests lead to virtually identical material rankings. Further comparisons show that aluminum, copper, and the stainless steels appear to have appreciably lower threshold temperatures to high velocity liquid impingement than to sonic gas flow. Again comparing Table XII and Table II data, a first glance would suggest that Inconel 718,

TABLE XII

MAXIMUM TEMPERATURES OF METAL SURFACES ON WHICH IMPACTING STREAMS OF LIQUID FLUORINE DO NOT RESULT IN IGNITION

Material	Approximate Nonignition Threshold Temperature, °F		
	LF_2 Velocity of 130 ft/sec	LF_2 Velocity of 240 ft/sec	LF_2 Velocity of 295 ft/sec
6061-T6 Aluminum	850*		
2219 Aluminum	850*	850*	
OFHC Copper	1150	1050	
301 Stainless Steel	1450	1100	1100
347 Stainless Steel	1300	1200	1300
321 Stainless Steel	1550	1550	1350
304-L Stainless Steel	1650	1650	1350
301 Cryo Stainless Steel	1550	1400	1400
A-286 Stainless Steel	1650	1600	1550
Inconel 718	1950	1850	1850
Monel K-500	1950	2000	2100
Nickel 200	2150	2100	2200

*Temperatures at which specimen would occasionally burn in air.

III, A, Liquid Impact on Heated Metals (cont.)

Monel K-500, and Nickel 200 are more resistant to impinging liquid fluorine than to sonic gas flow. However, the thresholds in Table II for these materials refer to a potential failure mode involving the onset of strong exotherms and the buildup of significant films of corrosion products only. No evidence of ignition was obtained in flowing sonic gas through Inconel 718, Monel K-500, and Nickel 200 even though pulse temperatures near 2400°F were observed.

B. LIQUID FLOW THROUGH AND IMPACT ON METALS AT LOW TEMPERATURES

Schmidt (Reference 7) has reported the results of tests in which specimens of various metals in selected geometric configurations were exposed to liquid fluorine under controlled conditions of flow and pressure. None of the metal samples eroded, decomposed, or exhibited any measurable physical or chemical changes. In a run made with a Teflon sample, instantaneous chemical reaction and decomposition occurred.

Fluorine was forced through 0.0135-in. ID metal orifices with pressures up to 1500 psi and velocities up to 376 ft/sec; the maximum cumulative flow time per specimen was 1 hr and the minimum was 22 min. Larger orifices were subjected to even higher velocities (over 400 ft/sec) for periods up to 60 sec. Only a slight yellowish color appeared on the upstream side of nickel and aluminum orifices. A brass orifice appeared slightly darker, and stainless steel appeared etched.

Impact plates of stainless-steel weld slag and aluminum sustained fluorine environments with pressures from 100 to 1350 psi and velocities from 136 to 355 ft/sec for nearly 60 sec without effects other than slight discoloration. No reaction was produced by sharpedged turbulence test wedges of stainless steel, aluminum, and brass at velocities up to 169 ft/sec.

The results of this investigation show that turbulence, fluid friction, and impact effects resulting from high-pressure, high-velocity liquid-fluorine flow through clean tubing or past irregularly shaped or sharpedged objects are not likely to initiate fluorine-system failures at low temperatures. The successful operations achieved in this series of compatibility tests can be attributed to the meticulous care that has taken in the assembly, cleaning, and passivation techniques used before exposure of the system to severe dynamic fluorine service. Therefore, improper choice of hardware, poor assembly techniques, and inadequate cleaning and pickling procedures appear to be the primary cause of fluorine-system failures. The results of these tests are summarized in Table XIII.

In related studies at Douglas Aircraft Company (Reference 8), experiments were conducted to evaluate the erosion and impingement resistance of aluminum-silicon alloy, A356-T6, in LF_2 (0.02 vol% HF). This was

TABLE XIII

COMPATIBILITY OF METALS WITH LIQUID FLUORINE UNDER HIGH VELOCITY FLOW AND IMPACT CONDITIONS

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
Leak-simulator orifice 0.0135-in. ID, L/D = 27.75	Aluminum (24 ST)	525	377	9.64	528	0.0183	184	Slight yellowish discoloration on upstream side of orifice
		1012	864	9.64	340	0.0283	293	
		1500	1432	12.43	436*	0.0285	287	
		1460	1436	15.25	424	0.0360	372	
		1339	1339	15.25	432	0.0353	365	
				62.21	2160 (36 min)			
	Stainless steel (347)	1386	1226	17.7	616*	0.0287	297	Slight frosted or etched effect on upstream side. Less affected on downstream side.
		1390	1206	17.7	578	0.0306	317	
		1500	1375	13.85	518*	0.0267	276	
		1510	1350	13.85	488	0.0284	293	
		1505	1443	13.85	472	0.0294	303	
		1512	1408	13.85	480	0.0289	299	
		1500	1398	13.85	500	0.0277	286	
				104.65	3652 (60.9 min)			
	Brass (64 SE)	1495	1395	12.43	344	0.036	376	
		1500	1390	15.25	670*	0.023	235	Slightly darker after exposure
		1465	1424	15.25	440	0.035	358	
				42.93	1454 (21.9 min)			
	Nickel	1100	1015	11.92	696*	0.01713	177	Slight yellowish discoloration on upstream side
		1413	1336	11.92	616*	0.01935	200	
				23.84	1312 (21.9 min)			

*Orifice clogged

Table XIII (cont.)

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
Leak-simulator orifice; 0.025-in. ID, L/D = 5	Aluminum (soft)	1453	1315	17.7	132	0.134	417	
		1465	1360	17.7	130	0.136	410	
		1486	1302	13.85	110	0.126	380	Slight frosted appearance on both sides
		1500	1282	13.85	110	0.126	379	
		1495	1326	13.85	107	0.130	390	
		1492	1391	13.85	108	0.128	386	
		1505	1375	13.85	106	0.131	394	
				104.65	803 (13.4 min)			
Sharp-edged orifice; 1/8-in. ID	Aluminum (soft)	785	505	10.45	6.8	1.54	185	
		1480	1203	10.45	4.4	2.38	286	
		1465	1169	10.45	4.6	2.27	273	Slightly coated on downstream side; frosty appearance. Slightly etched on upstream side
		1440	1144	10.45	4.6	2.27	273	
		1452	1159	10.45	4.0	2.61	315	
		1465	1196	10.45	4.6	2.27	273	
		1470	1192	10.45	4.0	2.61	315	
				73.15	33.0			
	Brass (64 SE)	1008	773	9.74	5.7	1.71	206	
		1482	1206	9.74	4.9	1.99	240	
		1505	1249	9.74	4.2	2.32	279	
		1498	1226	9.74	4.5	2.16	261	
		1504	1223	9.74	4.8	2.03	245	
		1494	1232	9.74	4.7	2.07	249	Purple discoloration on downstream side of orifice
		1500	1223	9.74	4.8	2.03	244	
		1493	1233	9.74	4.4	2.21	267	
		1450	1190	9.74	4.7	2.07	249	
		1485	1334	9.74	4.4	2.21	266	
		1500	1358	9.74	4.0	2.43	266	
				107.14	51.1			

TABLE XIII (cont.)

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
Sharp-edged orifice; 1/8-in. ID (cont.)	Stainless steel (304)	85	85	9.97	20.5	0.485	58.4	
		121	114	9.97	16.0	0.622	74.9	
		300	278	9.97	9.0	1.108	133.3	
		408	391	9.97	9.1	1.095	131.8	
		1005	811	9.97	6.0	1.66	200.0	
		1202	990	9.97	5.44	1.83	220.0	
				59.82	66.04 (1.1 min)			
Impact Plate with Round-edged orifice; 1/8-in. ID	Stainless steel weld slag (304)	1344	1206	11.92	3.78	3.17	355	
		1500	1362	11.92	4.5	2.65	349	
		102	85	9.74	8.6	1.13	136	Very slight etched effect but no apparent attack on impact sample. Slight yellowish discoloration on upstream side of orifice.
		1000	704	9.74	5.8	2.12	201	
		1475	1170	9.74	4.2	2.32	279	
		1485	1173	9.74	4.4	2.21	280	
		1480	1219	9.74	3.3	2.95	350	
		1471	1168	9.74	4.6	2.12	280	
		1495	1196	9.74	4.5	2.16	282	
		1480	1176	9.74	4.0	2.43	293	
		1495	1183	9.74	4.2	2.32	284	
		1490	1337	9.74	3.9	2.50	301	
		1500	1349	9.74	4.0	2.43	293	
				130.98	57.8			
	Aluminum (soft)	800	568	10.45	5.88	1.78	214	
		1470	1195	10.45	4.2	2.49	299	Slight etched effect on impact sample
		1475	1172	10.45	4.8	2.18	262	
		1470	1180	10.45	4.6	2.27	273	
	Stainless steel (304)	1465	1165	10.45	4.4	2.38	286	No effect on orifice except slight bluish cast on downstream side
		1455	1169	10.45	4.3	2.43	293	
		1460	1167	10.45	4.6	2.27	273	
				73.15	32.8			

TABLE XIII (cont.)

Configuration	Material	Experimental Conditions: Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Remarks
							Cycles per second*	
Rotating-vane flowmeter, ball-bearing (stainless steel rotor)	Stainless steel (316, 420, 430, 440)	85	--	9.97	20.5	0.465	46.5	Rotor-mount retainer rings slightly eroded and loose; would have affected running on continued operation.
		121	--	9.97	16.0	0.622	61.5	
		300	--	9.97	9.0	1.108	93.0	
		408	--	9.97	9.1	1.095	109.5	
		1005	--	9.97	6.0	1.66	165.0	
		1202		9.97	5.44	1.83	183.0	
				59.82	66.04 (1.1 min)			
	Aluminum (soft)	1443	1200	16.35	0.7	23.4	155.0	All four sides of sample had sooty film or coating. Not adherent; rubbed off easily. Did not seem to be in metal surface but on it; metal underneath was unchanged.
		1260	761	16.35	3.14	5.2	34.4	
		1370	872	16.35	3.10	5.3	39.4	
		1295	921	16.35	1.96	8.3	54.0	
		1360	873	16.35	2.75	5.9	39.5	
		1295	1057	10.20	0.58	17.6	117.0	
		1357	1067	10.20	0.67	17.9	118.0	
		1391	1103	10.20	0.40	25.5	169.0	
				112.35	13.20			
	Teflon	50	50	--	--	--	--	Immediate ignition on contact.

*100 cycles ∿ 1 lb liquid fluorine.

TABLE XIII (cont.)

Configuration	Material	Initial Pressure, psig	P, psi	Fluorine, lb	Time, sec	Flow Rate, lb/sec	Velocity, ft/sec	Reynolds Number, Re	Remarks
1/4-in. tubing; 0.1285-in. ID, length = 11.3 ft	Stainless steel (304)	0-120*	115	11.0	68.8	0.16	17.4	88,000	All runs with 1/4-in. tubing made without liquid-nitrogen bath. Initial temperature, 75°F.
		0-420*	397	11.0	26.4	0.417	45.4	232,000	
		0-1017*	837	11.0	18.24	0.603	65.7	337,000	
		0-1505*	1297	11.0	14.64	0.751	81.7	543,000	
				44.0	128.08 (2.13 min)				
1/4-in. tubing; 0.182-in. ID, length = 12.2 ft	Aluminum (5052 SO)	0-133*	118	11.0	25.6	0.43	24.4	176,000	All runs with 1/4-in. tubing made without liquid-nitrogen bath. Initial temperature, 75°F.
		0-410*	385	11.0	22.0	0.50	28.4	205,000	
		0-1010*	768	11.0	12.0	0.917	52.0	377,000	
		0-1500*	1275	11.0	7.36	1.495	84.8	614,000	
		0-1485*	1312	11.0	7.16	1.536	87.3	632,000	
				55.0	74.12 (1.24 min)				
3/4-in. tubing	Stainless steel (304)	1260	--	16.35	3.14	5.2	17.8	526,000	The 3/4-in. tubing was part of the test apparatus
		1370	--	16.35	3.10	5.3	20.3	600,000	
		1360	--	16.35	2.75	5.9	20.4	602,000	
		1340	--	16.35	1.96	8.3	28.5	843,000	
		1340	--	16.35	1.26	13.0	44.5	1,315,000	
		1330	--	16.35	1.14	14.3	46.3	1,370,000	
		1319	--	16.35	1.0	16.4	55.8	1,650,000	
		1391	--	10.2	0.9	18.2	62.1	1,835,000	
			--	16.35	0.7	23.4	71.4	2,110,000	
			--	10.2	0.4	25.5	87.3	2,580,000	
Turbulence test wedge (sharp-edged)	Stainless steel (347)	1340	862	16.35	1.14	14.34	90.0		No effect
		1340	740	16.35	1.26	12.97	86.4		
		1330	886	16.35	1.0	16.35	108.5		
		1404	978	16.35	0.9	18.16	120.5		
				65.4	4.3				
	Brass (64 SE)	1319	800	10.2	0.9	11.3	70		Very slightly frosted appearance; slightly lighter in color than parent metal
		1383	1036	10.2	0.5	20.4	135		
		1286	1028	10.2	0.57	17.9	113		
		1346	1100	10.2	0.66	15.5	102		
				40.8	2.63				

*Instantaneous pressure release.

III, B, Liquid Flow Through and Impact on Metals at Low Temperatures (cont.)

accomplished by flowing LF_2 through an orifice test coupon and impinging on another test coupon 3/16 in. downstream. Orifice and impingement specimens were exposed to F_2 at -235°F for 30 min at velocities of 50 and 150 ft/sec. No orifice change was observed but superficial impingement attack was observed at both velocities.

The test conditions and the results of the individual runs are summarized in Table XIV.

TABLE XIV

COMPATIBILITY OF AN ALUMINUM-SILICON ALLOY WITH LIQUID FLUORINE UNDER HIGH VELOCITY FLOW AND IMPACT CONDITIONS*

Material	Velocity, ft/sec	Orifice Diameter, in.		Final Condition of Impingement Coupon
		Initial	Final	
Al A356-T6 NASA Grade IIIF	50	0.065	0.065	Superficial attack
Al A356-T6 NASA Grade IIIF	150	0.039	0.039	Superficial attack

*LF_2 temperature, -235°F: LF_2 static pressure, 400 psig; flow rate, 0.50 gal/min; test time, 30 min.

SECTION IV

IV. METALS BEHAVIOR IN THE PRESENCE OF FLUORINE ADIABATIC COMPRESSION

As part of the program on the dynamic compatibility of halogen propellants with metals, Contract F04611-72-C-0031 (Reference 1), the Aerojet Liquid Rocket Company conducted adiabatic compression tests on gaseous fluorine in the presence of metals. The metal specimens used in the investigation were composed of the following alloys:

304-L Stainless Steel	6061-T6 Aluminum
347 Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
A-286 Stainless Steel	Monel K-500
	Nickel 200

The purpose of the tests was to determine the maximum allowable conditions of adiabatic compression of gaseous fluorine that can be tolerated in systems containing the metals listed above.

The apparatus used in the investigation was a U-tube adiabatic compression test apparatus which was modified to accommodate the introduction of gaseous halogen propellants and metal specimens and to incorporate a means of temperature conditioning the loaded U-tube. A schematic diagram of the apparatus is shown in Figure 8. The test specimen holder was a 1/4-in. solid AN plug used to seal the end of the U-tube. The test specimen was a strip of metal sheet 0.010-in. thick by 0.10-in. wide by 0.10-in. long which was spot welded to the end of the AN plug. The U-tube was fabricated from Inconcel X-750 1/4-in. tubing approximately 16-in. long.

The tests were conducted in the following manner. The U-tube was attached to the apparatus and the specimen holder used to seal the open-end of the U-tube. The tube was then evacuated to 1 torr or less, temperature conditioned, and then 15.7 psia of gaseous fluorine was gradually introduced into the assembly. The fluorine was allowed to remain in the U-tube for five minutes prior to the test to allow for initial passivation of the metal. The pneumatic line valve was then actuated and the nitrogen from the accumulator tank used to compress the fluorine vapor. The U-tube assembly was then vented and flushed with nitrogen and the test specimen was examined visually to ascertain if any attack occurred. Microscopic examination was used to evaluate the samples which were not totally consumed in the test. A 1000 lb burst disc made of 304-L stainless was used in each test to seal the pneumatic valve and check valve assembly from the halogen atmosphere prior to the test. The driving pressure in the accumulator tank and the initial fluorine temperature was varied with each material in order to define the pressures and temperatures at which the metals were susceptible to attack. The test specimen was replaced after each test to insure that comparable surfaces were being exposed to the test conditions. The pneumatic valve opened completely within 1.5 milliseconds and with an accumulator pressure of 1000 psia; the minimum pressurization rate was 6.7×10^5 psi/sec.

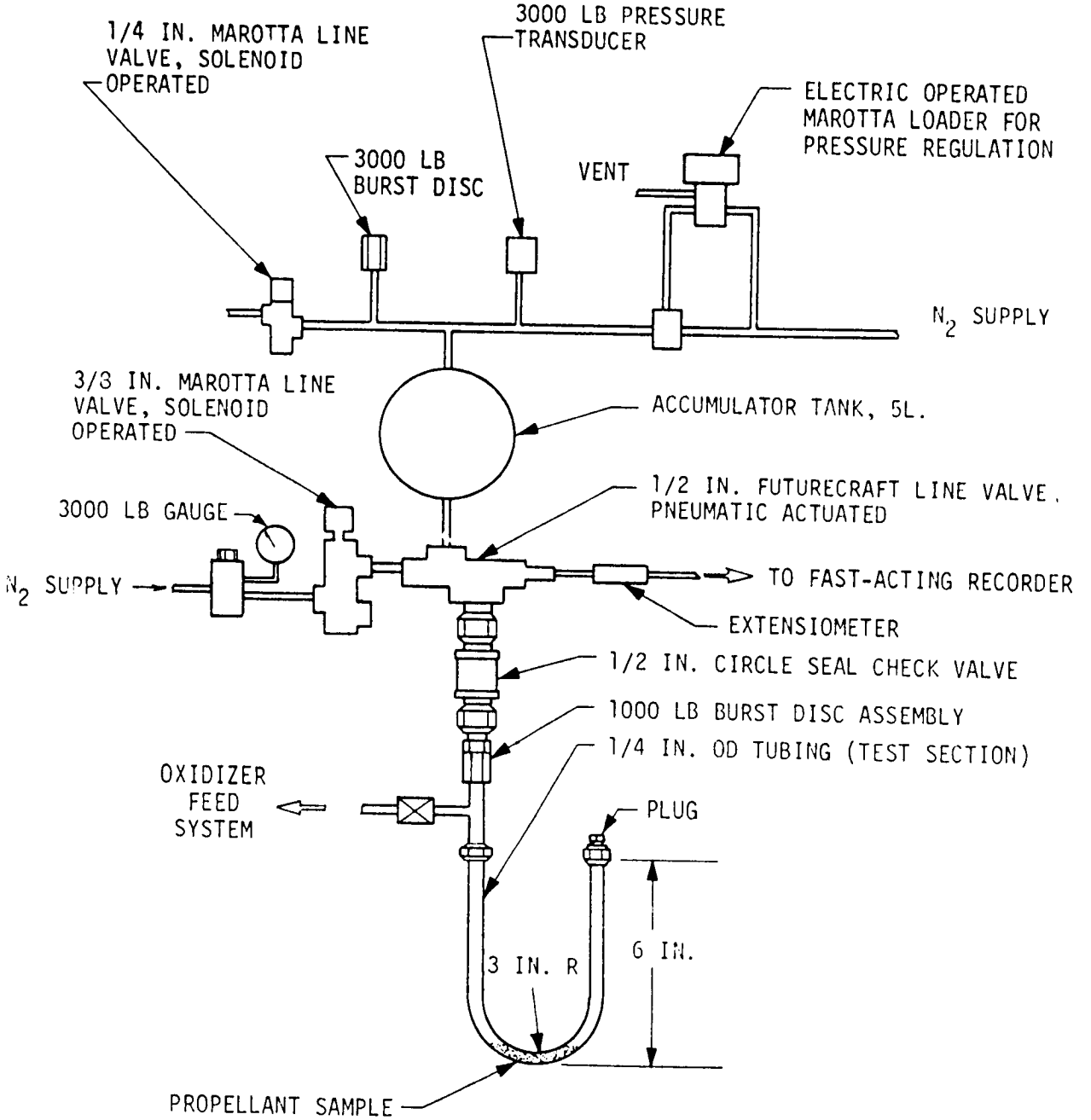

Figure 8. Schematic Diagram of U-tube Adiabatic Compression Apparatus

IV, Metals Behavior in the Presence of Fluorine Adiabatic Compression (cont.)

The results of 107 tests conducted on the specimens of the nine metals are summarized in Table XV. The initial fluorine temperature, T_o, and pressure, P_o, and the final pressure, P_f, are experimentally determined values. The final temperature, T_f, is calculated from Equation 1 assuming the fluorine to be a

$$T_f = T_o \left(\frac{P_f}{P_o}\right)^{\frac{\gamma-1}{\gamma}} \tag{1}$$

nondissociating ideal gas and where γ is defined by Equation 2 using values of Cp for fluorine from Reference 9.

$$\gamma = \frac{\left(\frac{Cp}{Cp - R}\right)_{T_o} + \left(\frac{Cp}{Cp - R}\right)_{T_f}}{2} \tag{2}$$

The estimated final density, ρ_f, is calculated from the perfect gas law and is evaluated at T_f and P_f. Test results denoted by a minus sign (-) indicate that attack is not evident by microscopic examination, those denoted by a single plus sign (+) indicate attack is apparent, and those denoted by a double plus sign (++) indicate the specimen was totally destroyed.

Specimens of OFHC copper and Nickel 200 were not visibly attacked under any of the test conditions. 304-L stainless steel and Inconel 718 were only slightly attacked. Monel K-500, 321 stainless steel, and A-286 stainless steel showed variable degrees of attack from superficial attack to total consumption. 347 stainless steel and 6061-T6 aluminum were totally consumed whenever attack was evident but each metal gave only one positive reaction out of 9 tests on each metal. The conditions under which the various metals can be expected to have approximately a 50% probability of reaction with gaseous fluorine subjected to adiabatic compression were derived from the data given in Table XV. These conditions are summarized in Table XVI. From the data presented in Tables XV and XVI, it is concluded that the metals can be ranked in categories in the following descending order of resistance to the effects of fluorine adiabatic compression: (1) Nickel 200 and OFHC copper, (2) Inconel 718, and (3) 304-L, 321 and A-286 stainless steels. The proper ranking of Monel K-500, 6061-T6 aluminum and 347 stainless steel is indefinite because of insufficient or irregular positive test results, but they appear to belong in the third category.

It is interesting to note that the results of these tests are in quite good agreement with gas flow and liquid impact data (see Tables II and XII, respectively) in terms of threshold temperatures and material rankings except that the adiabatic compression tests essentially reverse the order of Monel K-500 and OFHC copper. This significant reversal in relative resistance to attack has not been explained but it is also observed in connection with ignition temperatures in static fluorine (see Table III).

TABLE XV

BEHAVIOR OF VARIOUS METALS IN THE PRESENCE OF GASEOUS FLUORINE SUBJECTED TO ADIABATIC COMPRESSION

Metal	Initial Condition Temp. T_o, °F	Initial Condition Press., P_o, psia	Final Condition Press., P_f, psia	Final Condition Calc. Temp. T_f, °F	Final Condition Est. Density, ρ_f, lb/ft^3	Test Results
304-L Stainless Steel	62	15.7	1515	1085	3.48	-
	67	15.7	2515	1275	5.14	-
	68	15.7	2815	1310	5.64	-,+
	67	15.7	3015	1335	5.95	+,+
	212	15.7	1015	1310	2.03	-,-
	212	15.7	1515	1470	2.78	-,+
	212	15.7	1765	1530	3.14	-,+
	212	15.7	2015	1585	3.49	+
	369	15.7	3015	2235	3.97	-
	370	15.7	3015	2235	3.97	-
321 Stainless Steel	66	15.7	3015	1330	5.97	-
	70	15.7	3015	1345	5.92	-,-,-,-
	212	15.7	915	1270	1.87	-,-
	212	15.7	1015	1310	2.03	-,-,+
	212	15.7	1265	1395	2.42	-,++
	212	15.7	1515	1470	2.78	-
	212	15.7	2015	1585	3.49	-,++
	212	15.7	2515	1685	4.16	++,++
	212	15.7	3015	1760	4.81	+,++,+
	374	15.7	3015	2250	3.94	-
	375	15.7	3015	2250	3.94	-
347 Stainless Steel	212	15.7	2015	1585	3.49	-,-,-
	212	15.7	2265	1635	3.83	-,-
	212	15.7	2515	1685	4.16	-,++
	360	15.7	3015	2205	4.01	-
	366	15.7	3015	2225	3.98	-
A-286 Stainless Steel	62	15.7	2515	1260	5.18	-
	62	15.7	2715	1290	5.50	-
	68	15.7	2815	1310	5.64	-,+,+
	67	15.7	3015	1335	5.95	++
	212	15.7	3015	1760	4.81	-,-
	331	15.7	3015	2120	4.14	-
	332	15.7	3015	2125	4.13	-
6061-T6 Aluminum	62	15.7	2015	1180	4.36	-
	62	15.7	2515	1260	5.18	-
	66	15.7	3015	1330	5.97	-,++,-
	212	15.7	3015	1760	4.81	-,-
	369	15.7	3015	2235	3.97	-
	370	15.7	3015	2235	3.97	-

TABLE XV (cont.)

BEHAVIOR OF VARIOUS METALS IN THE PRESENCE OF GASEOUS FLUORINE SUBJECTED TO ADIABATIC COMPRESSION (Cont.)

Metal	Initial Condition Temp. T_o, °F	Initial Condition Press., P_o, psia	Final Condition Press., P_f, psia	Final Condition Calc. Temp. T_f, °F	Final Condition Est. Density, ρ_f, lb/ft^3	Test Results
OFHC Copper	66	15.7	3015	1330	5.97	-
	70	15.7	3015	1345	5.92	-
	212	15.7	3015	1760	4.81	-,-
	367	15.7	3015	2230	3.97	-
	368	15.7	3015	2230	3.97	-
Inconel 718	62	15.7	3015	1325	5.99	-,-
	212	15.7	2265	1635	3.83	-,-
	212	15.7	2515	1685	4.16	-,+
	212	15.7	3015	1760	4.81	-,+,-,-
	358	15.7	3015	2200	4.02	-
	360	15.7	3015	2205	4.01	-
Monel K-500	66	15.7	2515	1275	5.14	-,-,+
	67	15.7	2715	1300	5.47	-
	67	15.7	2815	1310	5.64	-
	67	15.7	3015	1335	5.95	++
	212	15.7	2015	1585	3.49	-,-
	212	15.7	2515	1685	4.16	+,+
	212	15.7	3015	1760	4.81	-,-,-,-
	367	15.7	3015	2230	3.97	-
	368	15.7	3015	2230	3.97	-
Nickel 200	63	15.7	3015	1330	5.97	-,-
	212	15.7	2765	1720	4.50	-,-
	212	15.7	3015	1760	4.81	-,-
	361	15.7	3015	2210	4.00	-
	362	15.7	3015	2215	4.00	-

TABLE XVI

TERMINAL ADIABATIC COMPRESSION CONDITIONS THAT RESULT IN A 50% PROBABILITY OF FLUORINE/METAL REACTION

Metal	Conditions for a 50% Probability of Reaction: Calc. Final Temp., °F	Calc. Final Density, lb/ft^3	Magnitude of Resulting Reaction
6061-T6 Aluminum	∿1330*	∿5.97	Major
A-286 Stainless Steel	1300	5.57	Variable
304-L Stainless Steel	1310	5.64	Slight
	1500	2.96	Slight
321 Stainless Steel	1475	2.90	Variable
347 Stainless Steel	∿1685*	∿4.16*	Major
Inconel 718	∿1685*	∿4.16*	Slight
Monel K-500	1305	5.55	Variable
	∿1635	∿3.82	Slight
OFHC Copper	Not Defined		Insignificant
Nickel 200	Not Defined		Insignificant

*Insufficient positive reaction data points to define reaction probability accurately.

IV, Metals Behavior in the Presence of Fluorine Adiabatic Compression (cont.)

It can be seen in Table XV that no positive reactions were obtained when fluorine temperatures prior to adiabatic compression were in the temperature range of 331 to 375°F. The corresponding temperature and density conditions upon adiabatic compression were 2120 to 2250°F and approximately 4 lb/ft^3, respectively; conditions considerably more severe than those achieved in many positive tests which involved lower initial temperatures. The failure of specimens to react with fluorine under these apparently more drastic conditions has not been explained but it is postulated that passivation-type reactions at the highest initial temperatures may have resulted in the formation of "passive films" which are sufficiently protective to be affected within the time span of an adiabatic compression.

The data obtained from all the tests indicate that the threshold temperatures for a fluorine/metal reaction resulting from adiabatic compression varies inversely with the final fluorine density for a given metal. However, the failure to achieve reaction under some apparently drastic conditions, indicate that some factor other than just final temperature and density has an important influence on a metal's susceptibility to reaction via adiabatic compression.

SECTION V

EFFECT OF A FLUORINE LIQUID PHASE SHOCK WAVE ON METALS

Tests were conducted at the Aerojet Liquid Rocket Company (Reference 1) to determine the effects of a shock wave promulgated through liquid fluorine (water hammer effect) on the metals listed below.

304-L Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
A-286 Stainless Steel	Monel K-500
6061-T6 Aluminum	Nickel 200

The tests were conducted in the adiabatic compression test apparatus shown schematically in Figure 8 with 2 to 3 ml of liquid fluorine condensed in the U-tube. The configuration of the test specimen of the metal was the same as described in Section IV to facilitate discrimination between the results of adiabatic compression and the "water hammer effect." Prior to the tests with fluorine, the apparatus was checked out with water in the U-tube and with various driving pressures. The resultant pressure spikes were recorded with a 6K Tabor transducer. With a 1000 psig driving pressure, a pressure spike of 8300 psig was measured showing that the pressure in the shock wave front was approximately eight times the driving pressure. Similar results were obtained with 2000 and 3000 psig of driving pressure; however, the transducer was mechanically stopped at 9500 psig and the absolute peak pressures were beyond the range of the transducer.

The experimental data obtained with liquid fluorine are presented in Table XVII. The significant items to be noted from the data are that: (1) 304-L stainless steel and Inconel 718 were apparently not attacked during the tests; (2) Monel K-500 showed discoloration due to localized heating; and (3) 321 and A-286 stainless steels, 6061 aluminum, OFHC copper, and Nickel 200 underwent very slight attack as evidenced by the removal of the sharp edges from the test specimen. It must be emphasized that none of the attack observed in these "water hammer" tests led to significant destruction of the metal. The effects were noted by microscopic examination of samples at 40X magnification. Baseline tests, using water with 301 cryoformed stainless steel and 6061 aluminum, showed no significant attack.

The results of a related shock wave test have been reported by Douglas Aircraft Company in Reference 8. An aluminum casting alloy, A 356-T6, Grade III-F, was exposed to an explosive shock of 120,000 psi after a 24-hr soak in LF_2 (0.02% vol HF) at -320°F using a test apparatus of the card-gap type. The test resulted in a reaction with no trace of the test coupon remaining.

Generally similar tests were made by Sterner and Singleton (Reference 10) to investigate the possibility of metal ignition in liquid fluorine under conditions of explosive shock. The runs were carried out in metal tubes 2-in. long x 5/8-in. ID x .065-in. wall thickness, with the tubes themselves being the samples. The tubes were closed at the ends by brass plugs, silver soldered in place, and fluorine was added through a 1/4-in. copper tube mounted in the sample tube wall. Two tubes of each material were tested, including Monel, nickel, brass, copper, 304 SS, 316 SS, 347 SS, and 1100 aluminum. The experimental procedure was as follows:

TABLE XVII

BEHAVIOR OF VARIOUS METALS
SUBJECTED TO A SHOCK WAVE OF LIQUID FLUORINE

METAL	INITIAL LIQUID TEMPERATURE, °F	DRIVING PRESSURE, psig	RESULT
304-L Stainless Steel	-321	2000	No observable effect (2 samples)
321 Stainless Steel	-321	2000	No observable effect
321 Stainless Steel	-321	2000	Slight erosion of sample edge
A-286 Stainless Steel	-321	2000	Erosion of sample edges
A-286 Stainless Steel	-321	2000	Erosion of sample edges
6061 Aluminum	-321	2000	No observable effect
6061 Aluminum	-321	2000	Erosion of sample edges
OFHC Copper	-321	2000	No observable effect
OFHC Copper	-321	2000	Erosion of sample edge
Monel K-500	-321	2000	Discoloration due to heating
Monel K-500	-321	2000	Discoloration due to heating
Inconel 718	-321	2000	No observable effect (2 samples)
Nickel 200	-321	2000	No observable effect
Nickel 200	-321	2000	Erosion of sample edges

V, Effect of a Fluorine Liquid Phase Shock Wave of Metals (cont.)

(1) The 1/4-in. tube was attached to the fluorine gas manifold and a No. 6 electric blasting cap was tightly fastened to the tube wall with nichrome wire.

(2) An insulated can was positioned and liquid nitrogen was added to the can, covering the cell completely.

(3) Fluorine gas was condensed into the cell, filling it completely with liquid.

(4) Ten minutes after the tube was filled, the blasting cap was set off.

The ends of the tubes were usually blown out by hydrostatic pressure generated by the deformation of the tube walls, but no evidence of fluorine reaction was observed in any run.

The reactivity of titanium filings with liquid fluorine was examined by placing filings in small Monel tubes, adding liquid fluorine, and exploding a dynamite cap outside the tube. Three tests were run. In two cases, there was no apparent explosion of the titanium, although the filings were completely transformed to the white titanium tetrafluoride. In the third case, a severe detonation occurred before the cap was exploded, and the tube was torn longitudinally from the force of the blast. No trace of the filings or reaction products was found.

From the composite results of these tests, it is concluded that the shock waves generated in liquid fluorine by driving the fluorine against a dead end at a driving pressure of 2000 psig or by the close-coupled explosive shock of a No. 6 blasting cap have little or no ability to initiate a significant reaction with aluminum, brass, copper, Inconel, Monel, nickel, and austenitic stainless steels. Aluminum casting alloy A 356-T6, Grade III-F, will react with liquid fluorine under the influence of an extreme shock wave (120,000 psi). Titanium, in finely divided form, is very reactive with liquid fluorine under the influence of little or no shock wave action.

SECTION VI

EFFECT OF ULTRASONIC AND LOW FREQUENCY VIBRATION ON THE INTERACTION OF METALS WITH FLUORINE

A. ULTRASONIC VIBRATION IN THE PRESENCE OF LIQUID FLUORINE

Tests were conducted at the Aerojet Liquid Rocket Company (Reference 1) to determine whether the "passive film" on the various metals undergoes appreciable degradation when subjected to ultrasonic vibration/cavitation in the presence of liquid fluorine. The metals investigated are listed below.

301 Cryo Stainless Steel	6061-T6 Aluminum
304-L Stainless Steel	OFHC Copper
321 Stainless Steel	Inconel 718
347 Stainless Steel	Monel K-500
A-286 Stainless Steel	Nickel 200

The tests were conducted in the following manner. A stainless steel cylinder was fabricated with four vertical rows of welded-on B-nut cap assemblies. The metal specimens were mounted by strapping to AN plugs which sealed the B-nut cap assemblies. In this manner, eighteen metal specimens could be tested concurrently. The assembled stainless steel cylinder was immersed in an ultrasonic cleaning bath which was driven with 400 watts at a frequency of 62.5 k Hz. The specimens were passivated in fluorine vapor overnight prior to exposure to the liquid. Prior to conducting the vibration tests, a control test was made wherein the metal specimens were immersed in static liquid fluorine for 5.5 hours, then weighed to determine whether weight changes occurred. New metal specimens were installed in the test fixture. The fixture with metal specimens in place was passivated overnight and then subjected to the vibration test. The vibration test cycle consisted of one-half hour of operation, one-half hour of shutdown, and this was continued for 6 cycles. Upon completion of the vibration test cycle, the specimens were weighed.

The results of the static exposure and vibration exposure tests with liquid fluorine are presented in Table XVIII. In addition, the results of a second control test obtained with Freon-113 under the vibrating conditions are included in the table for comparison. The specimens were examined at 60X magnification to determine if significant attack had occurred. Weight changes of $\pm$ 0.1 mg are considered to be the approximate sensitivity limits of the weighing procedure.

The significant items to be noted from the data on the control tests given in Table XVIII are: (1) ultrasonic vibration of the metal specimens in the "inert," Freon 113, results in no significant weight change (average weight change is +0.036 mg, σ = 0.073 mg, and the maximum weight change lies within 2σ of the average) and only slight superficial visual effects on the surfaces, (2) static exposure of the metals, except for 347 stainless steel, to liquid fluorine results in no significant weight change (average weight change is 0.000 mg, σ = 0.056 mg, and the maximum weight change, excluding

TABLE XVIII

EFFECT OF ULTRASONIC VIBRATION ON "PASSIVE FILMS" ON VARIOUS METALS IN THE PRESENCE OF LIQUID FLUORINE

Metal	Static Exposure in Liquid Fluorine			Vibration Exposure in Liquid Fluorine			Vibration Exposure in Freon 113		
	Initial Sample Wt., mg	Wt Chnge After Exposure mg	Observations	Initial Sample Wt., mg	Wt Chnge After Exposure mg	Observations	Initial Sample Wt., mg	Wt Chnge After Exposure mg	Observations
301 Cryo Stainless Steel	249.2	-0.1	No Change	253.9	0.0	No Change	-	-	-
304-L Stainless Steel	129.6	-0.1	Staining	123.8	0.0	No Change	-	-	-
304-L Stainless Steel	125.1	0.0	Staining	141.1	-0.1	No Change	-	-	-
321 Stainless Steel	130.9	0.0	No Change	133.7	0.0	No Change	-	-	-
347 Stainless Steel	141.8	+0.2	Staining	143.9	0.0	No Change	130.2	+0.1	Staining
347 Stainless Steel	152.3	+0.1	Staining	135.1	0.0	No Change	134.6	+0.1	Staining
A-286 Stainless Steel	181.9	0.0	Staining	189.0	0.0	No Change	184.0	+0.1	No Change
A-286 Stainless Steel	189.0	0.0	Staining	166.3	0.0	No Change	176.9	+0.1	No Change
6061-T6 Aluminum	47.9	0.0	No Change	48.9	0.0	No Change	44.0	-0.1	No Change
6061-T6 Aluminum	50.2	+0.1	No Change	53.2	+0.1	No Change	43.9	+0.1	No Change
OFHC Copper	143.7	0.0	Discolored	151.2	0.0	Discolored	153.1	0.0	Discolored
OFHC Copper	153.9	-0.1	Discolored	164.5	-0.1	Discolored	154.0	0.0	Discolored
Inconel 718	121.3	0.0	No Change	123.1	+0.1	Staining	137.4	0.0	No Change
Inconel 718	128.1	+0.1	No Change	126.4	-0.2	Staining	120.9	-0.1	No Change
Monel K-500	128.5	0.0	Staining	144.9	+0.1	No Change	158.5	+0.1	No Change
Monel K-500	132.6	0.0	Staining	142.3	+0.1	No Change	149.8	-0.1	No Change
Nickel 200	150.5	-0.1	No Change	147.0	-0.1	Staining	127.1	+0.1	No Change
Nickel 200	155.0	-0.1	No Change	127.8	-0.1	Staining	148.9	+0.1	No Change
Average		0.000			-0.011			+0.036	
Standard Deviation, σ		0.056			0.060			0.073	

VI, A, Ultrasonic Vibration in the Presence of Liquid Fluorine (cont.)

347 S.S., is within 2σ of the average), and (3) 347 stainless steel appears to suffer very slight attack by static fluorine as evidenced by a weight change that differs from the average of the other metals by 3.6σ. Using the above baseline statistical information, the following conclusions are reached regarding the effect of ultrasonic vibration on metals in the presence of liquid fluorine.

(1) None of the metals tested exhibit any appreciable change in weight or visual appearance other than staining or discoloration (average weight change = -0.011 mg, σ = 0.060 mg, maximum deviation = 3.2σ), and

(2) The weight change observed with Inconel 718 is very slight but may be statistically significant.

In related tests at Douglas Aircraft Company (Reference 8), the aluminum casting alloy, A 356-T6, was exposed to liquid fluorine (0.02% vol HF) at -320°F and subjected to vibration at 27.8 k Hz in an ultrasonic mechanical stepped horn apparatus in repeated cycles of 0.5 hr on and 3 hr off. Similar tests were conducted with water and liquid nitrogen for comparison. The average sample weight changes in water, LN_2, and LF_2 were 0.01, 0.02, and 0.04 mg/cm^2-min, respectively. Average corrosion pit depths in LN_2 and LF_2 were 18 and 40 microns, respectively.

It should be noted that the ultrasonic vibration involved in these tests was sufficiently powerful to disrupt the surface very significantly as evidenced by weight loss and pitting when the specimen was exposed to the inert liquid nitrogen. The fact that the presence of liquid fluorine in this same highly disruptive environment does not lead to gross fluorine/metal reaction very strongly indicates that the "passive flim" or loss of such is not an item of great importance in liquid fluorine/metal compatibility.

B. LOW FREQUENCY VIBRATION IN THE PRESENCE OF GASEOUS FLUORINE

In work reported by Sterner and Singleton (Reference 11), tubes made of copper, brass, stainless steel, nickel, and Monel which had been filled with liquid fluorine and impacted were immediately filled with gaseous fluorine after the impact test and subjected to a vibration test. The vibration test conditions were 30 Hz at 5 mm amplitude for periods up to 5 hr. In eight such tests, the vibrations produced no observable effect on the tubes. From these tests, it is concluded that low frequency vibration is insufficient to disrupt the "passive flim," or that the "passive film" is not particularly important in regard to ambient temperature gaseous fluorine/metal compatibility.

SECTION VII

RESPONSE OF METALS TO FLEXURE IN A FLUORINE ENVIRONMENT

A. ELASTIC FLEXURE IN GASEOUS AND LIQUID FLUORINE

Sterner and Singleton (Reference 11) investigated the effects of flexing thin metal strips of aluminum, brass, copper, and Monel within the elastic region in liquid fluorine using a specially designed testing cell. The tester utilized strip specimens ~3-1/2-in. long by ~3/8-in. wide by 0.001 to 0.010-in. thick. The strips had one end fixed to the bottom of the cell and the other end fastened to a reciprocating rod. This rod passed through a brass bushing in the top of the cell, and was powered by a solenoid. The solenoid was actuated by a signal from an electric timer which operated at the rate of 1 pulse/sec. The flexing tests were performed to provide information on the flexibility of a protective fluoride film. If increased corrosion resulted, this would have provided evidence that a fluoride film was present and that the film was not flexible. Evidence of corrosion was based on specimen weight change and microscopic examination at 60X magnification. The negative results actually obtained indicate that either the protective fluoride film is flexible or that a fluoride film is not required for protection. The results of these tests are summarized in Table XIX.

TABLE XIX

RESPONSE OF METALS TO ELASTIC FLEXURE IN LIQUID FLUORINE

Metal	Testing Time, min.	Flexure Cycles	Initial Specimen Wt., mg	Weight Change, mg	Observations
Aluminum (Alcoa Foil, 0.001-in. thick)	210	12600	35.8	+1.5	No change
Brass (yellow, 0.010-in. thick)	90	5400	908.4	-0.9	Sparse white coating
Copper (0.010-in. thick)	240	14400	900.3	+1.6	No change
Monel (0.002-in. thick)	290	17400	321.6	+2.0	Very sparse white splotches on convex side of sample

In related tests reported by Asunmea, et al., (Reference 12), metal specimens of 316 stainless steel and copper in the form of bellows were exposed to elastic flexure and/or cryoshock in gaseous and liquid fluorine environments to evaluate the mechanical stability of fluoride films. The basic test apparatus consisted of a double walled stainless steel test container, a specimen mount attached to the lid (to allow translational reciprocating motion of the specimens),

VII, A, Elastic Flexure in Gaseous and Liquid Fluorine (cont.)

a metal bellows seal on the reciprocating shaft, a variable eccentric cam to change the axial displacement of the shaft, and a variable speed power unit. The jacket of the test container contained no direct plumbing connections with the interior of the container and was used as a temperature control bath by flowing water or liquid nitrogen through it during different tests. A particle collector was connected at the bottom of the test chamber and was immersed in liquid nitrogen to maintain it at -320°F when necessary. The bellows specimens were formed from cold rolled, mill annealed (dead soft) sheet. The sheets were rolled into a tube, butt welded and hydroformed to contain three outside convolutions. During fabrication of the bellows, the weld was work hardened (1/8 to 1/4 full hard). During testing the axial displacement of bellows from the rest position was maintained such that the maximum stresses at the root of the convolutions was equal to 75% yield stress. This stress level is within the elastic region.

The mechanical stability of fluoride films was evaluated by low cycle fatigue tests, 5 cycles/sec, in the test apparatus according to the following four test procedures:

Test 1 - The metal bellows is exposed to gaseous fluorine at 1 atm for 1 hr, flexed for 500 cycles, and then thermally shocked and flexed in liquid nitrogen for an additional 1500 cycles. The liquid nitrogen containing any spalled-off fluoride film is drained into the cooled particle collector. The test chamber is reheated to room temperature and the low cycle fatigue and thermal shock treatment is repeated four more times. The particle collector is warmed up after the last test cycle. After the test chamber and particle collector are evacuated, the test chamber is flushed with 500 cc of filtered Freon TF which is drained into the particle collector. The contents of the particle collector are discharged through a 0.45-micron millipore filter unit. The millipore filter unit is capped-off and the 0.45-micron filter paper is subsequently removed in a dry box. The sample is subjected to metallurgical examination and analyses.

Test 2 - Test 1 procedure is repeated with the same metal bellows specimen but without flexing. The metal bellows and filter paper samples are subjected to metallurgical examination and analysis.

Test 3 - A new metal bellows is passivated and tested for 2000 cycles in gaseous fluorine at 2 atm. The fluorine is flushed out with gaseous nitrogen and particulate matter is flushed into the particle collector with Freon TF. The filter paper and metal bellows are subjected to metallurgical examination and analysis.

VII, A, Elastic Flexure in Gaseous and Liquid Fluorine (cont.)

Test 4 - A new metal bellows specimen is cooled to -320°F and liquid fluorine is condensed into the test chamber. The immersed bellows is flexed for 2000 cycles and the fluorine is subsequently drained into the particle collector. The test apparatus is purged free of fluorine with gaseous nitrogen and particulate is flushed into the particle collector with Freon TF. The filter paper sample and metal bellows are subjected to metallurgical examination and analysis.

A test of a 316 stainless steel bellows which involved repeated flexing in gaseous fluorine and liquid nitrogen according to the Test 1 procedure resulted in the recovery of a "structureless" material and test system contaminants. The "structureless" material was found to consist mainly of iron oxides but iron fluorides and their hydrates were identified. The same bellows was subjected to repeated gaseous fluorine and liquid nitrogen exposure without flexing according to the Test 2 procedure. This test yielded more system contaminants with adherent particulate material. The adherent material was primarily Fe_2O_3 and NiO with minor amounts of iron and nickel fluorides and iron fluoride hydrates. Examination of the bellows at approximately 30X and 100X magnification revealed only minor areas of attack on the bellows edges which were under maximum tension, and localized mechanical damage from handling.

Three different copper bellows were tested according to Test 1, Test 3, and Test 4 procedures, respectively. Analyses of recovered filter residues indicated the presence of copper, CuO, $Cu(OH)_2$, and a trace of CuF_2. Microscopic inspection failed to reveal any significant attack.

The combined data indicate that the fluoride films are stable to flexing in the elastic region of the metals in both gaseous and liquid fluorine and to cryoshock. The maximum depletion the fluoride film from the metal surface was estimated to be 0.007%.

B. PLASTIC FLEXURE IN GASEOUS AND LIQUID FLUORINE

Douglas Aircraft Company (Reference 8) conducted tests to evaluate the effects of the possible loss of the fluoride film on the surface of materials undergoing flexure/vibration in fluorine environments. The general concern was the reduction in cycle life of feed system components caused by breakdown of the passivation film.

The convoluted bellows constitute the most common form of flexible joint for state-of-the-art fluorine feed systems and was selected for testing. The test plan was designed to evaluate three potential bellows materials (Al 6061-T6, Inconel 625, and Armco 21-6-9) in gaseous and liquid fluorine and in ambient air and liquid nitrogen as control media and to test each material at three stress levels. A wide range of stress levels is used in

VII, B, Plastic Flexure in Gaseous and Liquid Fluorine (cont.)

designing conventional convoluted bellows. Commercial grade bellows are normally designed for a cycle life of 10^5 to 10^6 cycles, which result in fiber stresses that are in the elastic range for the material. Aerospace bellows, which are flight-weight feed systems, are normally designed for a cycle life of 10^3 to 10^4 cycles and, therefore, the fiber stress may be in either the elastic or in the plastic range of the material. Stress loadings that loaded the test specimens into the plastic range were selected for these tests. This decision was based on the three following factors: (1) aerospace bellows may be loaded in the plastic range, (2) adverse effects from exposure to fluorine would normally be more pronounced when the specimen is stressed in the plastic range, and (3) test time would be minimized.

The apparatus used for bellows testing consisted primarily of a specimen actuation shaft, which was actuated by an eccentric cam driven by a variable-speed electric motor. The complete drive mechanism was mounted on an unjacketed lid assembly. The original testing concept involving the use of the bellows specimens as the return mechanism for the eccentric drive became invalid when specimen loadings into the plastic range were selected for evaluation. Auxiliary return springs were added to the drive assembly to ensure proper return motion. With the addition of the return springs it was not possible to determine failure of a single test specimen by the loss of proper cam follower return action. Therefore, it became necessary to incorporate a different test technique to determine the first specimen failure. This alternate method consisted of operating the test assembly for a fixed number of cycles and then stopping the device, while the specimens were examined. This method resulted in test data points that had some scatter because the exact cycle of failure was not detectable.

Testing was conducted in four media: (1) ordinary air at ambient temperature and pressure; (2) liquid nitrogen at atmospheric pressure and its normal boiling point (-320°F); (3) gaseous fluorine at ambient temperature and 0.5 psig pressure; and (4) liquid fluorine at -320°F, pressurized with helium to 0.5 psig. The data show a consistent reduction in cycle life during the fluorine tests of approximately 30% as compared to the control runs. This percentage holds true for both ambient and cryogenic testing. The exact cause of the cycle life reductions was not determined.

The results of the flexure tests on 6061-T6 aluminum, Armco 21-6-9, and Inconel 625 bellows specimens in each of the test environments (ambient air, gaseous fluorine, liquid nitrogen, and liquid fluorine) are summarized in Table XX. These data, after appropriate analyses and reduction, have been correlated to yield fatigue strength-endurance cycle curves for each material in each environment. These correlations are presented in Figures 9, 10, and 11 for 6061-T6 aluminum, Armco 21-6-9, and Inconel 625, respectively.

TABLE XX

FATIGUE LIFE OF FLEXED METAL BELLOWS IN GASEOUS AND LIQUID FLUORINE

Bellow Material	Nominal Root Stress Level, psi x 10^{-3}	Ambient Air		Gaseous Fluorine		Liquid Nitrogen		Liquid Fluorine	
		Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}	Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}	Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}	Failure Frequency, Failures/Total	Fatigue Life, cycles x 10^{-3}
6061-T6 Aluminum	60.0	0/6	4*	1/2	2.5-3.0	4/4	35-40	2/2	<25
	90.0	1/4	1.0-2.5	1/2	1.0-1.5	--	--	2/2	<15
Armco 21-6-9	99.0	2/2	40-60	2/2	<20	--	--	--	--
	125.0	2/2	>10	--	--	1/1	>100	--	--
	175.0	2/2	10-20	2/2	12-17	2/2	<48	1/2	<21
								1/2	>48
	200.0	--	--	--	--	1/2	50-60	--	--
	268.0	--	--	1/2	2.0-4.0	2/2	20-30	2/2	25-30
Inconel 625	[illegible]	1/2	6-20	--	--	--	--	--	--
		1/2	>80						
	147.0	1/1	>10	--	--	1/4	45-50	--	--
						3/4	>100		
	200.0	1/2	10-20	1/2	12-15	2/2	<48	1/2	<21
								1/2	>48
	290.0	--	--	--	--	1/2	15-20	--	--
						1/2	20-30		
	2[illegible].0	2/4	<10	--	--	--	--	--	--
	3[illegible].0	--	--	2/4	2-4	2/2	7-10	2/2	8-12

* Mean value

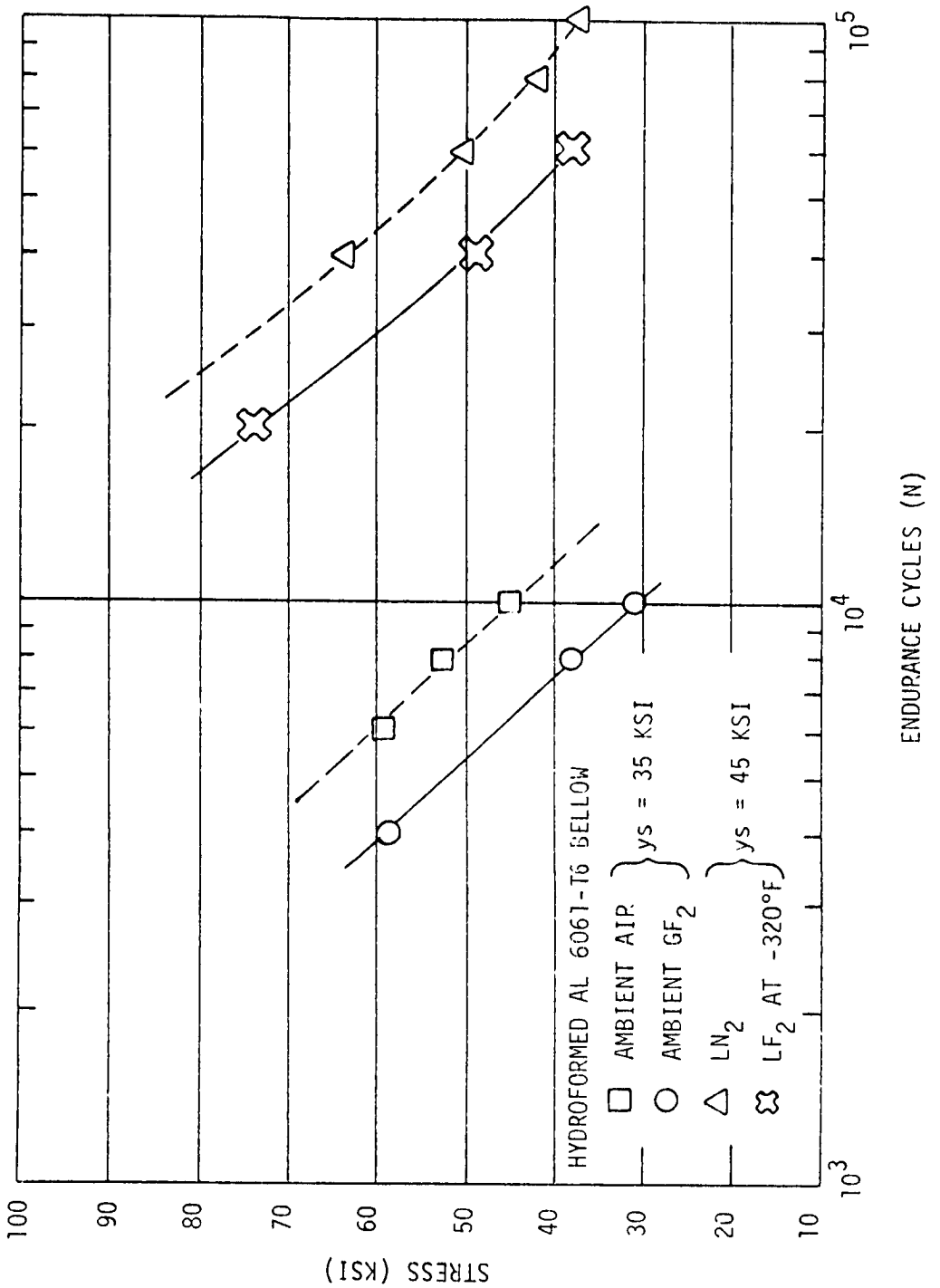

Figure 9. Fatigue Strength of Hydroformed 6061-T6 Aluminum Bellows in Fluorine Environments

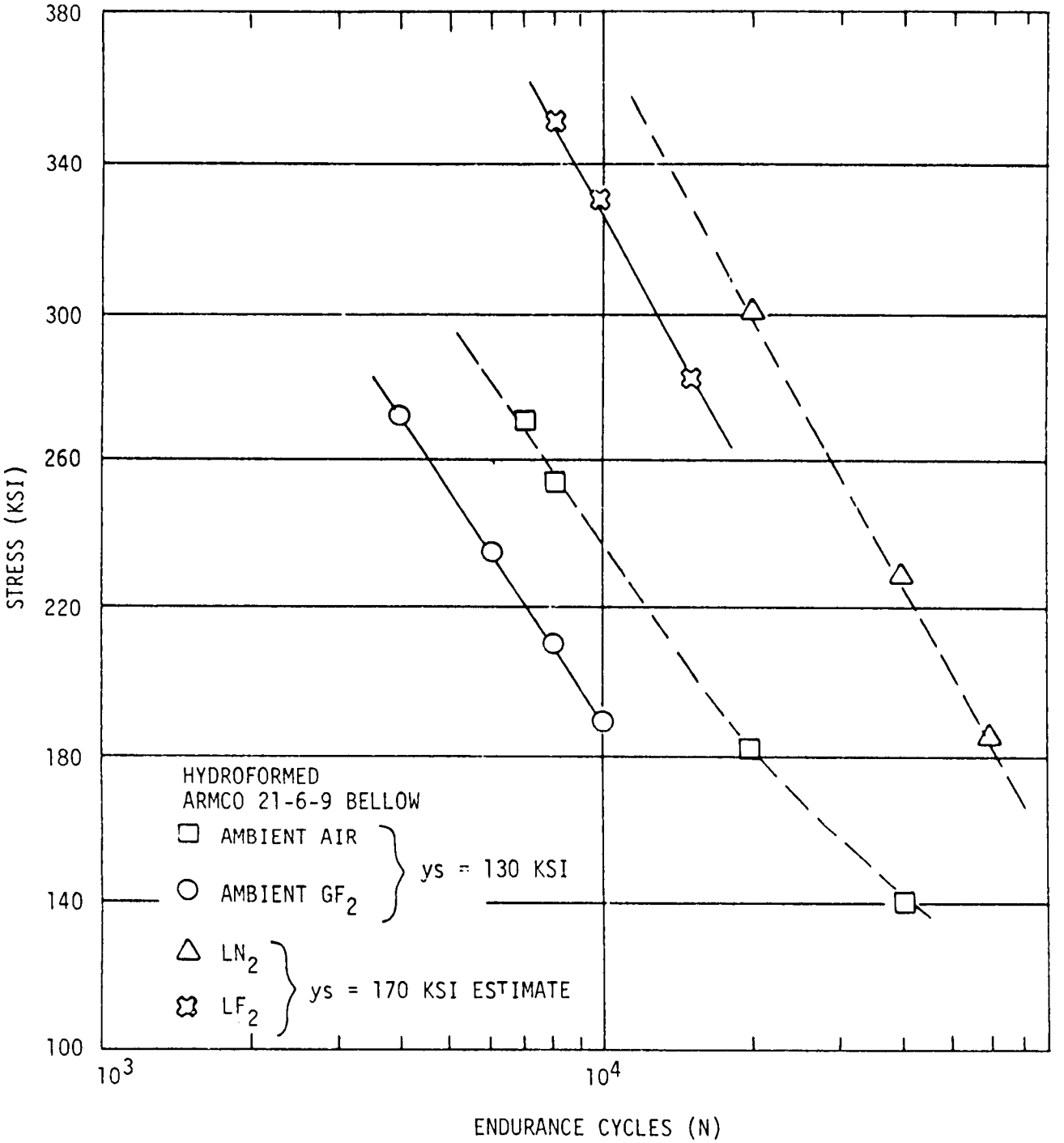

Figure 10. Fatigue Strength of Hydroformed Armco 21-6-9 Bellows in Fluorine Environments

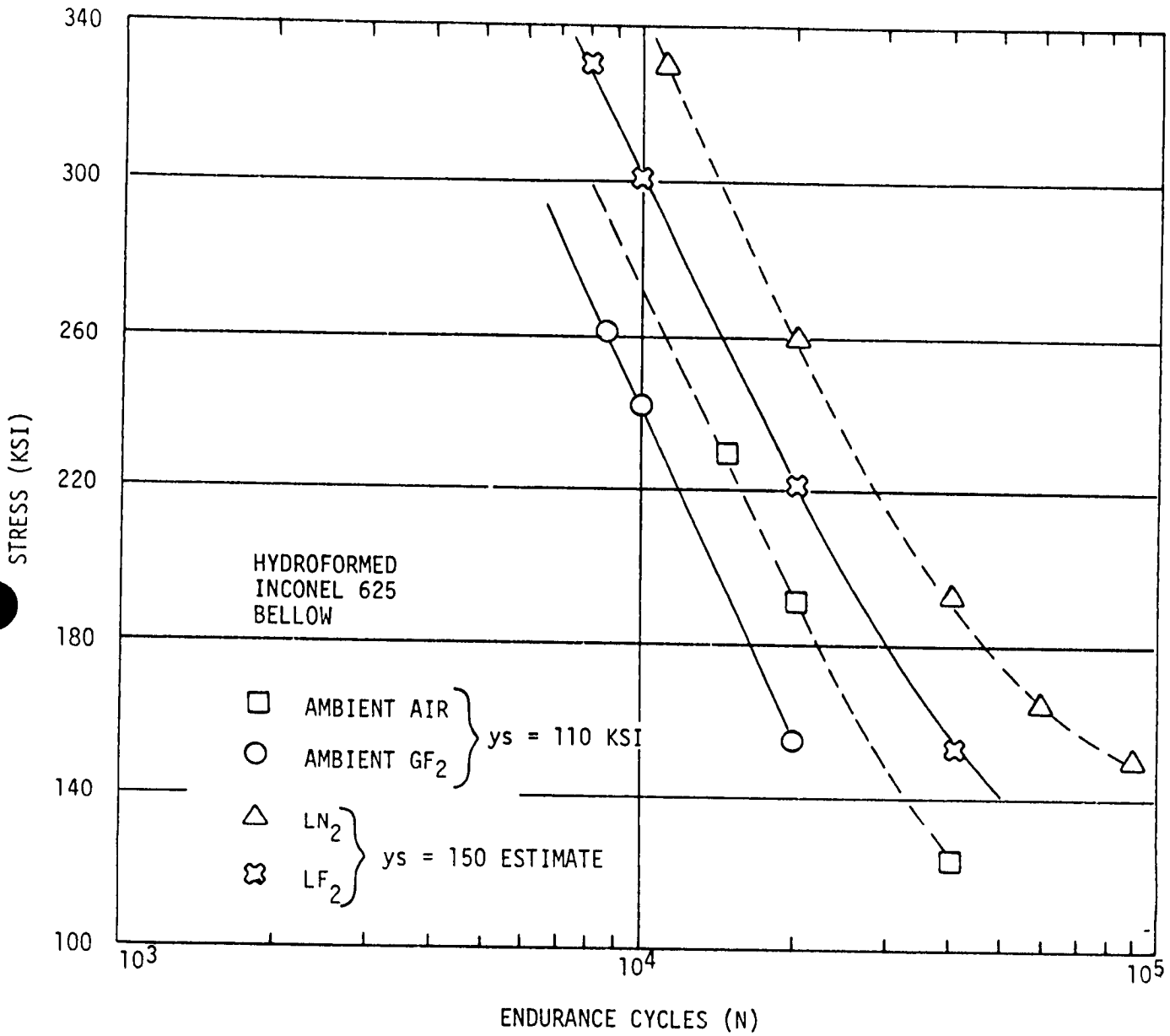

Figure 11. Fatigue Strength of Hydroformed Inconel 625 Bellows in Fluorine Environments

SECTION VIII

EFFECT OF MECHANICAL IMPACT ON METALS IN THE PRESENCE OF FLUORINE

Apparently, Sterner and Singleton (Reference 11) were the first to investigate the effect of mechanical impact on metals in the presence of fluorine. The metals they studied are listed below:

304 Stainless Steel	Brass
316 Stainless Steel	Copper
321 Stainless Steel	Monel
347 Stainless Steel	Nickel

The metal specimens were in the form of tubes cut to 2-in. lengths. Brass plugs were made up to fit the bore of each tube and they were silver soldered into the ends of the tube. A 1/4-in. copper tube was silver soldered into a hole drilled into the side of the tube. Tubes were cleaned after this with dilute hydrochloric acid, neutralized, rinsed and thoroughly dried. The tube was supported in a test cabinet in a horizontal position by a suitable mounting and a sharp conical stainless striker was positioned on the upper surface of the tube. The tube was evacuated, immersed in liquid nitrogen, and completely filled with liquid fluorine. Impact was provided by dropping either a 4- or a 6-lb weight onto the striker. Impact energies of approximately 1 to 10 ft-lb were used, depending on the thickness of the tube wall. In most cases, the impact was just below that necessary to rupture the tube wall, while in a few cases the wall was actually ruptured.

These tube impact tests were intended to test the hypothesis that a fluoride film protects the metal surface at low temperatures. It was reasoned that a severe blow on the tube wall would stretch the metal sufficiently to break the film and expose bare metal to the liquid fluorine. In many cases, the impact was severe enough to produce cracks on the inside wall of the tube and in 5 cases out of 20, the tube was ruptured. No ignition or increased corrosion was apparent or detected upon examining the impacted area microscopically with any of these metals.

At about this same time period it became known that titanium may ignite in liquid oxygen under the stimulus of a suitable mechanical impact (Reference 13). On the basis of that evidence, it was suspected that titanium and possibly some of the other metals would be sensitive to impact with liquid fluorine. Sterner and Singleton (References 10 and 11), therefore, performed tests to establish the energy level required to ignite titanium in liquid fluorine. In general, the tests were accomplished by dropping weights of various sizes from various heights or by releasing a compressed spring to obtain suitable impact energies. These energies ranged from 2.6 to 65 ft-lb. The samples and strikers were examined microscopically for evidence of ignition and the results were reported in a qualitative manner. The samples were polished 1/2-or 5/8-in. squares of metal and 0.050-in. thick. The sample and all of the components of the impact cell were scrupulously cleaned and dried before being placed into

VIII, Effect of Mechanical Impact on Metals in the Presence of Fluorine (cont.)

the cell. Several striker materials and a variety of striker faces were used in the tests. The preliminary work was performed using Monel strikers with titanium samples. Later work used titanium strikers with titanium samples. A few tests were conducted with aluminum and stainless steel strikers on aluminum samples. The types of strikers which were used are as follows:

Flat smooth	-	polished circular striking face, 1/8 to 3/8-in. diameter;
Flat rough	-	3/8-in. dia. circular striking face scarred with file marks;
Flat grooved	-	1/4-in. dia. circular striking face grooved similarly to phonograph record;
Chisel pointed	-	striking face was 1/4-in. knife edge;
Conical pointed	-	sharply pointed with 60° included angle;
Hollow pointed	-	small flat tip with 1/6-in. hole drilled into it;
Round	-	hemispherical striking face, 1/8 in. radius.

The results of these impact tests are summarized in Table XXI. The impact levels listed were calculated from the weight and distance dropped for the dropweight tests, and in the case of the spring-driven plunger, the energy level was calibrated by cocking the spring against a calibrated spring-scale. Ignition, when it was observed, was indicated by the formation of small craters and gullies together with droplets of melted metal on the sample or on the striker face. Usually the crater or gully formation on the sample was mirrored almost exactly on the face of the striker. The direction of ignition was generally away from the center of impact.

The preliminary tests with Monel metal strikers and titanium samples provided the surprising result that the striker tip reacted with the fluorine even at very low impact levels, but the sample did not. This indicated that the configuration of the striker face played as large a part in inducing ignition as did the impact energy level. This impression was strengthened in later tests as higher impact levels were used.

Various strikers were used in the hope of obtaining reasonably reproducible ignitions. The flat, smooth strikers were intended to provide a standard for comparison. The conical and chisel point strikers were intended to deliver all of the impact energy at one spot. The hollow, pointed and flat,

TABLE XXI

EARLY IMPACT TEST RESULTS ON ALUMINUM AND TITANIUM ALLOYS IN LIQUID FLUORINE AT -320°F

Striker Material	Striker Configuration	Impact Energy, ft-lb	Calc. Max. Energy Flux, ft-lb/in.^{2}-sec	Number of Tests: Positive Reaction	Number of Tests: No Reaction
	Titanium Samples (A 110 AT and C 120 AT)				
Monel	Flat, smooth	2.6	--	0	5
	Flat, rough	2.6	--	1	1
	Hemispherical	2.6	--	1	1
	Chisel-pointed	2.6	--	2	0
	Conical, pointed	2.6	--	3	0
				7	7
Titanium	Flat, smooth	40	--	2	0
		45	1.61×10^7	3	13
		52	1.86×10^7	5	11
		55	--	2	0
		58	--	1	3
		60	2.15×10^7	10	6
	Flat, grooved	5	--	2	0
		15	--	2	0
		30	--	2	0
		55	--	1	1
		58	--	2	0
		60	--	10	2
	Conical, pointed	2.6	--	1	2
		6	--	3	0
		9	--	2	0
		35	--	1	0
		50	--	2	0
		55	--	2	0
		58	--	1	1
		60	--	8	6
		61	--	0	1
	Hollow, pointed	6	--	1	3
		10	--	2	2
		38	--	1	0
	Aluminum Samples (Al 6061)				
Stainless Steel	Flat, grooved	58	--	1	11
	Conical, pointed	58	--	0	2
Aluminum	Conical, pointed	30	--	0	10

VIII, Effect of Mechanical Impact on Metals in the Presence of Fluorine (cont.)

grooved strikers were intended to trap some of the liquid and vaporized fluorine under the striker to provide high temperature by adiabatic compression. One problem with the conical pointed strikers at the higher energy levels was the welding of the tip to the sample surface. This made it difficult to detect whether ignition had occurred.

As can be seen in Table XXI, the results were not very reproducible and in no case did ignition become general. There was no apparent difference between the two titanium alloys tested. With aluminum, one ignition was obtained out of 24 tests. With titanium, ignition was initiated by all types of strikers at different impact levels. The effectiveness of ignition by the various striker configurations in increasing order was: flat; smooth; pointed; and grooved.

The next definitive work was reported by Douglas Aircraft Company (Reference 8) in 1967, by which time a modified ABMA impact test apparatus had become a relatively standard means of determining the impact sensitivity of materials in cryogenic oxidizers (particularly liquid oxygen). They performed open cup impact tests with liquid fluorine at -320°F and aluminum-silicon casting alloy, A356, (Types IV, III, II, and I, in order of increasing quality) using a modified ABMA impact test apparatus at an impact energy of 72 ft-lb*. Many of the test samples cracked upon testing (the frequency of cracking decreasing as the quality of the alloy increased) but even with the formation of new metal surfaces from sample cracking, reactions were not initiated. Samples which had previously been dye-penetrant inspected using both organic and inorganic dye penetrants and then thoroughly cleaned and baked in a vacuum prior to impact testing showed that the penetrants lead to increased impact sensitivity and, thus, are not safe quality inspection tests of cast materials for fluorine service. A closed-cup impact test at the 72 ft-lb impact level on aluminum A 356-T6, Grade III-F, which had been immersed in liquid fluorine at -320°F for 21 days showed no sign of reaction initiation but cracked similar to specimens used in open-cup tests. These tests showed quite conclusively that aluminum has a low level of sensitivity to impact in liquid fluorine but contaminants such as dye penetrants can increase the impact sensitivity.

Toy, et al., (Reference 14) have reported the results of three series of impact tests on 2014-T6 aluminum and Ti-6Al-4V(ELI) titanium in liquid fluorine. These tests are described in the following three paragraphs and the test results are summarized in Table XXII.

* Materials that are not initiated in liquid oxygen by an impact of 70 or 72 ft-lb on a modified ABMA impact tester are generally considered sufficiently impact insensitive to be considered for liquid oxygen service.

TABLE XXII

IMPACT TEST RESULTS ON 2014-T6 ALUMINUM AND Ti-6Al-4V(ELI) TITANIUM IN LIQUID FLUORINE

Metal Specimen	Striker Material	Sample Cup Material	Liquid Fluorine Temp., °F	Impact Energy, ft-lb	Number of Tests	
					Positive Reaction	No Reaction
Al 2014-T6	17-4 PH	Al 1100	-320	70	0	20
Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	-320	≤43	0	2
				47	1	7
				47.5	0	1
				48	1	1
				48.5	1	0
				49	1	0
				50	0	1
				≥51.5	2	0
Ti-6Al-4V	Ti-6Al-4V	Al 1100	-320	47	0	1
				58.5	1*	0
				70	1	0
Ti-6Al-4V	17-4 PH	Ti-6Al-4V	-320	≤72	0	5
Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	-240±10	≥40	3	0

* Reaction on rebound only

VIII, Effect of Mechanical Impact on Metals in the Presence of Fluorine (cont.)

Modified ABMA open cup impact tests were conducted on specimens of 2014-T6 aluminum at an impact energy of 70 ft-lb in liquid fluorine (-320°F) using 17-4 PH stainless steel strikers and Al 1100 sample cups. No reactions were observed in 20 tests.

Modified ABMA open cup impact tests on Ti-6Al-4V(ELI) titanium in liquid fluorine indicated it was impact sensitive when the following test combinations were used: (1) Ti-6Al-4V(ELI) sample, striker, and cup; and (2) Ti-6Al-4V(ELI) sample and striker and Al 1100 cup. The energy for a 50% probability of initiating a reaction with test combination (1) in liquid fluorine at -320°F was calculated to be 48 ft-lb. The test combination (2) was found impact sensitive at 70 ft-lb. The test combination Ti-6Al-4V(ELI) sample and cup and 17-4 PH striker pin was not impact sensitive in liquid fluorine at 72 ft-lb.

Three drop-weight closed cup impact tests were conducted with liquid fluorine at -240 ± 10°F (485 ± 15 psig) in the following manner: 86 cc of gaseous fluorine was condensed in the test unit at -320°F; the test assembly was allowed to warm up by letting the liquid nitrogen evaporate from the cryogenic bath; temperature and pressure were recorded and the drop-weight released when the pressure reached 500 psig. In these reactive impact tests, a 10 to 30 psi pressure drop in the test bomb was observed when impact occurred. Examination of the Ti-6Al-4V(ELI), sample, striker, and cup revealed numerous reaction sites. This impact energy value was deliverately chosen to be less than the open cup E_{50} of 48 ft-lb required for a 50% probability of initiating a reaction at -320°F in liquid fluorine. Qualitatively, the reaction found at 40 ft-lb impact energy level indicates that the titanium alloy is more impact sensitive in liquid fluorine at -240°F than at -320°F. This is borne out by the numerous reaction sites observed on the sample, striker, and cup.

Endicott and Donahue (Reference 15) have performed open cup impact tests with liquid fluorine (-320°F) and gaseous fluorine (65°F, ambient pressure) and titanium alloy, Ti-5Al-2.5Sn (ELI), with a modified ABMA impact test apparatus at an impact energy of 72 ft-lb. With liquid fluorine two reactions were observed in two tests and with gaseous fluorine no reactions were observed in 20 tests.

From all of the mechanical impact tests performed on metals in a liquid fluorine environment, it is concluded that the titanium alloys are the only ones among those studied that exhibit a significant sensitivity to impact at or below the 72 ft-lb energy level on a modified ABMA impact tester. The sensitivity of titanium to impact in the presence of liquid fluorine at -240°F appears to be greater than at -320°F but the sensitivity to gaseous fluorine at ambient temperature and pressure is less than for the liquid phase at -240 or -320°F. Aluminum alloys do not appear impact sensitive in the presence of liquid fluorine at -320°F and an energy level of 70-72 ft-lb (ABMA impact tester) unless the specimens are contaminated.

SECTION IX

RESPONSE OF METALS TO FRICTION, ABRASION, AND FRACTURE IN A FLUORINE ENVIRONMENT

A. METAL/METAL FRICTION IN GASEOUS FLUORINE

Theoretical analyses reported by Endicott and Donahue (Reference 15) indicate that a coefficient of friction of 0.40 would be expected for dissimilar metals operating in air and a value of 0.10 to 0.18 with a fairly good lubricant. To evaluate the silver-stainless steel combination in a gaseous fluorine environment, tests were conducted using a frictional-energy test device. To conduct this test, a frictional-energy test disk was refinished and given a silver plate. During the refinishing, a series of ventilation slots were cut into the test specimen so that gaseous fluorine exposure of the contact surfaces could be assured. After installation of the test specimen in the apparatus, the test section was pressurized with ambient gaseous fluorine and a series of friction runs was conducted up to the capacity of the machine. The results of the tests are shown on Table XXIII. During the last two tests, the samples were loaded so that the mechanism could not complete enough travel for a realistic value of friction coefficient to be determined. Post-test inspection of the test sample showed no evidence of galling on the specimen after all five tests. The silver fluoride film was a yellow-green fine-grained coating which transferred from the silver to the 316 stainless steel in small quantities. This was judged to be an acceptable condition for dry film lubrication. The measured coefficients of friction of 0.08 to 0.20 indicate that the fluoride film provides a reasonable measure of lubrication.

TABLE XXIII

RESULTS OF FRICTION TESTS OF SILVER-316 STAINLESS STEEL IN GASEOUS FLUORINE

Test No.	Load, psi	Coefficient of Friction
1	1,000	0.20
2	1,180	0.17
3	1,980	0.08
4	4,000	--
5	6,050	--

B. METAL ABRASION IN LIQUID FLUORINE

Film disruption studies were made by Sterner and Singleton (Reference 10) in which metal surfaces were continually wire brushed while immersed in liquid fluorine. The tests were carried out in a Monel cell 1-1/4-in. ID x 4-in. deep. A wire brush 1/2-in. x 1/2-in. was made with fine

IX, B, Metal Abrasion in Liquid Fluorine (cont.)

stainless steel bristles about 1/4-in. long and attached to a 1/4-in. Monel rod which passed through a brass bushing in the top of the cell. The metal sample, about 2-in. x 3/4-in. was supported in the bottom of the cell at an angle of about 30° with the vertical. The brush was caused to move up and down on the sample by a solenoid outside the cell. The rate was 1 stroke/sec and the travel was about 1-in. The Monel rod was hinged in the middle so that the brush was free to travel along the surface of the sample, and the force exerted by the brush on the sample was constant over the whole stroke. This normal force was due largely to gravity, and was about 0.05 lb. A helium purge was maintained on this cell during operation to prevent air from diffusing into the cell through the brass bushing. Ten tests were made with copper and two with magnesium alloy AZ-31. In addition, three blank tests were made with copper and one with magnesium. These control samples were exposed to liquid fluorine in exactly the same manner as the other samples except that the brush was not attached to the rod. The results of all the tests are presented in Table XXIV.

While the weight gains on these abrasion tests are scattered from 0 to 10 mg, the average for the copper and the magnesium samples is about the same as the weight changes observed on the blanks. Because the cell was not air tight, it is quite likely that small quantities of air with its accompanying moisture were able to diffuse into the cell and cause corrosion at a slightly higher level than is commonly observed in continuous immersion tests. The abrasion was severe enough to disrupt any protective fluoride film on the metals. The fact that no increase in corrosion was observed indicates that film protection is not the controlling mechanism in the corrosion resistance of these metals to liquid fluorine.

C. METAL FRACTURE IN FLUORINE

Tensile tear tests of metals immersed in liquid fluorine were conducted by Sterner and Singleton (Reference 11) with titanium, brass, copper, Monel, and aluminum. The titanium samples were 1/4-in. diameter rods which were machined in the center to about 0.030-in. diameter. The rod was threaded on both ends with one end screwed into a socket at the bottom of the test cell. The other end was fastened to a Monel metal rod which in turn protruded through a bushing in the top of the cell. A helium purge was used to reduce atmospheric contamination. A hand-operated lever fastened to the Monel rod was used to tear the sample after fluorine had been liquefied into the cell. The other four metals were tested in the same equipment, but the samples were in the form of thin strips 3-in. x 1/4-in. x 0.005-in. The torn edges of the samples were examined microscopically at 60X.

These tests were intended to present a freshly fractured surface to the liquid fluorine environment. Thus, there could be no possibility of a fluoride film protecting the surface at the time of fracture. It was expected that resulting ignition or corrosion products would indicate the need of a film

TABLE XXIV

RESULTS OF ABRASION TESTS OF METALS IN LIQUID FLUORINE

Sample	Alloy	Initial Weight, gm	Weight Change, mg	Exposure Time, hr	Remarks
1	Copper	28.2264	0.1	1	All samples, except where otherwise designated, were brushed with a coarse stainless steel brush continuously at one stroke/second while under liquid fluorine.
3	Copper	14.3360	0.9	1	
6	Copper	20.7717	5.2	1	
8	Copper	22.3695	9.9	1	
9	Copper	20.7949	3.8	1	
10	Copper	21.8593	4.3	1	
13	Copper	21.5263	-0.3	1	
14	Copper	22.2546	4.1	1	
15	Copper	22.2243	8.4	1	
16	Copper	22.1763	5.0	1	
		Avg.	4.14 (σ = 2.42)		
21	Copper	15.3295	3.9	1	*
22	Copper	20.8356	8.0	1	*
23	Copper	20.6760	1.0	1	*
		Avg.	4.3 (σ = 2.47)		
11	Mg AZ-31	5.8931	1.5	1	
17	Mg AZ-31	9.1126	2.9	1	
		Avg.	2.2		
20	Mg AZ-31	6.1560	2.0	1	*

* These samples were tested in the abrasion apparatus without brushing.

IX. C, Metal Fracture in Fluorine (cont.)

for protection. One barely observable ignition was obtained in six tests with titanium and this would tend to support the protective film theory. However, the ignition can also be explained by a process which involves the strain-heating of the specimen to its ignition temperature. No apparent reaction occurred when thin metal strips of copper, brass, Monel or aluminum were torn in tension under liquid fluorine.

Somewhat related test results have been reported by Richards and Hanson (Reference 16) wherein specimens of ASM 6434 steel; AM 350, 301, and 304-L stainless steel; 2014-T6, 6061-T6, and 7075-T6 aluminum, and Ti-6Al-4V titanium were fractured in liquid fluorine at -320°F in the course of tensile testing. There was no evidence of ignition on any of the specimens. Specimens of AM 350 stainless steel and Ti-6Al-4V titanium were similarly fractured in a high-velocity jet of gaseous fluorine at approximately 75°F. No indications of metal reaction were observed.

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