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INFORMATION REPORT

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RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH CRYOGENIC PROPELLANTS

FOREWORD

This report presents the first revision to "Recommended Materials and Practices for Use with Cryogenic Propellants" which was originally issued as SAE AIR 839 on 1/10/65. The original document has been completely updated, and two additional fluids - fluorine and nitrogen - have been incorporated in this latest edition.

The information presented in this document is meant to provide a basis for summary evaluation of selected cryogenic propellants. An attempt has been made to furnish a coverage which is broad in scope, yet comparatively brief in content, considering the amount of material involved. The information has been compiled from sources in the unclassified literature wherever possible; in this regard, extensive use has been made of material presented in The Handling and Storage of Liquid Propellants manual prepared for the Office of the Director of Defense Research and Engineering by a work group of the Advisory Panel on Fuels and Lubricants, the Liquid Propellant Manual prepared by the Liquid Propellant Information Agency at the Johns Hopkins University, Silver Spring, Maryland, and the Manual for Handling Missile Propellants (AFMTC TR 58-7) prepared for the Air Force Missile Test Center, Patrick AFB, Florida, by Pan American World Airways, Inc.

Inclusion of a comprehensive annotated bibliography and a tabular summary of the physical properties of each propellant - providing a ready source to the original references - allows the user to perform his own evaluation of the data if he so desires. The bibliography offers a more complete coverage of subject material than anything heretofore available in the literature; annotations should increase the value of this section. Physical property values presented in this work are "interim values" taken from selected references by the Cryogenic Data Center of the National Bureau of Standards Cryogenic Engineering Laboratory. An evaluation program is under way to determine the "most-probable" or "best" values.

Prepared by SAE Committee AGE-1, Military and Space Support Equipment (Fluid Systems Subcommittee). Particular acknowledgment is given to committee member Alan F. Schmidt for the selection, compilation, and organization of the information.

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- A Compilation from the Literature with Annotated Bibliography -

1. INTRODUCTION

1.1 General - Liquid propellant fuels and oxidizers are, in general, highly reactive chemicals. Consequently, the propellants and their reaction products possess certain hazardous properties which must be fully understood by all who are required to handle them. This manual is intended as a guide to help establish rules as needed to fit actual cases. The fitting of details into this framework must be left to personnel assigned to specific operations. Accordingly, information on the properties of these materials is given so that hazards will be recognized and understood.

1.2 Personnel Training and Supervision - All operating personnel shall be taught the nature of propellants and the general principles of safe conduct in handling, storage, and use of such materials. Propellants described here can be handled safely when certain simple basic principles are known and followed faithfully. On the other hand, ignorance or carelessness can result in permanent injury or death. Each person engaged in this work should be taught procedures of self-aid and first-aid, which if applied promptly afford a substantial measure of protection against injury in the event of accident.

2. HAZARDS

The three hazards to be dealt with in operations involving cryogenic propellants are health, fire, and explosion. Spills pose serious problems in inhabited areas since the low-temperature fluids and vapors may lead to physiological hazards such as frostbite and asphyxiation, and in some cases, to fires and explosions.

2.1 Health - Considering the response of the human body to its environment, appropriate engineering design and operating procedures must be exercised to minimize spills and leaks and to insure adequate ventilation. Local exhaust ventilation is usually preferable to general ventilation because it controls contamination of air at the source. The choice between the two types of ventilation will normally be dictated by the nature of the specific operation.

Adequate water supplies must be available for instant use in an appropriate form, such as showers and eye-wash fountains. Water is the best single agent for minimizing burns by propellants.

As a general guide to the control of toxic vapors, gases, and mists, hygenic standards such as Threshold Limit Values (often referred to as MAC's or Maximum Allowable Concentrations) are useful. There are other gases, such as hydrogen, nitrogen, and helium, which though not toxic in the usual sense, can cause asphyxiation by exclusion of oxygen from the immediate environment.

2.2 Fire - Each working area must be kept free of combustible materials. Ventilation is essential for keeping vapor and dust concentrations at a safe level. Fuels and oxidizers must be kept separated; fire-fighting equipment and extinguishing agents must be suited to the type of fire which may occur with a particular fuel or oxidizer. Where flammable vapors may be present, electrical equipment must be of the approved explosion-proof type and equipment and containers grounded. Nonstatic general wearing apparel should be provided and used where necessary. Approved lightning protection systems should be installed where required.

2.3 Explosion - Principles guiding the elimination and control of fire hazards are generally applicable to explosion hazards as well. In addition, earth, sand, concrete, or metal barricades of sufficient mass should be provided in appropriate places to lessen the effects of an explosion. Shock-sensitive materials must be protected from vibration and impact.

3. SAFETY MEASURES

Properly engineered systems are paramount to safe usage of propellants. In the construction of such systems, only materials compatible with the particular propellants for which the system is designed can be used. In order to eliminate the possibility of an accident, the entire system must be cleaned properly to eliminate any foreign matter.

Successful control of hazards requires thorough training of personnel in the following subjects:

1. The chemical and physical characteristics of the fuels and oxidizers.
2. The hazards peculiar to each fuel and oxidizer and the proper personal protective measures required.
3. The most efficient technique required for control of fires involving a specific fuel or oxidizer.

4. TRANSFER AND STORAGE

Fire and explosion hazards have an important influence on the design of main storage units and on their location with respect to each other and to populated buildings and areas. Fuels and oxidizers must be separated by distance or barriers, and ready storage quantities should consist only of the minimum amount necessary for the operation. Storage tanks should be diked, and ventilation should take advantage of prevailing winds and natural terrain.

Ample water for fire-fighting and decontamination must be provided. Cleanliness must be observed throughout the area, and rules regarding safe practices must be rigidly enforced.

All operations with cryogenic fluids should be planned carefully, and a set of preparatory, operating, and emergency procedures should be prepared for the operating personnel; these procedures should cover special cleaning and fire-fighting instructions, required clothing, safety devices, etc.

GENERAL BIBLIOGRAPHY

A general listing by title and mode of publication is presented below, followed by technical literature abstracts of each item.

Books
- Cryogenic Engineering
- Cryogenic Technology
- Applied Cryogenic Engineering
- Cryogenics
- Ground Support Systems for Missiles and Space Vehicles
- Rocket Propellant and Pressurization Systems

Conference Proceedings
- Advances in Cryogenic Engineering - Proceedings of the National Cryogenic Engineering Conferences
- Cryogenic Safety - A Summary Report of the Cryogenic Safety Conference
- Proceedings of the Propellant Thermodynamics and Handling Conference

Compendiums, Handbooks, Monographs
- A Compendium of the Properties of Materials at Low Temperatures (Phase I, Parts I, II, III)
- A Compendium of the Properties of Materials at Low Temperatures (Phase II, Part IV)
- Cryogenic Materials Data Handbook
- Mechanical Properties of Structural Materials at Low Temperatures
- Properties of Materials at Low Temperatures
- Specific Heats and Enthalpies of Technical Solids at Low Temperatures
- Thermal Expansion of Technical Solids at Low Temperatures
- Tensile and Impact Properties of Selected Materials from 20 to 300°K
- Cryogenic Data Book
- Compatibility of Rocket Propellants with Materials of Construction
- Metals and Alloys for Cryogenic Application - A Review
- Low Temperature and Cryogenic Steels

Manuals
- The Handling and Storage of Liquid Propellants
- Liquid Propellant Manual
- Manual for Handling Missile Propellants
- Liquid Propellants Safety Handbook
- Handling Hazardous Materials

Miscellaneous Papers
- Explosion and Fire Hazards associated with the Use of Low-Temperature Industrial Fluids
- Cryogenic Piping System Design Considerations
- Design of Cryogenic Storage Tanks for Industrial Applications
- Safe Handling of Cryogenic Fluids
- Air-Condensing Cryogenic Fluids
- Air-Solidifying Cryogenic Fluids
- Introduction to Cryogenic Engineering
- Cryogenic Safety

- Introduction to Cryogenics
- The Storage and Handling of Cryogenic Liquids

Miscellaneous Reports

- Sparking Characteristics and Safety Hazards of Metallic Materials
- Properties of Selected Rocket Propellants
- Effects of Low Temperature on Structural Materials
- Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids
- Review of Fire and Explosion Hazards of Flight Vehicle Combustibles
- Properties of Plastics and Related Materials at Cryogenic Temperatures

Miscellaneous Books

- Combustion, Flames and Explosions of Gases

Bibliographies

- Rocket Propellants, ASTIA (AD 233 500)
- Rocket Propellants, ASTIA (AD 315 500)
- Rocket Propellants, ASTIA (AD 263 000)
- Rocket Propellants, ASTIA (AD 325 000)
- Cryogenics and Low Temperature Research, ASTIA (AD 271 000)

Journals

- Cryogenics - An International Journal of Low Temperature Engineering and Research
- Cryogenic Engineering News
- Cryogenic Information Report
- Cryogenic Technology - Journal of the Cryogenic Society of America

CRYOGENIC ENGINEERING - Scott, R. B. - D. Van Nostrand Company, Inc., Princeton, New Jersey (1959) 368 pp.

Throughout the preparation of this book an objective always considered was to present the necessary information in such a manner that an investigator with a new idea involving cryogenic techniques can assess the feasibility of his project and gain some idea about the difficulties that he should expect. Because this book is intended primarily for the reader who is unfamiliar with low temperatures, the treatment is deliberately elementary, but it is not trivial. It is believed that considerations of practical importance can be presented in language that is easily understood. There is little or no attempt to deal with either the esoteric concepts of modern cryogenic physics or the refinements that engineering practice has established in some disciplines used by cryogenists such as heat exchange, distillation, or adsorption. References to authoritative information on such subjects are given. The emphasis here is upon both basic and applied information most important in engineering research and development at low temperatures.

Since this treatise emphasizes the practical aspects of low-temperature technology, it is hoped that the information will be most useful to the design engineer who has the responsibility of making "practical" equipment work.

CRYOGENIC TECHNOLOGY - Vance, R. W. - John Wiley & Sons, Inc., New York (1963) 585 pp.

The goal of this treatise is to provide a source or reference for those engaged either in applications of, or basic, theoretical studies. The text material contains an analysis of thermodynamic principles and cycles describing in detail how low temperatures are achieved, followed by discussions of the properties of liquids and solids, applications of phase equilibria relationships to industrial processes, heat transfer, thermometry, insulation techniques, and the fundamental theories involved in superconductivity. To augment this theoretical background are discussions of some of the principle applications of cryogenic engineering such as the cryotron and other superconductive devices, the solid-state maser, space simulation and cryopumping, nuclear propulsion, the safety aspects and explosive potentials of cryogenic propellants, and deep-space probes, including the cryogenic storage problems in extraterrestrial environments. An analysis of cryobiology technology provides an unusual climax.

APPLIED CRYOGENIC ENGINEERING - Vance, R. W. and Duke, W. M. - John Wiley & Sons, Inc., New York (1962) 510 pp.

This compilation of lectures is designed to enhance the knowledge of scientists and engineers engaged in research and development as well as operating personnel, in the field of cryogenics. It is particularly applicable to missile and space vehicle systems, but the basic theory explained is appropriate to all fields of endeavor requiring technical skills in the application of low temperatures to industrial processes.

The book has been divided into two parts: Part I - Basic Theory; Part II - Applications of Cryogenic Engineering.

Part I discusses basic theory, beginning with the properties of cryogenic fluids and covering mechanical properties of materials in cryogenic environments, low temperature thermometry, fluid flow and heat transfer, insulation techniques and some non-missile applications of cryogenic equipment. It consists of eight chapters in which the theories applicable to the use of cryogenic materials in ballistic missiles and space vehicles are condensed into engineering form augmented by organized experimental data.

Part II describes many of the applications of cryogenic theories to space vehicles and systems. Also, predictions have been made as to what the future propulsion systems might be for space vehicles.

CRYOGENICS - McClintock, M. - Reinhold Publishing Corp., New York (1964) 270 pp.

The purpose of this book is to give to the engineer or scientist with another specialty, or to the educated non-scientist, a qualitative understanding of the basic aspects and some of the representative applications of cryogenics.

GROUND SUPPORT SYSTEMS FOR MISSILES AND SPACE VEHICLES - Brown, K. and Weiser, P. - McGraw-Hill Company, Inc., New York (1961) 490 pp.

The aim of this book is to present a complete picture of the systems required to support either a missile or a space vehicle. Liquid propellant handling considerations are covered in Part IV (book is divided into five parts) and include a detailed discussion on cryogenics, hazards and safety, and the design and development of fast-fill propellant loading systems.

ROCKET PROPELLANT AND PRESSURIZATION SYSTEMS - Ring, Elliot (Editor) - Prentice-Hall, Inc., Englewood Cliffs, N. J. (1964) 310 pp.

Presented here are those subjects which make up the entire propulsion field, engine, propellant, feed systems, and pressurization systems, and the specific problems in each. Included are sections on cryogenic loading problems, geysering, stratification, special zero gravity fluid problems, propellant hardware, instrumentation, etc. The book is designed to deal in depth with such problems.

ADVANCES IN CRYOGENIC ENGINEERING - Timmerhaus, K. D. (Editor) - Advances in Cryogenic Engineering Vols. 1-11, Plenum Press, New York (1960-66)

A series of volumes dealing with low temperature phenomena and their applications; each volume constitutes the Proceedings of one Cryogenic Engineering Conference, beginning with Volume I - Proceedings of the First National Cryogenic Engineering Conference held at the National Bureau of Standards, Boulder, Colorado (September 1954) and covering all subsequent conferences to date.

CRYOGENIC SAFETY - A SUMMARY REPORT OF THE CRYOGENIC SAFETY CONFERENCE - Air Products, Inc., Allentown, Pa., (July 1959) 145 pp 77 fig 12 tab 61 ref.

This report covers material presented in five sessions and eleven seminars at the 1959 Cryogenic Safety Conference. The session topics included (1) Hazards of Cryogenic Systems, (2) Technical Character of Cryogenic Hazards, (3) Design and Construction for Safety, (4) Operations for Safety, and (5) Liquid Hydrogen Safety.

PROCEEDINGS OF THE PROPELLANT THERMODYNAMICS AND HANDLING CONFERENCE - Bollinger, L. E. and Lemmons, A. W. (Editors) Proc. of Propellant Thermodynamics and Handling Conference, Ohio State Univ. (July 20-21, 1959) O. S. U. Eng. Experiment Station Rept. No. 12.

The "Propellant Thermodynamics and Handling Conference" was one of the first "specialist" conferences held by the American Rocket Society. Coverage of two technical areas was planned originally for the conference: propellant thermodynamics and propellant handling. The propellant handling area had papers covering such aspects as materials problems, handling techniques, safety, and toxicity of high-energy and cryogenic liquid propellants and their combustion products. Included in this collection are the following titles:

The Large Scale Production, Handling, and Storage of Liquid Hydrogen.
Safety Aspects in the Handling and Storage of Liquid Hydrogen.
Experience with Handling Liquid Hydrogen in Engine Testing.
Transportation, Transfer and Storage of Liquid Fluorine.
Materials of Construction for Handling Fluorine.
Some Problems in Using Fluorine in Rocket Systems.
Safety and Handling of Ozone-Oxygen Mixtures.

A COMPENDIUM OF THE PROPERTIES OF MATERIALS AT LOW TEMPERATURES - PHASE I: Part I. Properties of Fluids (July 1960); Part II. Properties of Solids (Oct. 1960); Part III. Bibliography of References (Oct. 1960). Johnson, V. J. (General Ed.) Natl. Bur. Standards Cryogenic Eng. Lab., WADD Tech. Rept. 60-56, Contr. No. AF 33(616)58-4.

Phase I of the Compendium is divided into three parts: Part I, ten properties of ten fluids; Part II, three properties of solids; Part III, an extensive bibliography of references. Density, expansivity, thermal conductivity, specific heat and enthalpy, transition heats, phase equilibria, dielectric constants, adsorption, surface tension and viscosity for the solid, liquid and gas phases of helium, hydrogen, neon, nitrogen, oxygen, air, carbon monoxide, fluorine, argon and methane are given wherever adequate data could be collected. Thermal expansion, thermal conductivity and specific heat and enthalpy are given for a number of solids of interest in cryogenic engineering. Data sheets, primarily in graphic form, are presented from "best values" of data collected. The source of the material used, other references and tables of selected values with appropriate comments are furnished with each data sheet to document the data presented. Conversion tables and other helpful information are also included.

A COMPENDIUM OF THE PROPERTIES OF MATERIALS AT LOW TEMPERATURE - PHASE II, Part IV. Stewart, R. B. and Johnson, V. J. (General Ed.) Natl. Bur. Standards Cryogenic Eng. Lab. WADD Tech. Rept. 60-56 (1961) Contr. No. AF 33(616)59-6, 501 pp.

Phase II of the Compendium includes data sheets on compressibility factor, velocity of sound and entropy of fluids, vapor-liquid equilibrium concentration of binary mixtures of fluids, and electrical resistivity and thermal conductivity integrals of metallic solids. Data sheets are included for each of these properties for the following materials: Compressibility Factor (Helium, Hydrogen, Neon, Nitrogen, Air, Methane); Entropy (a T-S diagram for Neon); Velocity of Sound (in liquids: Helium, Hydrogen, Nitrogen, Oxygen, Argon, Methane; in gases: Helium, Hydrogen, Neon, Nitrogen, Oxygen, Air, Carbon Monoxide, Methane; Nitrogen in Oxygen, Carbon Monoxide, Argon, Methane); Electrical Resistivity (53 of the pure metallic elements); and Thermal Conductivity Integrals (44 pure metallic substances, 36 non-ferrous alloys, 9 ferrous alloys and 4 glasses and plastics). In general the data sheets present the data primarily in graphical form, and in addition include tables of selected values, references to the sources of the data and other references. Appropriate comments of interest to the user are also given.

CRYOGENIC MATERIALS DATA HANDBOOK - Durham, T. F., McClintock, R. M. and Reed, R. P. - Natl. Bur. Standards Cryogenic Eng. Lab., Contr. No. AF 04(647)-59-3, 556 pp 1107 ref.

This handbook of data on solid materials at low temperatures contains certain mechanical and physical properties of selected metals and non-metals over the temperature range minus 454°F to plus 500°F. The materials are mostly ones in current use for missile applications at cryogenic temperatures, but a few have been included because of their potential for such uses. The properties are those which are most generally useful to the designer. The compilation is believed to include all reliable data which have appeared in the literature from 1940 thru 1959 and recent data from test laboratories. In some cases the data reported have not yet been published. Information from a few papers published prior to 1940 has also been included.

MECHANICAL PROPERTIES OF STRUCTURAL MATERIALS AT LOW TEMPERATURES; A COMPILATION FROM THE LITERATURE - McClintock, R. M. and Gibbons, H. P. Natl. Bur. Standards Monograph 13 (June 1960) 180 pp 104 ref.

The tensile strength, yield strength, tensile elongation, and impact energy of about two hundred materials, metallic and non-metallic, are given graphically as functions of temperature between 4° and 300° Kelvin.

PROPERTIES OF MATERIALS AT LOW TEMPERATURES - Corruccini, R. J. - Chem. Eng. Progress 53, 262-67, 342-46, 397-402 (A three-part article) (1957).

This review summarizes the knowledge acquired from work at the (NBS) Boulder Laboratory on low-temperature data, organized and interpreted in the light of theory, and shows how useful estimation procedures may sometimes be derived from theory to fill gaps in the available data.

SPECIFIC HEATS AND ENTHALPIES OF TECHNICAL SOLIDS AT LOW TEMPERATURES; A COMPILATION FROM THE LITERATURE - Corruccini, R. J. and Gniewek, J. J. - Natl. Bur. Standards Monograph 21 (Oct. 1960) 20 pp 4 tab 165 ref.

Tables are given of the specific heat, cp, and the enthalpy of 28 metals, 3 alloys, 8 other inorganic substances, and 8 organic substances in the temperature range, 1° to 300°K.

THERMAL EXPANSION OF TECHNICAL SOLIDS AT LOW TEMPERATURES; A COMPILATION FROM THE LITERATURE - Corruccini, R. J. and Gniewek, J. J. - Natl. Bur. Standards Monograph No. 29 (May 1961) 22 pp 4 tab 246 ref.

Tables are given of the linear contraction relative to 293°K, $(L_{293} - L_T)/L_{293}$, and the linear expansion coefficient, $dL/L_{293}dT$, of thirty elements, forty-five alloys, twenty-two other inorganic substances and twenty plastics and elastomers in the temperature range, 0 to 300°K.

TENSILE AND IMPACT PROPERTIES OF SELECTED MATERIALS FROM 20 TO 300°K - Warren, K. A. and Reed, R. P. - Natl. Bur. Standards Monograph 63 (June 1963) - 51 pp 30 fig 7 tab 3 ref.

The tensile and impact properties of structural materials were experimentally determined at temperatures from 20 to 300°K. Tensile properties of a few materials were also determined at 4°K. The materials included forty-two commercial alloys of iron, aluminum, titanium, copper, nickel, and cobalt, and two metal-bonded carbides. The properties experimentally determined were the yield strength, tensile strength, elongation, and reduction of area, the stress versus strain curve, and the impact energy. The test equipment and procedures are described. The individual data are presented in tables, and the average results are displayed in graphs.

CRYOGENIC DATA BOOK (CGS UNITS) - Chelton, D. B. and Mann, D. B. (NBS-CEL, Boulder, Colo.) Calif. Univ., Radiation Lab., Berkeley, Rept. No. UCRL-3421) (May 1956) 116 pp.

Increased activities in Cryogenic Engineering have brought about the need for a compilation of available data. The purpose of the Cryogenic Data Book is to provide a condensed source of reliable data and reference information for those working in the cryogenic field. Specifically the data were compiled with a view toward the design of liquid hydrogen bubble chambers.

The compilation does not constitute a critical survey of the literature.

COMPATIBILITY OF ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION - Boyd, W. K. and White, E. L. - Battelle Mem. Inst., Defense Metals Inform. Center, Columbus, Ohio, DMIC Memo No. 65 (Sept. 1960) 65 pp. DDC AD 243 625.

This report summarizes the available information on the compatibility of liquid rocket propellants with prominent materials of construction. Fuels and oxidizers of current interest are discussed. The corrosion data which are presented will apply to storing, handling and control equipment outside of missiles and to missile components up to the combustion chamber. The compatibility of materials with reaction products in combustion chambers, nozzles, etc., has not been considered. The report has been subdivided into sections according to the propellant. Each material of construction is rated for a given medium as belonging to one of four classes, based primarily upon corrosion resistance. Consideration also is given to such factors as catalytic decomposition and sensitivity to impact.

METALS AND ALLOYS FOR CRYOGENIC APPLICATION - A REVIEW - Kendall, E. G. - Aerospace Corp., El Segundo, Calif., SSD-63-371 Rept. No. TDR-269 (4240-10)-6 (Jan. 1964) Contr. No. AF 04(695)-269, 61 pp 19 fig 11 tab 64 ref.

An up-to-date review of metals and alloys suitable for cryogenic aerospace structural applications has been made. The mechanical properties of austenitic stainless steels, other steels, aluminum alloys, titanium alloys, nickel alloys and cobalt alloys from +78 to -423°F are presented, including tensile and yield strengths, elongation and notch/tensile ratios. Mechanical properties of weldments are also presented. The question of notch toughness and the notch acuity factor, K_t, is discussed with respect to low temperature tensile testing. Compatibility with the liquid gases is discussed and alloys most suitable for containing liquid oxygen and hydrogen in aerospace vehicles are recommended.

LOW TEMPERATURE AND CRYOGENIC STEELS MATERIALS MANUAL - United States Steel, Pittsburgh, Pa. - 191 pp 81 fig 30 tab 218 ref.

This manual is designed to provide knowledge of steels produced for use in low-temperature and cryogenic service. It embodies a synopsis of material properties and fabrication techniques, as well as an economic evaluation of containers and other criteria required when designing cryogenic process equipment.

THE HANDLING AND STORAGE OF LIQUID PROPELLANTS - Chemical Propulsion Information Agency, Defense Research and Engineering, Wash., D. C. (Jan. 1963) 338 pp.

This manual is published as a source of information; it is intended for use as a basis for the preparation of regulations governing the handling and storage of liquid propellants.

Included in the contents are four chapters on cryogenic propellants (fluorine, oxygen, nitrogen, hydrogen), fifteen chapters on non-cryogenic propellants, and appendices covering fire fighting techniques, fire protection and extinguishment, cleaning procedures and hazard characteristics.

LIQUID PROPELLANT MANUAL - Liquid Propellant Info. Agency, Johns Hopkins Univ., Silver Springs, Md., Manual (March 1961) Contr. No. NOrd 7386.

The liquid propellant manual is a compendium of the properties of liquid propellants, and is intended to provide a survey of the physico-chemical properties of selected propellants and promising propellant candidates in order to assess their performance or feasibility in rocket applications. Additional information and revisions will be issued at frequencies depending upon the receipt of new data. Units for specific elements, compounds, and mixtures used as liquid propellants will contain information on the physical, chemical, thermodynamic, transport, and electromagnetic properties for these materials. In addition, information on safety, handling, compatibility of materials, and logistics will be included.

MANUAL FOR HANDLING MISSILE PROPELLANTS - Pan Am. World Airways, Patrick AFB, Fla., AFMTC Rept. No. TR 58-7 (1958) DDC AD 134 277.

This manual presents in a single authority the miscellaneous information available from diverse sources. It combines such data with practical experience and offers a standard of operation as current as possible. It deals with the hazards involved in the storage, handling, and the use of propellants employed in rocketry. The procedures and cautions recommended herein should be adhered to for the safety of personnel and property. It is intended as a guide and an outline of the most important precautions to be taken in operations involving certain hazardous fuels, oxidizers, and other chemicals. This publication is not to be considered as an engineering manual or as a design handbook; neither should it restrict development of new methods and procedures. It can be called a list of "things to do" and "not to do" for maintaining a reasonable degree of safety relating to the materials discussed. These procedures, in combination with the general principles of industrial safety, intelligently utilized should result in accident-free operations.

LIQUID PROPELLANTS SAFETY HANDBOOK - NASA-Kennedy Space Center (Safety Office), Cocoa Beach, Fla. - NASA Rept. SP-4-44-S (April 1, 1965).

This handbook contains the latest information concerning liquid propellants utilized by the NASA at the Kennedy Space Center at Merritt Island Launch Area as of the date of this publication. Changes will be issued periodically to keep the handbook current and accurate.

HANDLING HAZARDOUS MATERIALS - NASA - Technology Utilization Division - NASA Rept. SP-5032 (Sept. 1965), 93 pp.

This publication deals with highly reactive materials that have been studied in the search for fuels and oxidizers for space work: Liquid hydrogen, fluorine, ozone (and several non-cryogens). It describes both the hazards that have restricted the use of these materials and the procedures by which they have been handled and stored safely. References are given to work done by NASA and other investigators.

EXPLOSION AND FIRE HAZARDS ASSOCIATED WITH THE USE OF LOW-TEMPERATURE INDUSTRIAL FLUIDS - Burgoyne, J. H. - Trans. Inst. Chem. Engrs. (London) 185, CE 7-10 (Jan. - Feb. 1965).

Hazards of low-temperature fluids are considered under the headings of pressure bursts, gas explosion, fire, and explosion of liquid mixtures (e.g., of fuel and oxygen). The literature on these subjects is reviewed and an attempt is made to distinguish areas where gaps in knowledge exist and further systematic research should be rewarding. It is concluded that gas explosion properties at low temperatures and the explosibility of low-temperature liquid mixtures merit considerable attention.

CRYOGENIC PIPING SYSTEM DESIGN CONSIDERATIONS - Jacobs, R. B. - Heating, Piping Air Conditioning 32, 130-40, 142-56 (1960) (A two-part article).

Piping systems for transporting liquefied gases are not basically different from those for the more familiar fluids. But, some differences must be considered by the designer because of the temperature range encountered - room temperature down to almost absolute zero or -459.6°F. The topics presented (in the first article) include properties of materials and insulation techniques. How low temperatures affect the fluid-mechanical design, selection of pumping equipment, heat exchanger design, piping system instrumentation, and the fabrication and installation of the piping system are presented in the second article.

DESIGN OF CRYOGENIC STORAGE TANKS FOR INDUSTRIAL APPLICATIONS - Marsh, H. W. - Am. Soc. Testing Materials, Spec. Tech. Publ. No. 302 (March 1962) pp 172-83, 4 fig 1 tab 4 ref.

This is a discussion of the facets of cryogenic storage tank design directed toward those who have only limited experience in the field. Design considerations as to cost, suitability of materials for the temperatures and pressures involved, configuration of inner vessels and jackets, support systems, and types of insulation, evacuated and nonevacuated, for both shop-built and field-erected vessels are discussed in brief. The potential requirements for cryogenic storage for industrial applications are listed. Military applications for both ground and air-borne use are excluded as these involve unusual design conditions foreign to the usual industrial installation.

SAFE HANDLING OF CRYOGENIC FLUIDS - Neary, R. M. - Chemical Section, National Safety Congress, Chicago, Ill., (Oct. 16, 1961) paper 20 pp 8 ref.

Cryogenic fluids have been handled safely by a few companies since the early part of the century. Their use, and the number of people handling them, have increased tremendously in recent years. To ensure safety, old and new users alike require a thorough understanding of the properties of these fluids and a willingness to make use of reasonable safeguards in handling them. Since handling small quantities presents some safety considerations different from handling larger volumes, these subjects will be covered in separate sections of this paper.

AIR-CONDENSING CRYOGENIC FLUIDS - Neary, R. M. - Union Carbide Corp., Linde Division - Paper presented at National Safety Congress (Oct. 31, 1963).

With the recent advances in the missile and electronics industries and of numerous research applications, such as Telstar and space chambers, liquefied hydrogen and helium are fast becoming important cryogenic fluids. Unlike the more common cryogenic fluids, namely oxygen and nitrogen, the properties of liquefied hydrogen and helium are unusual and, as a result, special equipment and handling techniques are required. This paper briefly summarizes the properties, design of equipment, and practical procedures for the safe and efficient handling of these fluids.

AIR-SOLIDIFYING CRYOGENIC FLUIDS - Neary, R. M. Union Carbide Corp., Linde Division - Paper presented at 1964 ASME Winter Annual Meeting, N. Y., N. Y.

With the recent advances in the missile and electronics industries and of numerous research applications, liquefied hydrogen and helium are fast becoming important cryogenic fluids. Unlike the more common cryogenic fluids, namely liquid oxygen and nitrogen, liquefied hydrogen and helium are capable of solidifying air. This and other properties make it necessary to handle these products with different equipment and procedures. Personal protective equipment is reviewed. The design of small, medium and large tankage is reviewed briefly. Special emphasis is placed on design and safety devices for small liquefied helium containers commonly used in laboratories because several serious accidents have resulted from solid air plugging of the vents.

INTRODUCTION TO CRYOGENIC ENGINEERING - Reiff, D. D. - ASME Paper No. 64-WA/PID-8 (Nov. 1964) 12 pp 7 fig 11 ref.

The purpose of this report is to introduce a few of the essential disciplines in cryogenic engineering. The basic principles of liquefaction of gases and low-temperature heat transfer and insulation are briefly treated. The discussion of storage, transfer, and handling of cryogenic fluids has been slanted to hydrogen; however, the basic principles of cryogenic technology are embraced. In addition, mobile ground-service equipment is discussed briefly.

CRYOGENIC SAFETY - Spencer, E. W. - J. Chem. Education 41 (Sept. 1964) 4 pp 5 fig 1 tab 14 ref.

A general discussion on the hazards, storage, and general precautions pertinent to the handling of cryogenic fluids. This article is a portion of the paper which appeared previously in the Journal of American Society of Safety Engineers.

INTRODUCTION TO CRYOGENICS - Vance, R. W. - Machine Design 36, 169-192 (Oct. 8, 1964).

The principal engineering problems associated with cryogenics, including the fundamental relations, theories, equations and concepts, have been described in detail by many authorities. This article highlights some of these considerations and points the way toward practical solutions to selected design problems.

THE STORAGE AND HANDLING OF CRYOGENIC LIQUIDS - Zenner, G. H. - Progress in Cryogenics 2, 3-39, Academic Press Inc., New York (1960) 24 fig 6 tab 51 ref.

Included in the contents of this article are sections on the properties of liquids O_2, N_2, A, CH_4, F_2, H_2, He, storage and transport containers (stationary, truck, tank car), converters, meters, pumps (rotary and reciprocating), transfer methods and piping design.

SPARKING CHARACTERISTICS AND SAFETY HAZARDS OF METALLIC MATERIALS - Bernstein, H. and Young, G. C. - NAVORD Rept. 5205, Tech. Rept. NGF-T-57 (April 1957).

This report is a survey of the sparking characteristics and safety hazards of metallic materials. The fundamentals of sparking theory and methods of spark testing are presented. The ignition hazards associated with sparks are discussed. Attention is called to an alternate and possibly more significant source of ignition - impacts. The data indicate that sparks and impacts can result from the use of "non-sparking" materials. The authors conclude that no benefit is gained by employing non-sparking hand tools in place of steel to prevent explosions.

PROPERTIES OF SELECTED ROCKET PROPELLANTS - Vol. I (1963) Vol. II (1964) - The Boeing Company, Seattle, Washington - Document D2-11677 DDC AD 444 642.

The purpose of this document is to provide information on chemical, physical and thermodynamic properties, handling and safety characteristics, methods of production, and availability and cost of selected rocket propellants. (Cryogenic propellants hydrogen, fluorine, and oxygen are included in this work.)

EFFECTS OF LOW TEMPERATURES ON STRUCTURAL MATERIALS - NASA Tech. Utiliz. Rept., NASA SP-5012 (Dec. 1964) 55 pp 45 fig 37 tab 2 ref.

There are many problems, associated with the storage and handling of cryogenic fluids, which must be considered in the design and fabrication of tankage and other components of cryogenic rocket systems. Thus, a continuing program is being conducted by the Propulsion and Vehicle Engineering Laboratory of the Marshall Space Flight Center to evaluate the applicability of various metallic materials at cryogenic temperatures.

FIRE-HAZARD PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND VOLATILE SOLIDS - National Fire Protection Association, Rept. No. 325 (May 1960).

This tabulation of available data on the properties of flammable liquids and other materials listed is sponsored by the NFPA Committee on Flammable Liquids. The table summarizes available data on the fire-hazard properties of more than 1000 substances, listed alphabetically by their chemical name. The values selected are representative figures deemed suitable for general use.

REVIEW OF FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES - Van Dolah, W., Zabetakis, M. G., Burgess, D. S. and Scott, G. S. - ASD TR 61-278 (April 1961) (See also subsequent annual supplements).

The prevention of fires and explosions involving the combustibles and oxidants likely to be found in flight vehicles requires a knowledge of the flammability and related characteristics of these materials. This is a compilation of the available characteristics data for a series of combustibles and oxidants of current interest (including fluorine, oxygen and hydrogen).

PROPERTIES OF PLASTICS AND RELATED MATERIALS AT CRYOGENIC TEMPERATURES - Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, New Jersey, PLASTEC Rept. 20 (July 1965) 253 pp 46 fig 34 tab 319 ref.

This report reviews the effects of cryogenic temperatures on plastics and such related materials as elastomers and adhesives. It presents an annotated bibliography of 319 references from open literature, government project and contract reports, and conference papers. A detailed subject index and a number of supplemental indexes are included. Topics covered are: Molded Polymeric Materials (Plastics); Cryogenic Insulation; Structural Plastic Laminates; Elastomers, Seals and Sealants; Adhesives; Plastic Films, Film Laminations and Vapor Barriers; Fibers; Electrical Applications; Wear and Friction; Liquid Oxygen (LOX) Compatibility; Radiation and Combined Effects; and Miscellaneous Applications. Test Methods are not treated in a separate section in the discussion, but the subject index refers to many references with information on test procedures and apparatus.

COMBUSTION, FLAMES AND EXPLOSIONS OF GASES - Lewis, B. and Von Elbe, G. - Academic Press, Inc., New York (1961) 2nd Ed., 731 pp.

ROCKET PROPELLANTS - Armed Services Tech. Inform. Agency, Arlington, Va., Bibliography Rept. AD 233 500 (March 1960) 56 pp.

The bibliography is a compilation of approximately 292 abstracts of unclassified reports on liquid and solid propellants which were added to the ASTIA collection from 1953 to 15 Feb. 1960. The first part of the bibliography includes separate sections dealing with general information on solid rocket propellants and on liquid rocket propellants. The second part of the bibliography includes sections for each of the following compositions used in rocket propellants: (1) acetylenes, (2) amines, (3) ammonia, (4) ammonium perchlorate, (5) boron hydrides, (6) ethylene oxide, (7) fluorine, (8) hydrazines, (9) hydrocarbons, (10) hydrogen, (11) hydrogen peroxide, (12) lithium compounds, (13) methanol, (14) nitric acid, (15) nitrogen, (16) nitrogen-fluorine compounds, (17) nitrogen oxides, (18) nitro-paraffins, (19) oxygen, (20) ozone, (21) perchloryl fluoride, and (22) thiophosphites. Abstract entries in each subdivision of the first and second parts are arranged alphabetically by corporate author, numerically by contract number and by date. Only final or summary reports were included in the bibliography, except when the final report was not received or when a progress report contained significant information which was not included in the final report. A bibliography of confidential entries on solid and liquid propellants (AD 315 500) was compiled separately.

ROCKET PROPELLANTS - Armed Services Tech. Inform. Agency, Arlington, Va., Bibliography Rept. AD 263 000 (Aug. 1961) 75 pp.

A list of references was prepared as a sequel to previous ASTIA bibliographies on rocket propellants identified as AD 233 500 (unclassified) and AD 315 500 (confidential). Citations are limited to unclassified documents cataloged by ASTIA from February 1960 to August 1961. A classified edition of the bibliography was also published as AD 325 000. Entries are arranged in two broad categories of references: liquid, hybrid, solid or non-conventional propellant systems, and specific chemical components of propellants.

CRYOGENICS AND LOW TEMPERATURE RESEARCH. AN ASTIA REPORT BIBLIOGRAPHY - Armed Services Technical Information Agency, Arlington, Va., ASTIA AD 271 000 (Feb 62) 865 refs.

This bibliography was presented by ASTIA in response to numerous inquiries concerning cryogenics and low temperature research. Citations are included for documents cataloged by ASTIA from 1953 through 1 February 1962, and are restricted to unclassified, unlimited references. The classified section of the bibliography appears separately as a secret document, identified as AD-327 650. References are arranged alphabetically by subject areas pertaining to low temperature research, instrumentation, and materials. These subject areas are further subdivided into more specific topics which include references on superconductivity, thermochemistry, temperature measurement and control, adhesives, elastomers, liquefied gases, lubricants, metals, and propellant research.

CRYOGENICS - AN INTERNATIONAL JOURNAL OF LOW TEMPERATURE ENGINEERING AND RESEARCH - Mendelssohn, K., Scott, R. B., and Weil, L. (Editors) Heywood and Company, Ltd., London (Distributed in U.S. and Canada by Plenum Press, Inc., New York)

The purpose of CRYOGENICS is to publish original papers on all aspects of low temperature research, engineering, and development. Each issue also features an invited survey article, written by an authority on the subject, as well as shorter technical notes, letters and book reviews. The complete texts of all papers appear in English, with abstracts printed in English, French, German, and Russian.

The many different trends of low temperature research and development today are not only intensified, they are also divergent. However, all share the same cryogenic methods and techniques and all must rely on the same basic research and engineering data. Concentration of relevant information on these subjects in one journal should be invaluable to all those working in the field. It is the aim of CRYOGENICS to save time and labor of researchers and engineers in the field by providing them with significant and current information in one convenient publication.

CRYOGENIC ENGINEERING NEWS - (A controlled circulation publication printed monthly by Business Communications, Inc., Cleveland, Ohio).

A publication concerning the production and use of ultra-low temperatures.

CRYOGENIC INFORMATION REPORT - (Published by Technical Economics Associates, Estes Park, Colo.).

A monthly survey, bringing together information on the developments and activities in the various areas of the cryogenic field.

CRYOGENIC TECHNOLOGY - JOURNAL OF THE CRYOGENIC SOCIETY OF AMERICA - (Published bi-monthly by Cryogenic Technology Publications, Inc., Bel Air, Los Angeles, Calif.).

CRYOGENIC TECHNOLOGY is an official publication of the Cryogenic Society of America, devoted to the various technical and practical aspects of the several branches of cryogenics.

II. RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH LIQUID OXYGEN

- A Compilation from the Literature with Annotated Bibliography -

1. HAZARDS

1.1 Health - The health hazards of liquid oxygen arise from its very low temperature. If liquid, or cold gaseous, oxygen contacts the skin, damage resembling burns can result. The extent of such damage can range from relatively minor burns to complete embrittlement and destruction of exposed tissue. The immediate effects of freezing by liquid oxygen can be minimized by soaking affected parts in tepid water. Extensive burns require prompt medical attention.

Oxygen gas will not cause toxic effects in propellant operations, except that inhalation of the very cold gas may cause some upper respiratory irritation.

1.2 Fire - Liquid oxygen will not burn but vigorously supports combustion. Its low temperature causes cooling and freezing of liquid fuels if both liquids are brought together. Such mixtures are shock sensitive and are capable of reaction with the violence of a detonation.

Liquid oxygen is capable of saturating normal clothing and rendering it flammable. Workers must not smoke or strike fires in oxygen storage or handling areas or while wearing clothing saturated with oxygen, since the clothing may retain a high concentration of oxygen for a considerable period of time.

Two types of combustion reactions may occur depending on conditions of mixing and ignition. Intensity of combustion reaction is dependent on the type of fuel involved. Although the mixing of fuel and liquid oxygen may be accomplished without fire, a detonation occurs upon ignition or mechanical shock excitation. Where combustion is initiated prior to or concurrently with fuel-oxygen contact, flare type combustion occurs, accompanied by repeated explosions.

Putting out fires involving liquid oxygen requires procedures varying with the type of fire conditions. Where the fire results from a leak or flow of liquid oxygen onto wood, paper, waste, or similar combustible material, first stop the flow if possible. For small spills, or after the leak or flow of liquid oxygen has been stopped, use enough water to put the fire out quickly. Where the fire involves liquid oxygen and liquid fuels, control it as follows:

(a) When liquid oxygen leaks or flows into large quantities of fuel, shut off the flow of liquid oxygen, and put the remaining fuel-fire out with Class B fire fighting agents.

(b) When fuel leaks or flows into large quantities of liquid oxygen, shut off the fuel flow.

(c) When fuel and liquid oxygen have been mixed, or are mixing, but not yet burning, isolate the area from ignition sources and get out quickly, allowing the oxygen to evaporate. Where large pools of water-soluble fuel are present, use water to dilute the fuel and to reduce the intensity of the fire. This method cannot be used with fuels which do not mix with water. Do not use on fires in deep pools of liquid oxygen as this causes more rapid release of gaseous oxygen. Appropriate extinguishing agents may be used to put out fuel fires after the oxygen has evaporated.

NOTE: Mixtures of liquid oxygen and fuels present an extreme detonation hazard. Such materials as wood pulp, cotton, lampblack, hydrocarbons, metal powders, sulfur and coal dust are often used in combination with liquid oxygen as a relatively cheap explosive; the latter combination produces an effect similar to 40% nitroglycerine dynamite. It seems likely that almost any combustible material might detonate when in contact with liquid oxygen. Several incidents may illustrate this: A leak developed in a pipe joint in a liquid oxygen line and the liquid flowed onto an asphalt-paved surface. When a workman attempting to repair the leak struck the joint, the impact was transmitted from the joint to the pavement below and the pavement detonated. A similar incident has been reported where gravelled asphalt detonated when a man walked across an area where liquid oxygen had previously been spilled.

1. 3 Explosion - All materials that will burn, especially rocket fuels, present an explosion hazard when mixed with liquid oxygen. Such mixtures can usually be exploded by static electricity, mechanical shock, electrical spark, and similar energy sources. Under most conditions, the ordinary burning of rocket fuels or other combustible materials, when mixed with liquid oxygen, may progress to a detonation.

Liquid oxygen forms high concentrations of oxygen gas from spills or leaks. During transfer operations large volumes of gas are formed due to "boil-off." In confined areas, gaseous oxygen can form mixtures with fuel vapors that can be exploded by static electricity, electrical spark, or flame.

Pressure rupture can occur when the liquid is held in a closed system with no refrigeration. Oxygen cannot be maintained as a liquid if its temperature rises above the critical temperature (-181°F) regardless of confining pressure. Liquid oxygen trapped between valves can cause violent rupture of the pipe or tube, while loss of refrigeration can cause a storage tank to rupture if the pressure is not relieved by suitable devices. Loss of vacuum in vacuum-jacketed tanks can cause increased evaporation and overload the normal venting system, resulting in high pressures.

All sources of ignition or heat must be kept away from oxygen transferring and servicing operations and from areas where spills have occurred. All tanks and equipment must be provided with proper grounding to remove static electricity. It is absolutely essential to keep combustible or other reactive materials to a minimum in liquid oxygen storage and handling areas. Porous combustible materials such as clothing may retain hazardous quantities of gaseous oxygen, creating a dangerous fire hazard.

Pressure rupture of equipment can be avoided by checking all parts of the oxygen system to see that refrigeration and/or vacuum jacketing is maintained. Closed systems and "dead ends" must be avoided unless properly protected with pressure relief valves and blow-out discs. Such devices protect the system in the event of refrigeration or vacuum failure. Blow-out discs, or their equivalent, are also required on vacuum-insulated equipment jackets.

2. SAFETY MEASURES

2. 1 General - All hazardous operations or experiments involving the handling of liquid oxygen shall be performed by two or more persons working in a group. Trained supervision of all potentially hazardous activities involving liquid oxygen is essential.

2. 2 Personnel Education - The following subjects shall be explained to all persons concerned with liquid oxygen handling, transfer, and storage:

(a) Nature and properties of oxygen in both the liquid and the gaseous phases.

(b) Approved materials which are compatible with liquid oxygen.

(c) Proper equipment and its operation.

(d) Use and care of protective equipment and clothing.

(e) Safety, self-aid and first-aid instructions.

2. 3 Personal Protection - The principal hazards associated with the handling of liquid oxygen are fire and the extremely low temperature of the liquid.

For hand protection, gauntlet type gloves which can be easily and rapidly removed are satisfactory. These gloves may be either of asbestos or degreased chrome leather with an inner liner of impermeable material. For protection of the feet, leather shoes which can be readily removed should be used. These can be high top or low top; the choice depends entirely on the area in which the individual will be working. If high top boots are used, pants legs will be outside the boot tops. Where soles of shoes have been exposed to the liquid, the footwear should be removed immediately to prevent delayed frostbite.

Head and face protection requires the use of acid-type goggles (preferably) or a face shield to stop splashes. Flame resistant and static-free clothing should be worn by personnel conducting hazardous operations or experiments with liquid oxygen because of the fire hazard. In addition, an apron of approved material shall be worn if the liquid is being handled in an open system.

3. TRANSFER AND STORAGE

3. 1 General - Liquid oxygen must be stored in containers (either fixed or mobile) of approved design, materials, and construction.

Storage, transfer, and test areas must be kept neat, and free from combustibles. These areas must be inspected frequently.

An adequate water supply or fire extinguishers must be available for combating fires. Approved deluge-type personnel showers should be properly located for immediate use in an emergency.

3. 2 Materials - The ability of materials to maintain satisfactory physical properties and to withstand thermal stresses caused by large temperature changes is of prime importance.

3. 2. 1 Metals - The ferrous alloys, except the austenitic chromium-nickel alloys, lose their ductility when subjected to the low temperatures of liquid oxygen and depending on their form and the application to which they are applied they may become too brittle for use with liquid oxygen. Metals suitable for this service are aluminum, copper,

nickel, and most of their alloys, as well as the "300 series" austenitic stainless steels.

3. 2. 2 Non-Metals - Non-metals which are suitable for use with liquid oxygen are given in several of the references provided in the Bibliography. A rather extensive list of materials to be used for gaskets, packaging, sealants, lubricants, solvents, etc., is now available; however, use is occasionally qualified by the intended application - a fact which points to the desirability of reviewing the original information source concerning material compatibility with liquid oxygen. Applications involving mechanical impact are of particular concern.

3. 3 Equipment - Liquid oxygen handling equipment shall be degreased by washing with approved grease-removing solvents before being used. Equipment taken out of service for maintenance or modification shall be inspected and cleaned before being returned to service.

Liquid oxygen may be stored in either fixed or mobile tanks of approved design and materials. Storage and shipping containers designed for non-cryogenic fluids shall not be used in this service. Storage tanks shall be tested in accordance with the provisions of applicable ASME, ASTM, or ICC specifications for pressure vessels. Containers for shipment, storage, and transfer of liquid oxygen should be fabricated in accordance with the physical and structural requirements dictated by the use for which they are intended. Insulated, vacuum-jacketed tanks shall be used with a non-combustible insulating material such as diatomaceous silica, synthetic aerated silica, rock wool, magnesia, or fiberglass - properly cleaned to remove all grease and dirt. Pressure relief devices (valves and/or rupture discs) must be provided to protect all compartments from overpressure failure. Welded construction and bottom outlets are recommended for all tanks.

The general conditions applicable to tanks are also applicable to pipes and fittings.

3. 4 Transfer Procedures - Prior to transferring liquid oxygen from one container to another, all hose adapters, couplings, transfer lines and accompanying equipment shall be inspected for foreign particles. When there is a suspicion of hydrocarbons in any form, or when foreign particles are present in above equipment, the equipment shall be cleaned and inspected as indicated in Section 3. 5.

After inspecting the area to determine if it is safe to commence transfer operations, hose fittings are connected to the respective container counterparts and checked for proper seating and tightness. Drip pans shall be placed under vents and connections of liquid oxygen vessels to contain spills. Liquid oxygen must not be spilled on asphalt pavement. Containers must not vent in the vicinity of combustible material.

When the transfer operation has been completed, the liquid valves on both vessels are closed and the transfer line is vented by opening an appropriate relief valve. The hose is then disconnected and allowed to warm up and preferably dry out before it is used again. Care should be taken that the hose and other accessories do not touch the ground. Dust caps are to be replaced and exposed sections of other connectors covered, insuring that dirt, moisture, and other foreign matter cannot get into the hose and ultimately into the liquid oxygen.

3. 5 Cleaning Procedures

3. 5. 1 General - The nature of liquid oxygen, a strong oxidizer which vigorously supports combustion, presents several unique problems when cleaning lines and storage tanks through which it passes.

Cleanliness, in the usual sense, is not a sufficient criterion when dealing with liquid oxygen systems. The high purity required prohibits the presence of solid particles of specified micron size, in addition to limiting the quantity of organic material, due to the highly reactive nature of such material in contact with liquid oxygen.

Cloth or brushes, where the material may be separated from the base, shall never be used in any cleaning operation. The acceptable types of solvent for cleaning liquid oxygen systems are chlorinated hydrocarbons such as ethylene dichloride, trichlorethylene or Freon. With the exception of Freon, which is relatively non-toxic, the problem of toxicity exists with these compounds. Carbon tetrachloride is extremely toxic and shall not be used in any cleaning operation. Relative to other solvents, operators shall not be exposed to them for long periods and safety measures must be taken for protection against vapors. When a detergent, such as a solution of tri-sodium phosphate, is used to clean liquid oxygen systems, the problem of toxicity does not exist. (NOTE: Tri-sodium phosphate is not to be used on aluminum or its alloys.)

Consideration shall be given to detached parts of liquid oxygen systems to prevent contamination of the parts or of the system from which they were removed. The best method is to encase the opening in a securely and properly applied polyethylene bag. In the absence of such a bag, wide plastic tape may be applied. Material should never be stuffed in a liquid oxygen system opening. Make-shift methods must not be used in these operations.

Since it is not possible to predict the hydrocarbon build-up rate in most liquid oxygen systems, and since it is necessary to hold extremely low hydrocarbon concentration levels in these systems, periodic inspection for contamination will determine when cleaning again becomes necessary.

3. 5. 2 Methods - As substitution for a lengthy detailed résumé of cleaning methods and inspection techniques for oxygen systems - presentation of which will not achieve universal acceptance - segments of two books referenced in the General Bibliography section of this document are suggested for further reading. These are:

(a) APPLIED CRYOGENIC ENGINEERING - Vance, R. W. and Duke, W. M. (Ed.) - Appendix C - Contamination Control in Cryogenic Fluids and Systems.

(b) GROUND SUPPORT SYSTEMS FOR MISSILES AND SPACE VEHICLES - Brown, K. and Weiser, P. (Ed.) - Chapter 11 - Cryogenic Missile System Hazards.

Quoting from the first of these: "There has been and still is a great variance throughout industry in the type and size of equipment requirements, cleaning techniques, work flow, inspection methods, definition of a clean atmosphere and contamination criteria. This lack of standardization initially imposed a severe hardship on the ballistic missile effort, but standardized specifications have now been established which should reduce confusion, inefficiency, and costly recleaning operations. AIR FORCE TECHNICAL ORDER, T. O. 42C-1-11, Cleaning and Inspection Procedures for Rocket Propellant Systems (Liquid and Gaseous), governs the cleaning methods. Copies can be obtained by writing to Olmstead Air Force Base, MAOQ."

From the second: "As a result (of the extreme cleanliness requirements in the missile industry) many cleaning specifications and inspection procedures are in existence, most of them similar, but still of sufficient difference as to create confusion in the installation and acceptance of missile propellant loading systems.

"To minimize this confusion the Aerospace Industries Association, at the instigation of many of the prime contractors, sponsored a meeting .... in an effort to formulate one set of standards which could be applicable to all missile programs. After much planning and coordinating, the AIA issued their recommendations for cleaning and inspection procedures in a pamphlet: Handbook for Contamination Control of Liquid Rocket Propulsion Systems, Aerospace Industries Association, March 7, 1960."

"In the meanstime the Air Force Ballistic Missile Division issued another set of instructions governing component cleaning methods and criteria for the initial acceptance of ground support systems: Specification for Cleaning Components of Liquid Oxygen-Hydrocarbon Fuel Propellant Systems, AFBMD, ARDC, July 5, 1960."

From this it is evident that one completely acceptable set of standards does not yet exist and therefore cannot be reported here. It is recommended again, however, that the references cited at the beginning of this subsection be reviewed for extensive discussion of the topic (including cleaning and inspection procedures and techniques).

BIBLIOGRAPHY

QUALITY CONTROL OF OXYGEN PROPELLANT LIQUID OXYGEN, AVIATOR'S LIQUID BREATHING OXYGEN, AND AVIATOR'S GASEOUS BREATHING OXYGEN - Air Force Tech. Order 42B6-1-1 (May 15, 1963).

The purpose of this technical manual is to provide information, guidance, instructions, and procedures for on-base quality control of liquid oxygen used as a missile propellant, and liquid and gaseous oxygen used for aviator's breathing purposes. Included in the contents are sections on hazards and safety precautions in handling liquid and gaseous oxygen.

COMPATIBILITY OF METALLIC MATERIALS WITH LIQUID OXYGEN - Aerojet-General Corp., Rept. No. DVR 64-459 (Oct. 1964), 15 pp 4 tab 27 ref - DDC AD 459 269.

Investigation of the reactivity of metals with both liquid and gaseous oxygen were reviewed and summarized, as were theories of the ignition and propagation of combustion of metals in oxygen. Aluminum, stainless steels and nickel-based alloys were found to be compatible with liquid oxygen, but magnesium and titanium alloys were not.

OPTIMUM DESIGN OF LIQUID OXYGEN CONTAINERS - Arnett, R. W., Warren, K. A. and Mullen, L. O. - Natl. Bur. Standards, WADC TR 59-62 (Aug. 1961) Contr. AF 33(616)56-15, 235 pp 87 fig 14 tab 73 ref.

The basic parameters influencing the design of liquid oxygen containers are considered and their design interrelation evaluated. Factors considered include materials, configuration, insulation, support members, instrumentation, valves, piping, weight, evaporation loss, and accessory items such as vacuum pumps and transfer hoses. Means for evaluating and optimizing the combination of the various factors are presented together with experimental work conducted in areas where information was lacking. Description of the design and construction of a liquid oxygen container together with the thermal test results on the container is included.

CONTAMINANTS IN LIQUID OXYGEN AS RELATED TO SAFETY IN LIQUID OXYGEN PRODUCTION AND DISTRIBUTION EQUIPMENT - Arrick, C. D. - Advances in Cryogenic Engineering 3, 218-25 (Proc. of 1957 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) Paper D-8, 1 fig 3 tab.

If suitable precautions are taken in production and distribution there is very little hazard from the traces of combustible contaminants present in liquid oxygen. However, these contaminants could contribute to serious fires or explosions if they are allowed to increase to dangerous levels. Combustible materials may get into liquid oxygen from the atmospheric air processed, from oil lubricated air compressor, from improperly cleaned equipment, and from equipment parts such as gaskets, packings, etc. This discussion is limited to the contaminants introduced from the air processed in a low temperature air separation plant. The bulk of the combustible materials in the liquid oxygen product usually comes from this source if reasonable attention has been paid to the other sources. It is quite practical and desirable to keep the concentration of combustibles in liquid oxygen far below dangerous levels. It is difficult and unnecessary to eliminate them completely.

STUDY OF LIQUID OXYGEN CONTAMINATION - Bailey, B. M., Sterner, C. J. and Vignale, V. J. - Air Products, Inc., Allentown, Pa., Summary Progr. Rept. No. 4 (July 1960) Contr. AF 33(616)6730, 107 pp 25 fig 12 tab 56 ref. DDC AD 253 231.

The significance of contamination in liquid oxygen is discussed. The three types of contaminants of concern in this program include: (1) combustible compounds, solid or

dissolved, which may constitute a fire or explosion hazard to both general safety and equipment; (2) solid inert contaminants which may contribute to mechanical malfunction of the propellant loading system or the rocket engine; and (3) dissolved inert contaminants which may affect the rocket thrust or, under certain circumstances, might interfere with engine ignition. The major sources of contamination consist of the air stream to the separation plant which produces the liquid oxygen, transfer of liquid oxygen from the plant to storage, and nitrogen pressurization. Nominally minor sources include vent lines and relief valves, residual contamination, and equipment deterioration. Current specifications are given for liquid oxygen and equipment.

CONTAMINATION CONTROL IN LIQUID OXYGEN SYSTEMS - Ball, W. L. - Air Products & Chemicals, Inc.

CONTAMINATION IN THE PRODUCTION & HANDLING OF CRYOGENIC FLUIDS - Smith, C. P. - Linde Company - Jour. Am. Assoc. Contamination Control 3 (Aug. 1964) pp 10-15, 19, 32.

SAFETY IN AIR AND AMMONIA PLANTS - CEP Technical Manuals (Vol. 1-6), published by A. I. Ch. E.

Includes both published and previously unpublished data on the topic of safety in air and ammonia plants--primarily discussions and resumés of past plant operating experiences and current practices.

CORROSION EFFECTS OF LIQUID FLUORINE AND LIQUID OXYGEN ON MATERIALS OF CONSTRUCTION - Fink, F. W. and White, E. L. - Corrosion 17, 58t-60t (1961) 2 fig 1 tab 9 ref.

The corrosion behavior of materials of construction for handling liquid fluorine and liquid oxygen is summarized. This is an important matter in rocket construction. Even though both of these elements are very reactive, most of the common metals are sufficiently resistant for many applications. The compatibility with these oxidizers of alloys of iron, nickel, copper, aluminum, magnesium, titanium, and zirconium is discussed. Corrosion rate data compiled from both published and unpublished sources are presented. The compatibility of non-metals and organic materials is also reviewed. Attention is given to the effect of initiating rapid reactions, or burning of both metals and organic materials by compressive impact, tensile impact, friction, wear, and other mechanisms.

STUDY OF LIQUID OXYGEN CONTAMINATION - FINAL REPORT - Foster, R. H. - Air Products & Chem., Inc., Allentown, Pa., Final Rept. SSD-TD 62-8 (May 1961) Contr. AF 33(616)6730, 144 pp 31 fig 14 tab 62 ref DDC AD 272 377.

The purpose of this study was to develop a better understanding of the physical, chemical and mechanical relationships involved in developing realistic parameters for specification purposes for the application of oxygen to missiles. The significant sources and degree of contamination are supplied as a background survey and the current specifications for liquid oxygen and ground support equipment are discussed. Recommendations for liquid oxygen specification and for equipment operation are presented. Sources and mechanisms for ignition of liquid oxygen systems, factors related to solid contaminants, cleaning and purification of oxygen equipment and handling systems, have been included. Also as part of this contract, the contractor developed safety standards for use in high pressure oxygen and helium gases for later incorporation in the Liquid Propellant Safety Manual published by the Liquid Propellant Information Agency. As part of this program, a three-month analytical survey was made at Cape Canaveral and summarized herein.

MECHANICALLY INITIATED REACTIONS OF ORGANIC MATERIALS IN MISSILE OXIDIZERS - Hauser, R. L., Sykes, G. E. and Rumpel, W. F. - Martin Co., Denver, Colo., ASD Tech. Rept. 61-324 (June 1960 - June 1961) Contr. AF 33(616)7271, 281 pp 50 fig 137 tab 8 ref.

This report presents the results of impact testing of 24 organic materials with liquid oxygen. In addition, nine of these materials were tested with nitrogen tetroxide. Pure polymers, plasticizers, and antioxidants were studied and their threshold sensitivity levels and detonation energies were determined. Procedures and equations for calibrating impact testing machines were developed and used to calculate the rates of energy transfer into test materials. A full record of test procedures is included. In addition, 18 of the given materials in contact with liquid oxygen were subjected to shear forces with a modified Shell Four-Ball Wear Tester to determine whether reactions could be initiated by friction.

REACTIONS OF ORGANIC MATERIALS WITH LIQUID OXYGEN - Hauser, R. L. and Rumpel, W. F. - Advances in Cryogenic Engineering 8, 242-50 (Proc. of 1962 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1963) Paper E-2, 5 fig 2 tab 4 ref.

This paper summarizes the pertinent results of a scientific study of the nature and magnitude of detonation reactions involving organic materials and liquid oxygen. The study is more complete than any available in current literature. Theoretical analysis and instrumentation techniques now permit calibration of impact testing machines and calculation of energy transfer rates. A number of pure polymers, particularly elastomers, were found to be less reactive than their commercial counterparts; some plasticizers and antioxidants were observed to propagate in liquid oxygen, and none was initiated in gaseous oxygen.

Relative measures of detonation energies were obtained for a number of organic materials; this information provides a safer basis for selection of materials than has been available solely from reaction frequency data.

CORROSION IN CRYOGENIC LIQUIDS - Jackson, J. D. - Chem. Eng. Progress 57, 61-64 (1961) 6 fig 10 ref.

The large use of liquid propellants in missile systems has brought many serious problems to the missile designer and the materials engineer. One important problem is the corrosion behavior of materials of construction under the various exposure conditions of the missile and the auxiliary equipment. In the missile, short-term exposure occurs; however, the materials may be stressed almost to their yield strength. In the auxiliary equipment (such as storage tanks, pipelines, and pumps), long term exposure, under much less severe strength requirements, occurs. This article discusses corrosion behavior and mechanical properties of metals used in handling liquid oxygen and liquid fluorine.

REACTIVITY OF METALS WITH LIQUID AND GASEOUS OXYGEN - Jackson, J. D., Boyd, W. K. and Miller, P. D. Battelle Memorial Inst., Defense Metals Information Center, Columbus, Ohio, DMIC Memo No. 163 (Jan. 1963) 26 pp DDC AD 297 124.

Since the first observation of a violent reaction in early 1959, the compatibility of titanium and its alloys with liquid oxygen (LOX) has received considerable attention. Initially, laboratory investigations were primarily limited to impact studies utilizing the ABMA impact tester or modifications thereof. Later the Air Force initiated a program to determine the mechanism of the reaction. The results of these early studies were previously summarized in DMIC Memorandum 89, dated March 6, 1961.

More recently, the factors necessary to promote reactions between titanium and liquid or gaseous oxygen have been studied under conditions similar to those which would be encountered in missile and space service. It is the purpose of this memorandum to summarize the present state of the art in the light of both past and present developments.

HAZARD LEVEL OF HYDROCARBON FILMS IN SYSTEMS CONTAINING LIQUID AND GASEOUS OXYGEN - Kehat, E. - Advances in Cryogenic Engineering 7, 163-69 (Proc. of 1961 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1962) Paper E-4, 8 fig 1 tab 8 ref.

The object of this work was to determine realistic standards of cleanliness in systems containing liquid and gaseous oxygen. An arbitrary figure of 4 mg/ft^2 had been set by examination of systems that had caused no trouble in the past. It was felt that this figure was too low and that experimental determination of the safe level should be made to set such standards.

EFFECT OF LIQUID NITROGEN DILUTION ON LOX IMPACT SENSITIVITY - Key, C. F., Gayle, J. B. - NASA-George C. Marshall Space Flight Center, Huntsville, Alabama - NASA TMX-53208 (Feb. 15, 1965).

An experimental investigation was carried out to study the decrease in reactivity of materials with liquid oxygen (LOX) that is caused by dilution of the LOX with liquid nitrogen (LN$_2$). A wide range of materials was selected for testing, each of which previously had been shown to be sensitive to impact in LOX. Tests were made with the ABMA LOX Impact Tester using LOX/LN$_2$ mixtures ranging in concentration from 20 percent LOX in LN$_2$ to pure LOX. The results showed that relatively large proportions of LN$_2$ were required to effect an appreciable decrease in reactivity; however, all materials tested were insensitive to impact at 10 Kg-m in liquid air.

COMPATIBILITY OF MATERIALS WITH LIQUID OXYGEN - Key, C. F. and Riehl, W. A. - NASA - George C. Marshall Space Flight Center, Huntsville, Ala., Internal Report MTP-P&VE-M-63-14 (Dec 4, 1963).

The test instrument and procedure developed by Lucas and Riehl was used to determine the compatibility of a wide variety of materials with liquid oxygen (LOX). This method is based upon the tendency of materials to react with LOX on impact and is commonly known as the "ABMA Tester" Within the past eight years' use, over 100,000 individual test drops have been made on approximately 1,000 different materials.

Pertinent data from these tests have been compiled and the findings are presented in this report. Recommendations are made for guidance of designers and others in selection of safe materials for use in oxygen systems. Materials are discussed according to the following classifications: (1) Lubricants, (2) Sealants and Threading compounds, (3) Thermal and Electrical Insulation, (4) Elastomers, Plastics and Adhesives, (5) Gaskets and Packing, (6) Metals, Alloys and Solders, (7) Dye Penetrants, and (8) Solvents, Cleaning Solutions and Miscellaneous.

COMPATIBILITY OF MATERIALS WITH 7500 PSI OXYGEN - Union Carbide Corp., Linde Division, AMRL-TDR-64-76 (Oct. 1964) Contr. AF 33(657)-11686, 89 pp 43 fig 12 tab 17 ref.

PRECAUTIONS AND SAFE PRACTICES FOR HANDLING LIQUEFIED ATMOSPHERE GASES - Linde Company, Div. of Union Carbide Corp., Publication F-9888.

The purpose of this booklet is to outline the basic techniques for the safe handling of liquefied atmospheric gases.

LONG-TERM STORAGE OF LIQUID OXYGEN - Little, Arthur D., Inc. (July 1958) Contr. AF 04(647)-130, 24 pp 4 fig 5 tab 2 ref - DDC AD 267 782.

This report covers an investigation of the hazards produced by the long-term storage of liquid oxygen. Possible contamination in the transfer process from the plant to the storage tank was not of concern here, but only those hydrocarbons occurring in the liquid oxygen received from the air-separation plant.

SURVEY OF HAZARDS OF HANDLING LIQUID OXYGEN - McCamy, C. S. - Ind. Eng. Chem. 49, No. 9, 81A-82A (Sept. 1957) 15 ref.

With the increased industrial use of liquid oxygen, the importance of knowing about its compatibility with other materials is very much accented. Included in this article are properties of liquid and gaseous oxygen, materials compatibility with oxygen, flammability and ignition characteristics, etc.

OXYGEN PLANT SAFETY PRINCIPLES - McKinley, C. and Himmelberger, F. - Chem. Eng. Progr. 53, No. 3, 112-21 (March 1957) 6 fig 6 tab.

Safe operation of air separation equipment is a subject of growing importance because of the vastly increased rates of tonnage oxygen and nitrogen usage by the chemical and metallurgical industries. Much of the large new demand is at locations under heavy and increasing air pollution - conditions requiring fullest application of present technology. Reduction of hazards requires understanding. To this end, past published data provides limited knowledge.

Original data developed at Air Products by controlled explosion tests and solubility studies upon combustible contaminants permit the formulation of new safety principles consistent with historical findings.

This article presents new information on the character of materials and explosions in oxygen plants, and is not intended as a review of design and operating practice.

STANDARD FOR BULK OXYGEN SYSTEMS AT CONSUMER SITES - National Fire Protection Association, Rept. No. 566 (May 1962) 8 pp.

These Standards cover the general principles recommended for the installation of bulk oxygen systems on industrial and institutional consumer premises. It covers requirements for bulk oxygen systems including design, location, operation and maintenance. The Standards do not apply to oxygen manufacturing plants or other establishments operated by the oxygen supplier or his agent for the purpose of storing oxygen and refilling portable containers, trailers, mobile supply trucks or tank cars.

COMPATIBILITY OF MATERIALS WITH LIQUID OXYGEN - Peckham, H. M. and Hauser, R. L. - Advances in Cryogenic Engineering 4, 26-46 (Proc. of 1958 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) Paper A-3, 6 fig 1 tab.

Insuring the compatibility of materials with liquid oxygen has been a problem with the missile industry from the first use of LOX in propellant systems. Many materials are compatible under static conditions; however, when they are used in missile systems where dynamic or shock producing conditions are ever present, a severe hazard of detonation exists. The cryogenic industry has been aware of this problem for some time, although the study to date has been restricted to solving the immediate problems of producing and transporting the fluid.

The first active study of the compatibility problem in the missile industry was focused on lubricants. Investigations began in early 1957 when it was found that most commercial lubricants were impact sensitive in combination with LOX.

This paper reviews the application of (compatibility tester) standards to a test apparatus constructed for the Materials Engineering Laboratory at Martin-Denver and presents results of (materials compatibility) tests conducted by Martin-Denver and others.

SAFETY ASPECTS IN THE DESIGN AND OPERATION OF OXYGEN SYSTEMS - Reynales, C. H. - Douglas Aircraft Co., Eng. Paper No. 713 (Jan 1959).

COMPATIBILITY OF MATERIALS WITH OXYGEN - Reynales, C. H. - Douglas Aircraft Co., Rept. D81-444 (Oct. 1958) 78 pp 26 ref.

The contents of this report represent the result of a rapid survey made to meet an immediate need for general information on the behavior of oxygen in conjunction with the materials used in the construction of WS-315A, ground support equipment. The study covers the review of technical literature, test reports and unpublished data concerning the behavior of gaseous and liquid oxygen.

SELECTION OF LUBRICANTS AND THREAD COMPOUNDS FOR OXYGEN MISSILE SYSTEMS - Reynales, C. H. - Advances in Cryogenic Engineering 6, 117-29 (Proc. of 1960 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1961) Paper B-6, 34 fig 7 tab.

The missile industry has been concerned from the beginning about the presence of lubricants in oxygen systems because the use of some of these compounds may lead to burnouts and to disastrous explosions. This brief study aims to analyze the reasons behind the special role played by these compounds in missile oxygen systems and to find means of reducing the hazards resulting from their usage by evolving criteria for selecting safe compounds.

REACTIVITY OF TITANIUM WITH OXYGEN - Riehl, W. A., Key, C. F. and Gayle, J. B. - NASA - George C. Marshall Space Flight Center, Huntsville, Ala. Internal Report MTP-P&VE-M-62-13 (Nov. 30, 1962).

The reactivity of titanium with oxygen was studied by several test methods and under a variety of conditions associated with space vehicles.

Titanium is highly sensitive to impact in contact with LOX, and this method was used to study the effects of surface treatments, coatings, and numerous other factors upon the reactivity. The comparative reactivities of titanium, aluminum, and stainless steel alloys with oxygen were investigated by impact, shock, puncture, and spark sensitivity testing. Punctures resulting from bullets, darts, pins, or artificial meteoroids usually caused explosions. Coatings which reduced titanium reactivity in impact or shock tests were not beneficial under puncture conditions. Aluminum and stainless steel failed to react on impact or puncture.

The shock stimuli produced by small detonator caps alone were sufficient to initiate explosive reaction of titanium in contact with oxygen. An extremely heavy shock was necessary to cause aluminum to react under the same test conditions, and stainless steel did not react under the most drastic shock conditions employed. The titanium/oxygen combination is considerably more susceptible to spark initiation than aluminum/oxygen. A comparatively high energy spark was necessary for reaction of 0.010-inch-thick sheets of titanium with oxygen.

Under the particular test conditions used, titanium was insensitive to reaction with oxygen when subjected to vibration, pressure cycling, or to rupture with pressurization of thin-walled tanks containing LOX.

IGNITION OF METALS IN OXYGEN - White, E. L. and Ward, J. J. - Battelle Mem. Inst., Defense Metals Inform. Center, Columbus, Ohio - DMIC Memo. No. 224 (Feb. 1, 1966) 55 pp 12 fig 13 tab 46 ref.

The report deals with the ignition of metals in oxygen and oxygen-containing atmospheres. The ignition of metals is reviewed from the viewpoints of (a) methods that have been used to study behavior, (b) experimental values that have been obtained, and (c) the status of theories that permit the calculations of ignition temperatures. A number of experimental methods have been used to determine the ignition temperature of solid metals and alloys in oxygen gas, air, various mixtures of inert gases with oxygen, and liquid oxygen. In addition to the input of energy from heat sources, the effects of electrical-energy input, and various types of mechanical-energy input on the ignition temperature have also been reported. Experimental values of ignition temperature are discussed for alloys of titanium, aluminum, copper, nickel, iron, cobalt, magnesium, tin, and lead; stainless steels, silver and silver solders, and other metals and alloys are also discussed.

SAFETY IN THE USE OF OXYGEN - Voit, R. - Linde Ber. Tech. u. Wiss. 9, 46-55 (Sept. 1960) 10 fig.

This paper discusses the three following tasks undertaken by the author's company:

1. The investigation of the dangers concomitant with the liquefaction of air and the fractionation into its constituent parts.
2. Determination of the causes of burns and injuries to attendants in oxygen plants, - there being no simultaneous injury to the plant - and the elimination of these accident possibilities.
3. Investigation of the causes of fires and explosions at oxygen valves, lines and plants, and their elimination.

SAFETY ENGINEERING AS APPLIED TO THE HANDLING OF LIQUEFIED ATMOSPHERIC GASES - Zenner, G. H. - Advances in Cryogenic Engineering 1, 291-95 (Proc. of 1954 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) Paper H-5, 4 fig.

In the development of the present large-scale production and distribution of liquefied atmospheric gases many unusual hazards were encountered. The following discussion is intended to clarify these hazards and to outline some of the means used to overcome them.

PROPERTY VALUES OF OXYGEN
AT SELECTED CONDITIONS

Nomenclature and Conditions

TP = Triple Point
NBT = Normal Boiling Temperature (and 1 atm.)
NTP = Normal Temperature and Pressure
(70°F, 14.7 psia)
273.15°K* = 0°C = 32°F = 491.67°R

The term "mole" as used here means "gm-mole."

a. Calculated from density of the liquid and dP/dT of fusion line by the Clapeyron equation.

b. The Advisory Committee on Thermometry of the International Committee on Weights and Measures has agreed on 90.17°K as the present most probable value of thermodynamic temperature for the normal boiling point of oxygen; see Brickwedde, F. G., "International Practical Temperature Scale," Physics Today 16, 24-26 (1963).

c. C_p (vapor)$_{NBT}$ could be used here.

d. Value taken at 90°K(-297.67°F).

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*Changes have been made to correct data to this scale where necessary.

Property Values of Oxygen at Selected Conditions

Property				Value	Reference
Molecular Weight				31.9988	1
Triple Point Values	Temperature, °K			54.353	2, 3
	Pressure, mm Hg			1.14	2, 3
	Density, mole/cc	Solid		0.0430	[a]
		Liquid		0.0413	4, 5
		Vapor		0.000000336	4, 5
Normal Boiling Values	Temperature (T_b), °K			90.180 [b]	2, 3
	Density, mole/cc	Liquid		0.03565	5, 6, 22
		Vapor		0.0001396	5, 22
Critical Values	Temperature, °K			154.77	2; 3
	Pressure, mm Hg			38109	2, 3
	Density, mole/cc			0.013333	3, 22
One Liter Liquid (NBT) Equivalents	Weight, kg			1.141	6, 22
	Volume of Gas, liters		NBT	255.4	6, 22
			NTP	860.1	4, 6, 2
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	255.4	6, 22
			NTP	860.1	4, 6, 2
Heat of Fusion, Cal/mole			TP	106.3	4, 7, 8
Heat of Vaporization, Cal/mole			NBT	1630.9	5, 7, 22
Specific Heat Cal/mole-°K	C_s	Solid	TP	11.1	5, 8
		Liquid	NBT	13.0	5, 8
		Vapor	NBT	[c]	
	C_v	Liquid	NBT	7.7 [d]	9
		Vapor	NBT	5.0 [d]	10, 11
		Gas	NTP	5.03	2
	C_p	Liquid	NBT	13.0	6, 8
		Vapor	NBT	7.1 [d]	11
		Gas	NTP	7.03	2
Specific Heat Ratio	$\frac{C_p}{C_v}$	Liquid	NBT	1.69	6, 8, 9
		Vapor	NBT	1.42	10, 11
		Gas	NTP	1.40	2
Thermal Conductivity K Cal/cm-sec-°K		Liquid	NBT	0.0003575	12, 13
		Vapor	NBT	0.00001930	14
		Gas	NTP	0.0000626	15, 14, 2
Viscosity μ Gm/cm-sec		Liquid	NBT	0.00190	16, 17, 21
		Vapor	NBT	0.0000692	18, 19, 13
		Gas	NTP	0.000203	15, 13, 2, 20

Property Values of Oxygen at Selected Conditions

Property				Value	Reference
Molecular Weight				31.9988	1
Triple Point Values	Temperature, °F			-361.83	2, 3
	Pressure, psia			0.0220	2, 3
	Density, lb/ft^3	Solid		85.9	[a]
		Liquid		82.5	4, 5
		Vapor		0.000671	4, 5
Normal Boiling Values	Temperature (T_b), °F			-297.35	2, 3
	Density, lb/ft^3	Liquid		71.2	5, 6, 22
		Vapor		0.2789	5, 22
Critical Values	Temperature, °F			-181.08	2, 3
	Pressure, psia			736.90	2, 3
	Density, lb/ft^3			26.63	3, 22
One Gallon Liquid (NBT) Equivalents	Weight, lb			9.520	6, 22
	Volume of gas, ft^3		NBT	34.15	6, 22
			NTP	115.1	4, 6, 2
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	255.4	6, 22
			NTP	860.1	4, 6, 2
Heat of Fusion, Btu/lb			TP	5.976	4, 7, 8
Heat of Vaporization, Btu/lb			NBT	91.738	5, 7, 22
Specific Heat Btu/lb-°F	C_s	Solid	TP	0.346	5, 8
		Liquid	NBT	0.405	5, 8
		Vapor	NBT	[c]	
	C_v	Liquid	NBT	0.24 [d]	9
		Vapor	NBT	0.16 [d]	10, 11
		Gas	NTP	0.157	2
	C_p	Liquid	NBT	0.406	6, 8
		Vapor	NBT	0.22 [d]	11
		Gas	NTP	0.220	2
Specific Heat Ratio	$\frac{C_p}{C_v}$	Liquid	NBT	1.69	6, 8, 9
		Vapor	NBT	1.42	10, 11
		Gas	NTP	1.40	2
Thermal Conductivity K Btu/hr-ft-°F		Liquid	NBT	0.08643	12, 13
		Vapor	NBT	0.004666	14
		Gas	NTP	0.01515	15, 14, 2
Viscosity μ Centipoise		Liquid	NBT	0.190	16, 17, 21
		Vapor	NBT	0.00692	18, 19, 13
		Gas	NTP	0.0203	15, 13, 2, 20

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III. RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH LIQUID HYDROGEN

- A Compilation from the Literature with Annotated Bibliography -

1. HAZARDS

1.1 Health - The health hazards of liquid hydrogen arise from its very low temperature and the fact that the gas can exclude oxygen, thus causing asphyxiation. If liquid, or cold gaseous, hydrogen contacts the skin, damage resembling burns can result. The extent of such damage can range from relatively minor burns to complete embrittlement and destruction of exposed tissue. The immediate effects of freezing by liquid hydrogen can be minimized by soaking affected parts in tepid water. Extensive burns require prompt medical attention.

1.2 Fire.

1.2.1 General - An unconfined mixture of hydrogen and air will burn but not detonate if it is exposed to a limited ignition source such as a spark. In confined areas or when ignition is accomplished by a shock source, equivalent to a blasting cap or a small explosive charge, a detonation, or an explosion of the mixture can occur. A hydrogen flame has one-tenth the radiation effect and one-tenth the duration of hydrocarbon fuels such as gasoline and kerosene. When no impurities are present, hydrogen burns in air with an invisible flame. Hydrogen-air mixtures containing as little as 4 percent or as much as 74 percent hydrogen by volume are readily ignited. Hydrogen-oxygen mixtures are flammable over the range of 4 to 94 percent hydrogen by volume.

Quantity-distance relationships for the storage and use of hydrogen have been prepared and published by the U.S. Bureau of Mines, National Fire Protection Association, U.S. Air Force and others; however, to date, general acceptance for any one of these guides has not been achieved. Each requirement, therefore, should be examined and evaluated with current information from the above sources in mind, and with the understanding that only the best engineering judgment is good enough to make necessary decisions in this matter.

1.2.2 Control - The most effective control of hydrogen fires is the shutting off of the supply. Equipment should be designed for effective control and isolation in case of failures. Fires from hydrogen gas can be controlled effectively with the common extinguishing agents such as water, carbon dioxide and steam. It should be remembered, however, that if hydrogen flame resulting from leaks are extinguished, hydrogen will continue to leak and form a cloud of combustible gas which may explode if ignited. Where large spills occur, vacate the area at least 400 ft radius from the source. It should be emphasized that the outer limits of the flame, or fire, cannot generally be seen. If leaks occur in enclosed areas, care should be exercised to eliminate ignition possibilities, and adequately ventilate before entering.

1.2.3 Prevention - The following sources of ignition must be eliminated to prevent the occurrence of fires:

1. Open Flames - smoking, welding, or open flame shall be prohibited when hydrogen is being processed.

2. Electrical Equipment - all electrical equipment must be of the explosion-proof type or must be purged continuously with an inert gas.

3. Metallic Sparks - all handling tools should be of the spark resistant, non-ferrous type or should be covered with a non-conducting material.

4. Static Electricity - all equipment must be properly grounded, and the use of conductive floors and shoes is recommended.

1.3 Explosion.

1.3.1 General - Liquid hydrogen is not in itself explosive but if contaminated with oxygen it is unstable and an explosion is likely to occur. The liquid is hazardous, however, because the gas is always present due to evaporation. An explosive hazard exists when the hydrogen-air mixture is completely or partially confined. Such a mixture will propagate a detonation wave when initiated by an explosive. A deflagation will occur when this mixture is ignited from a spark source. However, either type of ignition will cause serious damage. Explosive hazards also exist when oxygen enriched solid air or when strong oxidizers are present. Pressure rupture, with severe consequences, can occur when the liquid is held in a closed system with no refrigeration. Hydrogen cannot be maintained as a liquid if its temperature rises above the critical temperature (-400 F) regardless of confining pressure. Liquid hydrogen trapped between valves can cause violent rupture of the pipe while loss of refrigeration can cause a storage tank to rupture if the pressure is not relieved by suitable devices. Liquid hydrogen does not present a detonable hazard when it evaporates and mixes with air in an unconfined space, although certain mixtures are subject to rapid combustion with a very high rate of flame propagation.

1.3.2 Prevention - All sources of ignition shall be kept away from areas where liquid hydrogen is being stored or handled. This means no smoking, use of approved explosion-proof electrical equipment where available and proper grounding of equipment to remove static electricity. Venting of hydrogen vapors should be accomplished at a remote location and storage tanks and other containers should be kept under positive pressure to insure that air does not enter the system. An "Underwriter Approved" automatic device for detecting hazardous concentrations of hydrogen should be installed where appropriate. Pressure rupture of materials can be avoided by the proper use of pressure relief valves and blow-out discs. Pressure gages should also be used for system monitoring. Enclosures of any type that would allow trapping of hydrogen should be either eliminated or ventilated. Careful pressure and leak testing of all lines should occur periodically.

2. SAFETY MEASURES

2.1 General - Liquid hydrogen is difficult to handle because of its low temperature, which causes many materials to become brittle. The low temperature also constitutes a freezing hazard to personnel who come into direct contact with the fluid or any unprotected equipment. However, the most serious hazard associated with the use of liquid hydrogen is the danger of fire or explosion. Liquid hydrogen is extremely volatile; the flammable and detonation limits of gaseous mixtures of air and hydrogen are wide; and the potential energy release per pound of reactants is very large. All operations involving the handling of liquid hydrogen shall be performed by two or more persons working in a group Trained supervision of all potentially hazardous activities involving liquid hydrogen is essential.

2.2 Personnel Education - The following subjects shall be explained to all personnel concerned with liquid hydrogen handling, transfer, and storage:

(a) Nature and properties of hydrogen in both the liquid and the gaseous phases.

(b) Approved materials which are compatible with liquid hydrogen.

(c) Proper equipment and its operation.

(d) Use and care of protective equipment and clothing.

(e) Safety, self-aid, and first-aid instructions.

2.3 Personal Protection - The principal hazards associated with the handling of liquid hydrogen are fire and the extremely low temperature of the liquid.

For hand protection, gauntlet type gloves which can be easily and rapidly removed are satisfactory. These gloves may be either of asbestos or chrome leather with an inner liner of impermeable material. For protection of the feet, leather shoes which can be readily removed should be used. These can be high top or low top; the choice depends entirely on the area in which the individual will be working. If high top boots are used, pants legs will be outside the boot tops. Where soles of shoes have been exposed to the liquid, the footwear should be removed immediately to prevent delayed frostbite.

Head and face protection requires the use of acid-type goggles or a face shield to stop splashes. Flame-resistant and static-free clothing should be worn by personnel working with liquid hydrogen because of the fire hazard.

Respiratory protection is not required; however, the possibility of asphyxiation in closed areas should be recognized. The use of oxygen breathing equipment in a hydrogen atmosphere will create an explosion hazard and shall be avoided.

3. TRANSFER AND STORAGE

3.1 General - Liquid hydrogen must be stored in containers (either fixed or mobile) of approved design, materials, and construction.

Storage, transfer, and test areas must be kept neat and free from combustibles. These areas must be inspected frequently.

An adequate water supply or fire extinguishers must be available for combating fires (of combustibles other than hydrogen). Approved deluge-type personnel showers should be properly located for immediate use in an emergency.

3.2 Materials - The ability of materials to maintain satisfactory physical properties and to withstand thermal stresses caused by large temperature changes is of prime importance.

3.2.1 Metals - The ferrous alloys, except the austenitic chromium-nickel alloys, lose their ductility when subjected to the low temperatures of liquid hydrogen and depending on their form and the application to which they are applied they may become too brittle for use with liquid hydrogen. Metals suitable for this service are aluminum, copper, nickel, and most of their alloys, as well as the "300 series" austenitic stainless steels.

3.2.2 Non-Metals - Several of the non-metals suitable for use with liquid hydrogen are Teflon, Kel-F, Dacron, Nylon, Mylar and Micarta. The most commonly used insulating materials for cryogenic application (with due recognition being given to the classic high-vacuum insulation) are expanded perlite, silica aerogel, diatomaceous earth, fiberglass, polystyrene and polyurethane plastic foams, cork, balsa and asbestos.

3.3 Equipment - Liquid hydrogen handling equipment shall be degreased by washing with approved grease-removing solvents before being used. Equipment taken out of service for maintenance or modification shall be inspected and cleaned before being returned to service.

Liquid hydrogen may be stored in either fixed or mobile tanks of approved design and materials. Storage and shipping containers designed for non-cryogenic service shall not be used in this service. Storage tanks shall be tested in accordance with the provisions of applicable ASME, ASTM, or ICC specifications for pressure vessels. Containers for shipment, storage, and transfer of liquid hydrogen should be fabricated in accordance with the physical and structural requirements dictated by the use for which they are intended. Insulated, vacuum-jacketed tanks shall be used with a non-combustible insulating material. Pressure relief devices (valves and/or rupture discs) must be provided to protect all compartments from overpressure failure. Welded construction and bottom outlets are recommended for all tanks.

The general conditions applicable to tanks are also applicable to pipes and fittings.

3.4 Transfer Procedures - Prior to transferring liquid hydrogen from one container to another, all hose adapters, couplings, transfer lines and accompanying equipment shall be inspected for cleanliness. Connector O-rings shall be examined for cracks or other signs of damage and replaced when necessary; these seals should be lightly coated with silicone vacuum-grease.

After inspecting the area to determine if it is safe to commence transfer operations, hose fittings are connected to the respective container counterparts and checked for proper seating and tightness. Static grounding cables shall always be used, between both the transferring vehicles and strategically located ground rods, in transfer and storage of liquid hydrogen.

The system should now be put through a sequence of evacuation and purge cycles - initially with an inert gas such as dry nitrogen and then with hydrogen. The first cycle may also be used as a means of detecting and correcting leaks. Alternate cycles of hydrogen pressurization and vented depressurization are, upon occasion, also useful in reducing system gas contamination to an acceptable level when evacuation is impossible or impractical. After the system has finally been charged with hydrogen, it should be maintained at slight positive pressure to prevent infiltration, or inward diffusion, of undesirable fluids (air, water, etc.).

Upon completion of the transfer, the system may be "inerted" by permitting, or causing, it to warm above the liquefaction temperature of nitrogen, followed by an adequate number of evacuation and nitrogen gas purge cycles. Again it is to be left under slight positive pressure, and consideration must be given to subsequent warming of the contained gas with resultant pressure rise.

If the lines are to be disconnected upon completion of the transfer operation, disregard the preceding paragraph. Close valves on both vessels and vent the transfer line by opening an appropriate relief valve. After disconnecting the line, dust caps are to be replaced and exposed sections of other connectors covered, insuring that dirt, moisture or other foreign matter cannot get into the hose and ultimately into the liquid hydrogen.

Several approaches have developed on the subject of venting hydrogen gas. One constitutes deliberate burning or flaring of the escaping gas, while the other involves venting without burning. A certain degree of hazard exists in both cases, however, and the final choice rests with conditions existing at the facility - flow rates, location of vent stack, solid contaminant concentration level in vent gas, etc. If the gas is flared, provision must be made to prevent flashback down the stack; if it is not flared, reasonable assurance should exist that ignition will not occur due to electrostatic phenomena. One means of preventing a flow of air down the stack during periods of minimum, or no, venting is to provide a continuous nitrogen purge up the stack. When possible, and economically feasible, it is desirable to recover the gas, which would otherwise be discharged to atmosphere, by collecting it in gasholders and compressing it to high pressure storage.

BIBLIOGRAPHY

SAFETY ASPECTS OF LIQUID HYDROGEN - Allan, D. S. - Little, Arthur D., Inc. - Society of Automotive Engineers Paper No. 994B (Jan. 1965) 5 pp 3 fig 5 ref.

The results of both research and practical experience that have provided a working basis for the safe storage and handling of liquid hydrogen are reviewed. The hazards involved in the use of liquid hydrogen, including those related to both its cryogenic characteristics and its reactivity with air, are discussed. General recommendations are made as to precautionary measures which shall be considered in the design and operation of liquid hydrogen facilities.

TEST EQUIPMENT AND PROCEDURES USED IN THE DEVELOPMENT OF LIQUID OXYGEN - HYDROGEN ROCKET ENGINES - Anschutz, R. H. - *Advances in Cryogenic Engineering* 5, 62-8 (Proc. of 1959 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960).

The development of rocket engines utilizing cryogenic fluid propellants involves many specialized tests and the use of much specialized test equipment. This is particularly true where one of the propellants used is liquid hydrogen with its extremely low temperature and wide flammability limits. Pratt & Whitney Aircraft is currently developing for the Air Force under NASA direction the XLR 115 liquid oxygen-liquid hydrogen rocket engine. This paper discusses some of the test equipment and procedures which are being employed in the XLR 115 engine development program at the Florida Research and Development Center near West Palm Beach, Fla.

HAZARDS OF LIQUID HYDROGEN IN RESEARCH AND DEVELOPMENT FACILITIES - Atlantic Research Corporation, Alexandria, Va., ASD-TDR-62-1027 (Dec. 1962), Contr. No. AF 33(657)-8952, 75 pp 1 fig 4 tab 27 ref.

It is the objective of this report to establish the hazards associated with the use of liquid hydrogen in research and development facilities, and to review the applicable techniques of hazard prevention and control. For this purpose the physical and chemical properties of hydrogen have been summarized with emphasis on the relation of these properties to combustion and detonation processes, and information has been collected on experiences and practices in numerous facilities. Hazards comprise the possibility of pressure rupture of containers, initiation of flammable mixtures formed by release of hydrogen due to vessel failure or other causes, and explosion of hydrogen and contaminating oxygen under cryogenic conditions. It is shown that the theory of chemical reaction provides a complete understanding of the combustion and detonation characteristics of hydrogen-oxygen systems and defines the chemical and physical requirements for inhibition and control of combustion and detonations. Experiences and practices in research and development facilities have been analyzed, general safety procedures have been suggested and subjects warranting further investigation have been determined.

HYDROGEN - Atomic Energy Commission, Washington, D. C., Safety & Fire Protection Bull. No. 5 (Aug. 1956) 10 pp 3 fig 16 ref.

The Atomic Energy Commission and its contractors have experienced a number of serious accidents involving hydrogen gas. These have included, variously, hydrogen cooled equipment, by-product hydrogen, hydrogen generated as a result of water-metal reactions, process hydrogen, and the pressure-testing of hydrogen containers. This bulletin covers properties, uses, handling and explosion characteristics of gaseous and liquid hydrogen, and provides various listings of precautions and safe practices to be observed in working with hydrogen.

HAZARDS DUE TO HYDROGEN ABOARD A SPACE VEHICLE - Caras, Gus. J. - Redstone Scientific Information Center Rept. 291 (Sept. 1964) 17 pp 23 ref.

This bibliography consists of 23 annotated references on the subject of hazards to space vehicles as a result of hydrogen leaks. The references treat such topics as hydrogen-leak detection and suppression of fires and explosions. Since the subject of hydrogen safety is rather broad, an attempt was made to include only those references which were related in some way to safety of space cabins or similar compartments.

HYDROGEN - Compressed Gas Association, Inc., New York (1955) Pamphlet G-5 15 pp 3 fig.

This pamphlet is one of a series of publications compiled by the Compressed Gas Association, Inc. to satisfy the demand for information relative to the transportation, handling and storage of compressed gases.

In this pamphlet an attempt has been made to present general information regarding the characteristics of hydrogen and its handling.

TENTATIVE STANDARD FOR LIQUEFIED HYDROGEN SYSTEMS AT CONSUMER SITES - Compressed Gas Association, Inc., New York - Pamphlet G-5.2T (Aug. 1965), 8 pp 2 tab.

This standard covers the general principles recommended for the installation of liquefied hydrogen systems on consumer premises.

A STUDY OF THE HAZARDS IN THE STORAGE AND HANDLING OF LIQUID HYDROGEN - Cassutt, L. H., Maddocks, F. E. and Sawyer, W. A. - *Advances in Cryogenic Engineering* 5, 55-61 (Proc. of 1959 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) 3 fig 11 ref.

This paper describes the results of a research program initiated to develop realistic safety criteria for the storage and handling of liquid hydrogen. Such criteria could bring about substantial savings in the capital equipment costs of production and storage facilities and could point out safety devices which would prevent major losses. Also a reduction in the required area for a production or storage facility might be effected, thus decreasing the costs of such facilities.

ELECTROSTATIC HAZARDS ASSOCIATED WITH THE TRANSFER AND STORAGE OF LIQUID HYDROGEN - Cassutt, L., Biron, D. and Vonnegut, B. - Advances in Cryogenic Engineering 7, 327-35 (Proc. of 1961 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1962) Paper H-1, 7 fig 1 tab 17 ref.

This paper summarizes the results of an experimental program to investigate the potential hazards of static charge generation and accumulation in well-grounded liquid hydrogen storage and transfer systems. Results of previous investigations of hydrogen hazards indicate that, because of the very low ignition energy requirements and wide range of flammability for mixtures of hydrogen and air (or oxygen), extreme care must be taken to remove all possible ignition sources from hydrogen facilities. The elimination of static electricity as an ignition source, however, required greater knowledge than was available concerning the conditions governing its occurrence in liquid hydrogen service.

LIQUID HYDROGEN TECHNOLOGY - General Dynamics/ Astronautics, San Diego, Calif. - Rept. No. AE62-0774 (Sept 1962) 294 pp 143 fig 24 tab 144 ref. STIF N64-10128.

This report summarizes a continuing study of liquid hydrogen technology being conducted by General Dynamics/ Astronautics in company-funded research and in development of the hydrogen-fueled Centaur space vehicle for the National Aeronautics and Space Administration. The report is intended to serve as a standard reference on liquid hydrogen properties, handling and storage with primary emphasis on space vehicle applications. The following 14 areas are included: manufacture, transportation, hydrogen safety, materials compatibility, cryogenic insulation, transfer, cryogenic measurements, propulsion methods, sloshing, vortexing, propellant heating, zero-gravity behavior, space storage, properties.

DESIGNING FOR SAFETY IN HYDROGEN BUBBLE CHAMBERS - Hernandez, H. P., Mark, J. W. and Watt, R. D. - Rev. Sci. Instr. 28, 528-35 (July 1957).

The principal hazards of operating a liquid hydrogen bubble chamber are failure of equipment (due to overpressure) and uncontrolled escape of hydrogen gas, which may cause an explosion. If safety conditions are incorporated in planning from the job beginning, components can be designed to reduce or eliminate the probability of accidents arising from the known hazards. The degree of safety, the hydrogen safety-vent system, and the hazards and operation of the liquid hydrogen bubble chambers at UCRL are discussed.

SAFETY REVIEW: LIQUID HYDROGEN SERVICING SYSTEM PAD 37B SATURN C-1 - CAPE CANAVERAL, FLORIDA - Himmelberger, F. and Vander Arend, P. C. - Air Products & Chem., Inc., Allentown, Pa., Contr. No. NAS 8-1546, 35 pp 5 fig 1 tab 9 ref.

This written Safety Review discusses the underlying principles of liquid hydrogen safety in Part I, and then, in Part II, defines how these principles have been applied to the design of the Liquid Hydrogen Servicing System on Pad 37B (Cape Canaveral, Florida). Since the safety aspects of fuel handling are well known, greater emphasis has been placed on the cryogenic factors governing liquid hydrogen safety.

HANDLING LIQUID HYDROGEN ON A PILOT-PLANT SCALE - Laquer, H. L. - Advances in Cryogenic Engineering 5, 85-94 (Proc. of 1959 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) 12 fig 4 ref.

The following discussion summarizes experience obtained during the last three years while handling liquid hydrogen in 5500 - liter batches. The work was not an objective in itself, nor is it complete or exhaustive, but was done only coincidentally while developing and operating a liquid hydrogen-cooled electromagnet. The quantities of liquid handled are small by missile standards, but the problems encountered on this pilot-plant scale are much nearer to those of large-scale usage than those of normal laboratory usage. The scaling of volumes would be from 1 gal. in the laboratory to 1000 gal. in our magnet to perhaps 100, 000 gal. for missile testing.

PROCEDURES FOR THE DESIGN AND OPERATION OF HAZARDOUS RESEARCH EQUIPMENT - U.S.A.E.C., Lawrence Radiation Lab., Univ. of Cal., Berkeley, Cal., UCRL-9711 (Oct. 1961) 73 pp 12 fig 7 ref.

This manual sets forth the procedures for the safe design and operation of hazardous research equipment, such as hydrogen targets, bubble chambers, high-pressure gas apparatuses, and the like. These procedures are in addition to the LRL general safety requirements set forth by the Plant Safety and Emergency Service Department.

PRECAUTIONS AND SAFE PRACTICES FOR HANDLING LIQUID HYDROGEN - Linde Company, Div. of Union Carbide Corp., Publication F-9914.

The purpose of this booklet is to outline the basic techniques for the safe handling of liquid hydrogen.

INTERIM REPORT ON AN INVESTIGATION OF HAZARDS ASSOCIATED WITH LIQUID HYDROGEN STORAGE AND USE - Little, Arthur D., Inc. (Jan. 1959) Contr. AF 18 (600)1687, 92 pp 24 fig 5 tab 14 ref.

Over the years there has been accumulated in various quarters a considerable, but nevertheless limited, experience with the hazards associated with handling of liquid hydrogen in gallon quantities. There have been several explosions and accidents reported (appendix A) - some explained and others from unknown causes - but there has never been a satisfactory basis for predicting the magnitude of hazard associated with the large-scale production, storage and handling of liquid hydrogen.

It was the purpose of the current assignment to establish through an experimental program the criteria for storing and transporting large quantities of liquid hydrogen and - on the basis of the findings - to recommend realistic quantity-distance relationships and safe-handling procedures.

FINAL REPORT ON AN INVESTIGATION OF HAZARDS ASSOCIATED WITH THE STORAGE AND HANDLING OF LIQUID HYDROGEN - Little, Arthur D., Inc. (March 1960) Contr AF 18(600)-1687.

The material presented in this report summarizes the efforts of a program designed to provide a more satisfactory basis for establishing reasonable safety procedures for the storage and transportation of large quantities (up to 100,000 lb.) of liquid hydrogen. Experience of others, including accident records and safety practices, were studied and an experimental program to gather much needed additional information was conducted. Details of the experimental program are presented in Appendix A. The conclusions and recommendations concerned with safe handling and proper storage criteria derived from the results of the program are presented in the main body of the report.

FINAL REPORT ON AN INVESTIGATION OF HAZARDS ASSOCIATED WITH THE STORAGE OF LIQUID HYDROGEN IN CLOSE PROXIMITY TO LIQUID OXYGEN AND RP-1 (CONFIDENTIAL) - Little, Arthur D., Inc., (July 1960) Contr. AF 18(600)1687.

LIQUID HYDROGEN SAFETY MANUAL - Little, Arthur D., Inc., Detachment No. 2, (Oct. 1959) Cont. AF 18 (600)1687.

This document covers general properties, hazards, safety measures, transfer and storage, shipping of, and recommended safety instruction format for use with, liquid hydrogen.

HYDROGEN HANDBOOK. A COMPILATION OF PROPERTIES, HANDLING AND TESTING PROCEDURES, COMPATIBILITY WITH MATERIALS, AND BEHAVIOR AT LOW TEMPERATURES - Little, Arthur D., Inc., Cambridge, Mass., AFFTC TR 60-19 (April 1960) (Subcontract to Parker Aircraft Co., Los Angeles, Calif.) Contr. No. 33(616)6710; 246 pp 89 fig 20 tab 29 ref. DDC AD 242 285.

This report summarizes (1) experience with and the available technical information on the development of two prototype valves, one for a cryogenic gas service and the other for a cryogenic liquid service (these valves are under development by Parker Aircraft Co. for a government agency); (2) bibliographical information on the physical and mechanical properties of specific construction materials for a temperature range of -420°F to +200°F (these materials include some austenitic stainless steels and Teflon plastics); (3) the thermodynamic properties of helium, hydrogen, and nitrogen fluids with which the valves may be used or tested; (4) the hazards associated with the transportation and storage of hydrogen and with its use for testing the prototype valves for leakage across the seals; and (5) the sources and availability of hydrogen, and the Los Angeles regulations that apply to its transportation and use.

HANDBOOK FOR HYDROGEN HANDLING EQUIPMENT - Little, Arthur D., Inc., WADC TR 59-751 (May 1961) Contr. AF 33(616)5641, 583 pp 226 ref. DDC AD 235 123.

This handbook provides engineering data concerning the most adequate, safe, and economical procedures and equipment for liquid hydrogen storage, transfer, and ground servicing systems. The engineering data developed centers on the requirements for (1) storage vessels, (2) transfer lines, (3) pumping systems, (4) valves, (5) instruments, and (6) recondensing systems. Results, conclusions and recommendations are reported in separate chapters classified in accordance with the above listed hardware items.

STORAGE, TRANSFER, AND SERVICING EQUIPMENT FOR LIQUID HYDROGEN - Little, Arthur D., Inc., WADC Tech Rept. 59-386 (July 1959) Contr. AF 33(616)5641, 772 pp 237 ref.

The purpose of this study is to provide engineering data concerning the most adequate, safe, and economical procedures and equipment for liquid hydrogen storage, transfer, and ground servicing systems.

Investigations have centered on the requirements for (1) storage vessels, (2) transfer lines, (3) pumping systems, (4) valves, (5) instruments, and (6) recondensing systems. Results, conclusions and recommendations are reported in separate chapters classified in accordance with the above listed hardware items.

STORAGE, SERVICING, TRANSFER AND HANDLING OF LIQUID HYDROGEN - Little, Arthur D., Inc., AFFTC TR 61-18 (May 1961) Contr. No. AF 33(616)7330, 162 pp 26 ref.

This report documents the results of investigations into six technical areas pertaining to the handling of large quantities of liquid hydrogen. The engineering data developed are reported in six separate sections. Section I establishes the current availability and specifications for liquid hydrogen pumps and cites the operational experience reported by the major users of these items. Section II sets forth a tested method for predicting the hydrogen gas required for the pressurized transfer of liquid hydrogen. Section III recounts the known facts relating to the safety and reliability of hydrogen gas cylinders as used in typical operations for the pressurized transfer of liquid hydrogen. Section IV presents the design specifications and performance characteristics of gravity-fed and boosted pressure-fed vaporizers for liquid hydrogen transfers established as a result of an integrated program of theoretical analysis and tests. Section V includes an economic comparison of systems using pumps, hydrogen vaporizers and high pressure hydrogen gas bottles to transfer liquid hydrogen. Section VI presents the results of a further investigation of the single parting line coupling for vacuum-jacketed transfer lines originally reported in WADC TR 59-386.

STANDARD FOR GASEOUS HYDROGEN SYSTEMS AT CONSUMER SITES - National Fire Protection Association, Rept. No. 567 (1963) 11 pp.

This Standard covers the general principles recommended for the installation of gaseous hydrogen systems on consumer premises. It covers requirements for gaseous hydrogen systems including design, location, operation and maintenance.

The Standard does not apply to hydrogen manufacturing plants or other establishments operated by the hydrogen supplier or his agent for the purpose of storing hydrogen and refilling portable containers, trailers, mobile supply trucks or tank cars.

LIQUID HYDROGEN HANDLING AND SAFETY - Maddocks, F. E. - Little, Arthur D., Inc., Santa Monica, Calif. (No date) 29 pp 16 fig 1 tab 12 ref.

The history of liquid hydrogen production is reviewed from the first liquefaction in liter quantities until current production of many tons per day. Some of the interesting physical and thermal properties of the liquid are discussed with particular emphasis on those of most interest to the missile and space designer. A typical process for liquid hydrogen production is described and the growth of the U. S. production capacity is reviewed. A description of current storage vessel and transfer line design practice is given. Some of the limitations of metals, both ferrous and non-ferrous, and non-metals when used at liquid hydrogen temperature are pointed out. The paper concludes with a detailed review of safety problems including detonation, deflagration and radiation hazards as well as recommendations for safe handling of the material.

SAFETY INSTRUCTION AND SAFETY GUIDE FOR HANDLING GASEOUS AND LIQUID HYDROGEN AT THE BOULDER LABORATORIES - Natl. Bur. Standards Memo. Rept. No. CM-4 (Jan. 1960) 30 pp 12 ref.

The Safety Instruction outlines organizational responsibilities and application of the Safety Guide for the safe use of hydrogen in the Boulder Laboratories. The Safety Guide outlines safety considerations pertinent to the various situations and conditions in which liquid and gaseous hydrogen is used in the Boulder Laboratories. The subject matter covered is developed with the intent of increasing personnel awareness of the hazards involved in handling hydrogen and pointing out practical methods of minimizing the hazards. It is not intended to prohibit or inhibit the use of hydrogen for experimental purposes.

HANDLING OF LIQUID AND GASEOUS HYDROGEN - Schmidt, A. F. - Presented in the panel on Handling of Propellants and Gases, SAE National Aeronautic Meeting, Los Angeles, Calif., (Oct. 11, 1960) 7 pp.

Problems associated with the use of hydrogen are discussed in the light of present-day cryogenic fuel handling technology; an examination of several characteristics of hydrogen is made - specifically those concerned with its ignition and subsequent detonation or deflagration.

LIQUID HYDROGEN - Schmidt, E. W. - Raketentechnik und Raumfahrtforschung 5, 24-26 (1961); also available in English translation as: Tech. Memo. 1028, Feltman Research Laboratories, Picatinny Arsenal, Dover, New Jersey (August 1962) 18 pp 1 fig 1 tab 9 ref.

The problems in the manufacture, storage, and handling of liquid hydrogen are examined. Cited are the operations of a number of American firms, including Pratt and Whitney. The primary problem discussed is the loss through evaporation and the pipes, valves, fittings, and storage tanks designed to counteract this loss in order that the liquid hydrogen may be used to better advantage as a rocket propellant.

CRYOGENIC HYDROGEN - Pratt and Whitney Aircraft Div., United Aircraft Corporation - Booklet S-945 (Mar. 1965).

Engineers at Pratt and Whitney Aircraft's Florida Research and Development Center have handled millions of gallons of liquid hydrogen during years of active experience with this material. Some of the techniques they have learned are published in the hope they may be of interest to those associated with projects employing this fuel. Sections of the booklet deal with preparation, storage, handling, physical and thermodynamic properties of hydrogen.

THE SAFE HANDLING OF LIQUID HYDROGEN - Scharle, W. J. - Trans. Inst. Chem. Engrs. (London) 185, CE 16-24 (Jan.-Feb. 1965).

This paper presents an up-to-date summary of current practices in the U. S. A. on the safe storage and handling of liquid hydrogen. Present yearly consumption in the U.S.A. is over 50 million gallons.

A brief review of the properties of hydrogen and general procedures for safe handling is given. Quantity-distance relationships for liquid-hydrogen storage tanks, both for production facilities and missile test stands are given. Safe methods for disposal of varying quantities of liquid hydrogen require special consideration, and criteria are presented.

Quality-control aspects for liquid hydrogen are becoming more rigid. The hazards of oxidants present in liquid hydrogen are discussed. A brief description of purity requirements is given along with a standard method for sampling and analysis.

A description of methods of transfer and transfer equipment is given.

THE STORAGE AND HANDLING OF HYDROGEN WITH SAFETY - Stoll, A. P. - Trans. Inst. Chem. Engrs. (London) 185, CE 11-16 (Jan. - Feb. 1965).

Safety precautions during the handling of hydrogen, whether liquid or gaseous, are dictated by the relative ease of ignition of hydrogen whether in air or in oxygen. Considerable pressures can be built up if reaction of combustion is contained and protection is primarily based on preventing the formation of explosive mixtures of hydrogen with air both inside and outside the equipment. Further, probable sources of ignition should be segregated or eliminated altogether. The effects of burning liquid hydrogen and methods of dealing with such fires are discussed.

The storage and handling of liquid hydrogen at - 253°C requires special techniques, which are by now well established. Details are given of how liquid hydrogen should be handled in the laboratory, showing that with due care such work can be carried out quite safely.

TECHNOLOGY AND USES OF LIQUID HYDROGEN - Scott, R. B., Denton, W. H., Nicholls, C. M. (Editors) Pergamon Press, Oxford, England (1964) 415 pp.

This book is a compilation of advanced technical information from the foremost laboratories of the United States, England, Switzerland, and West Germany on the production and uses of liquid hydrogen. It covers technical aspects of production of hydrogen gas for liquefaction, hydrogen liquefiers, properties of hydrogen, insulation requirements for storage and transport, safety practices, and uses ranging from refrigerant to rocket fuel.

LARGE-SCALE PRODUCTION, HANDLING, AND STORAGE OF LIQUID HYDROGEN - Vander Arend, P. C. - Advances in Cryogenic Engineering 5, 49-54 (Proc. of 1959 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) Paper A-4, 1 fig.

With the engineering, design, and construction of large-scale liquid hydrogen production facilities under direction of the Air Force, liquid hydrogen has become a propellant available on a sustained and economic basis. A short review of the past few years shows how tremendous the progress in hydrogen technology has been.

CONTROL OF LIQUID HYDROGEN HAZARDS AT EXPERIMENTAL FACILITIES: A REVIEW - Weintraub, A. A. - AEC Health and Safety Laboratory Rept. 160 (May 1965) 249 pp 26 fig 4 tab 60 ref.

The hazards of liquid hydrogen at experimental facilities are described and current techniques are presented for their control. As background, the uses of hydrogen, its general properties (Appendix A notes specific properties) and the design and materials for liquid hydrogen systems are discussed. Flame propagation, deflagration and detonation, ignition in free space and under confined conditions are considered under fire and explosion hazards.

The techniques of hazard control are examined in relation to hydrogen detection systems, ventilation, liquid hydrogen dump systems, flaring, ignition sources, explosion suppression, inerting, fire control and personnel exposures. Storage, transfer and transportation are also discussed. Appendix B contains case histories of hydrogen accidents. Two of the liquid hydrogen safety guides, cited among the 60 references, are reproduced in Appendix C.

THE APPLICATION OF COMMERCIAL ELECTRICAL EQUIPMENT TO LOCATIONS WHERE HYDROGEN GAS MAY EXIST IN QUANTITIES SUFFICIENT TO PRODUCE EXPLOSIVE OR IGNITABLE MIXTURES - Woodard, K. A. - Advances in Cryogenic Engineering 1, 144-47 (Proc. of 1954 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) Paper C-6.

The purpose of this paper is to summarize the type of electrical equipment and methods of installation chosen for industrial plants and miscellaneous equipment installations used in processing liquid or gaseous hydrogen. An attempt has been made to set up systematic design procedures built around the National Electrical Code wherever practicable. This paper is not intended to be used as a rule book, but only as a guide and as a record of past problems and their solutions in order to expedite future design problems and to help insure the safest performance possible.

An expanded version of this paper was written in 1955 by the author for the Stearns-Roger Manufacturing Company, Denver, Colo., under the title: A SAFETY GUIDE FOR THE APPLICATION OF COMMERCIAL ELECTRICAL EQUIPMENT IN LIQUID HYDROGEN FACILITIES.

HAZARDS IN THE HANDLING OF CRYOGENIC FLUIDS - Zabetakis, M. G. - Advances in Cryogenic Engineering 8, 236-41 (Proc. of 1962 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1963) Paper E-1, 1 tab 28 ref.

The general safety precautions to be used in the liquefaction, handling, storage, and use of compressed gases are reviewed briefly. Physiological effects of cryogenic fluids and their behavior in air and in contact with various structural materials are considered in some detail. The usual hazards associated with inerts, combustibles and oxidants are treated in terms of fluids that are initially at low temperatures.

RESEARCH ON THE HAZARDS ASSOCIATED WITH THE PRODUCTION AND HANDLING OF LIQUID HYDROGEN - Zabetakis, M. G. and Burgess, D. S. - U.S. Bur. Mines, WADD Tech. Rept. 60-141 (June 1960) Contr. AF 33(616) 58-5, 76 pp 39 fig 10 tab 22 ref.

The use of liquid hydrogen as a high-energy fuel introduces numerous hazards not ordinarily associated with the use of other more conventional fuels. These hazards are attributable to the unique properties of hydrogen in the liquid and gas states. Since little work has been conducted on explosion and related hazards of cryogenic fuels, a research program was undertaken to obtain basic data on such dangers for hydrogen and other combustibles under these conditions. The data were used to outline emergency procedures for protecting personnel and equipment when an accident spillage of liquid hydrogen occurs and to establish a quantity-distance table for the storage of this fuel.

EXPLOSION HAZARDS OF LIQUID HYDROGEN - Zabetakis, M. G., Furno, A. L., and Martindill, G. H. - Advances in Cryogenic Engineering 6, 185-94 (Proc. of 1960 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1961) Paper D-2, 7 fig 1 tab 12 ref.

The use of liquid hydrogen as a low temperature fluid and as a high energy fuel presents explosion hazards not ordinarily encountered with other cryogenic fluids. These hazards arise because of the many unique properties of this combustible in both the liquid and gaseous states. A program was started in 1958 by the Federal Bureau of Mines to determine the nature and extent of the above hazards. The data obtained from this program have been used to formulate emergency procedures and safeguards for the prevention of a disaster following the accidental spillage of liquid hydrogen. These data, emergency procedures and safeguards are summarized in this report.

RESEARCH ON THE HAZARDS ASSOCIATED WITH THE USE OF LIQUID HYDROGEN IN BUBBLE CHAMBERS - Zabetakis, M. G., Furno, A. L. and Perlee, H. E. - U.S. Bur. Mines, Dept. of Interior, Explosives Research Lab., Pittsburgh, Pa., Final Rept. No. 3861 (May 1962) 53 pp 24 ref.

In the present study, certain of the hazards associated with the use of liquid hydrogen in enclosed spaces were investigated in some detail. Of particular interest were those hazards associated with the use of the liquid in bubble chambers. These could arise from the failure of a glass window, container, vacuum tank, vent system, etc. Accordingly, special efforts were made to determine the nature of glass window failures, the results to be expected from the impingement of glass fragments on materials found in bubble chamber vacuum tanks, the performance of vent systems, the desirable characteristics of hydrogen gas detection systems, the method of ignition of hydrogen-air mixtures, and finally, the results to be expected from the ignition of such mixtures in enclosed spaces.

HAZARDS IN USING LIQUID HYDROGEN IN BUBBLE CHAMBERS - Zabetakis, M. G., Furno, A. L. and Perlee, H. E. - U.S. Bur. Mines, Dept. of Interior, Explosives Research Lab. Pittsburgh, Pa., RI 6309 (1963) 39 pp 27 fig 29 ref.

(Similar in content to preceding report; slightly different arrangement of material.)

PROPERTY VALUES OF NORMAL HYDROGEN AT SELECTED CONDITIONS

Nomenclature and Notations

TP = Triple Point
NBT = Normal Boiling Temperature (and 1 atm.)
NTP = Normal Temperature and Pressure
(70°F, 14.7 psia)
273.15°K* = 0°C = 32°F = 491.67°R

The term "mole" as used here means "gm-mole."

a. The Advisory Committee on Thermometry of the International Committee on Weights and Measures has agreed on 20.384°K as the present most probable value of thermodynamic temperature for the normal boiling temperature of normal hydrogen; see Brickwedde, F. G., "International Practical Temperature Scale," Physics Today 16, 24-26 (1963).

b. C_p (vapor)$_{NBT}$ could be used here.

c. Extrapolated value.

d. C_s (liquid)$_{NBT}$ could be used here.

e. Assuming b above is done, the value of C_p/C_v (liquid)$_{NBT}$ is then 1.6.

f. Value taken at 20°K (-423.67°F).

Property Values of Normal Hydrogen at Selected Conditions

Property				Value	Reference
Molecular Weight				2.01594	1
Triple Point Values	Temperature, °K			13.95	2, 3, 4
	Pressure, mm Hg			54.0	3, 4
	Density, mole/cc	Solid		0.0430	3, 4
		Liquid		0.0383	3, 4
		Vapor		0.0000631	4
Normal Boiling Values	Temperature (T_b), °K			20.38 [a]	2, 3, 4
	Density, mole/cc	Liquid		0.0352	2, 3, 4
		Vapor		0.000661	4
Critical Values	Temperature, °K			33.18	2, 3, 4
	Pressure, mm Hg			9865	3, 4
	Density, mole/cc			0.0149	2, 3, 4
One Liter Liquid (NBT) Equivalents	Weight, kg			0.0710	1, 2, 3
	Volume of Gas, liters		NBT	53.3	2, 3, 4
			NTP	850	2, 3, 5
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	53.3	2, 3
			NTP	850	2, 3, 5
Heat of Fusion, Cal/mole			TP	28.0	3, 4
Heat of Vaporization, Cal/mole			NBT	216	3, 4
Specific Heat Cal/mole-°K	C_s	Solid	TP	1.37	3
		Liquid	NBT	4.6	3
		Vapor	NBT	[b]	
	C_v	Liquid	NBT	2.9	3
		Vapor	NBT	3.0 [c]	6
		Gas	NTP	4.90	6
	C_p	Liquid	NBT	[d]	
		Vapor	NBT	5.8	3, 4
		Gas	NTP	6.89	6, 4
Specific Heat Ratio	$\frac{C_p}{C_v}$	Liquid	NBT	[e]	
		Vapor	NBT	1.9	3
		Gas	NTP	1.41	6
Thermal Conductivity K Cal/cm-sec-°K		Liquid	NBT	0.000284	7
		Vapor	NBT	0.000038 [f]	6, 4
		Gas	NTP	0.000427	6, 4
Viscosity μ Gm/cm-sec		Liquid	NBT	0.000135	8, 3
		Vapor	NBT	0.0000109 [f]	3, 6, 4
		Gas	NTP	0.0000884	3, 6, 4

Property Values of Normal Hydrogen at Selected Conditions

Property				Value	Reference
Molecular Weight				2.01594	1
Triple Point Values	Temperature, °F			-434.56	2, 3, 4
	Pressure, psia			1.04	3, 4
	Density, lb/ft^3	Solid		5.41	3, 4
		Liquid		4.82	3, 4
		Vapor		0.00794	4
Normal Boiling Values	Temperature (T_b), °F			-422.99 [a]	2, 3, 4
	Density, lb/ft^3	Liquid		4.43	2, 3, 4
		Vapor		0.0832	4
Critical Values	Temperature, °F			-399.95	2, 3, 4
	Pressure, psia			190.8	3, 4
	Density, lb/ft^3			1.88	2, 3, 4
One Gallon Liquid (NBT) Equivalents	Weight, lb			0.592	1, 2, 3
	Volume of gas, ft^3		NBT	7.12	2, 3, 4
			NTP	113.7	2, 3, 5
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	53.3	2, 3
			NTP	850	2, 3, 5
Heat of Fusion, Btu/lb			TP	25.0	3, 4
Heat of Vaporization, Btu/lb			NBT	193	3, 4
Specific Heat Btu/lb-°F	C_s	Solid	TP	0.679	3
		Liquid	NBT	2.3	3
		Vapor	NBT	[b]	
	C_v	Liquid	NBT	1.4	3
		Vapor	NBT	1.5 [c]	6
		Gas	NTP	2.43	6
	C_p	Liquid	NBT	[d]	
		Vapor	NBT	2.9	3, 4
		Gas	NTP	3.41	6, 4
Specific Heat Ratio	$\frac{C_p}{C_v}$	Liquid	NBT	[e]	
		Vapor	NBT	1.9	3
		Gas	NTP	1.41	6
Thermal Conductivity K Btu/hr-ft-°F		Liquid	NBT	0.0687	7
		Vapor	NBT	0.0092 [f]	6, 4
		Gas	NTP	0.103	6, 4
Viscosity μ Centipoise		Liquid	NBT	0.0135	8, 3
		Vapor	NBT	0.00109 [f]	3, 6, 4
		Gas	NTP	0.00884	3, 6, 4

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*Changes have been made to correct data to this scale where necessary.

PROPERTY VALUES OF PARAHYDROGEN AT SELECTED CONDITIONS

Nomenclature and Notations

TP = Triple Point
NBT = Normal Boiling Temperature (and 1 atm.)
NTP = Normal Temperature and Pressure (70°F, 14.7 psia)
273.15°K* = 0°C = 32°F = 491.67°R

The term "mole" as used here means "gm-mole."

a. Calculated with the assumption that the volume change on fusion is the same for normal and parahydrogen with the value of ΔV from reference 3.

b. The Advisory Committee on Thermometry of the International Committee on Weights and Measures has agreed on 20.267°K as the present most probable value of thermodynamic temperature for the normal boiling temperature of parahydrogen; see Brickwedde, F. G., "International Practical Temperature Scale," Physics Today 16, 24-26 (1963).

c. C_p (vapor)$_{NBT}$ could be used here.

d. C_v (gas)$_{NTP}$ of normal hydrogen could be used here.

e. C_p (gas)$_{NTP}$ of normal hydrogen could be used here.

f. Assuming c and d above are done, the value for C_p/C_v (gas)$_{NTP}$ is then 1.41.

g. Value taken at 20°K (-423.67°F).

h. The difference between the viscosities of normal and parahydrogen is less than 1% from 15° to 90°K; see references 16 and 17. Therefore μ (gas)$_{NTP}$ of normal hydrogen could be used here assuming the trend of normal-to-para difference.

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*Changes have been made to correct data to this scale where necessary.

Property Values of Parahydrogen at Selected Conditions

Property				Value	Reference
Molecular Weight				2.01594	1
Triple Point Values	Temperature, °K			13.803	2,9
	Pressure, mm Hg			52.8	9
	Density, mole/cc	Solid		0.0429	[a]
		Liquid		0.0382	2,9,14
		Vapor		0.0000624	9,14
Normal Boiling Values	Temperature (T_b), °K			20.268 [b]	2,9
	Density, mole/cc	Liquid		0.03511	2,9,14
		Vapor		0.000664	9,14
Critical Values	Temperature, °K			32.976	9,14
	Pressure, mm Hg			9697	9,14
	Density, mole/cc			0.0156	9,14
One Liter Liquid (NBT) Equivalents	Weight, kg			0.07078	9
	Volume of Gas, liters		NBT	52.9	2,9
			NTP	848	2,6,9
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	52.9	2,9
			NTP	848	2,6,9
Heat of Fusion, Cal/mole			TP	28.1	10
Heat of Vaporization, Cal/mole			NBT	214.8	9,10,14
Specific Heat Cal/mole-°K	C_s	Solid	TP	1.36	3,10
		Liquid	NBT	4.63	12
		Vapor	NBT	[c]	
	C_v	Liquid	NBT	2.72	13,14
		Vapor	NBT	3.13	14
		Gas	NTP	[d]	
	C_p	Liquid	NBT	4.7	14
		Vapor	NBT	5.86	14
		Gas	NTP	[e]	
Specific Heat Ratio	$\frac{C_p}{C_v}$	Liquid	NBT	1.72	13,14
		Vapor	NBT	1.902	14
		Gas	NTP	[f]	
Thermal Conductivity K Cal/cm-sec-°K		Liquid	NBT	0.000284	7,4
		Vapor	NBT	0.000038	6,15
		Gas	NTP	0.000440	6,15
Viscosity μ Gm/cm-sec		Liquid	NBT	0.0001317	8
		Vapor	NBT	0.0000109[g]	3,6,16,17
		Gas	NTP	[h]	

Property Values of Parahydrogen at Selected Conditions

Property				Value	Reference
Molecular Weight				2.01594	1
Triple Point Values	Temperature, °F			-434.83	2,9
	Pressure, psia			1.02	9
	Density, lb/ft^3	Solid			[a]
		Liquid		4.81	2,9,14
		Vapor		0.00784	9,14
Normal Boiling Values	Temperature (T_b), °F			-423.187 [b]	2,9
	Density, lb/ft^3	Liquid		4.42	2,9,14
		Vapor		0.0835	9,14
Critical Values	Temperature, °F			-400.30	9,14
	Pressure, psia			187.6	9,14
	Density, lb/ft^3			1.96	9,14
One Gallon Liquid (NBT) Equivalents	Weight, lb			0.5907	9
	Volume of gas, ft^3		NBT	7.07	2,9
			NTP	113.3	2,6,9
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	52.9	2,9
			NTP	848	2,6,9
Heat of Fusion, Btu/lb			TP	25.07	10
Heat of Vaporization, Btu/lb			NBT	191.7	9,10,14
Specific Heat Btu/lb-°F	C_s	Solid	TP	0.674	3,10
		Liquid	NBT	2.30	12
		Vapor	NBT	[c]	
	C_v	Liquid	NBT	1.35	13,14
		Vapor	NBT	1.55	14
		Gas	NTP	[d]	
	C_p	Liquid	NBT	2.3	14
		Vapor	NBT	2.91	14
		Gas	NTP	[e]	
Specific Heat Ratio	$\frac{C_p}{C_v}$	Liquid	NBT	1.72	13,14
		Vapor	NBT	1.902	14
		Gas	NTP	[f]	
Thermal Conductivity K Btu/hr-ft-°F		Liquid	NBT	0.0687	7,4
		Vapor	NBT	0.0092	6,15
		Gas	NTP	0.106	6,15
Viscosity μ Centipoise		Liquid	NBT	0.01317	8
		Vapor	NBT	0.00109[g]	3,6,16,17
		Gas	NTP	[h]	

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IV. RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH FLUORINE

- A Compilation from the Literature with Annotated Bibliography -

1. HAZARDS

1.1 Health

1.1.1 General - Liquid fluorine exhibits a slight green fluorescence giving it a yellow green appearance. Pure gaseous fluorine has a pale yellow color. A fluorine cloud released into the atmosphere generally has a dense, medium brown appearance. This changes rapidly to a milky-white appearance as the fluorine reacts with the water in the atmosphere to form hydrogen fluoride.

Fluorine has the characteristic halogen odor; however, under most circumstances, HF is formed by the time its odor can be detected, which adds a faint ozone odor.

1.1.2 Toxicity - Both liquid and gaseous fluorine are exceedingly corrosive to body tissues. The low boiling point of fluorine makes it unlikely that the liquid will get in contact with the body, but if this accident should occur, skin injury resembling burns will follow. These are likely to be severe, deep, and slow in healing.

Gaseous fluorine in high concentrations will result in thermal burns to the skin. This type of burn would be similar to that caused by an oxyacetylene flame and could be treated like any combination chemical and thermal burn. Gaseous fluorine in moderate concentrations in contact with the skin will result in burns more chemical in nature and closely resembling those caused by hydrofluoric acid. A latent period depending upon the degree of exposure is usually associated with fluorine burns. Several hours may elapse before the patient is conscious of pain or injury. The lesion becomes first reddened and then swollen and pale with a macerated appearance. It is accompanied by severe throbbing pain. Adequate treatment will usually stop the pathological changes at this stage; otherwise necrosis and ulceration will ensue.

Because treatment of fluorine burns is specific and highly efficient, it should be instituted immediately, even in cases of questionable severity. The skin should be flushed with copious amount of tepid tap water for at least 15 minutes, the washing should not be interrupted even while removing contaminated clothing. Medical attention should be summoned and, if in the opinion of the physician the burn is mild, a water base paste containing magnesium salts may then be applied (A commercial paste on the market consisting of 20% magnesium sulfate, 6% magnesium oxide, 18% glycerin, 1.2% procaine hydrochloride, q.s. water base). If the physician considers even a slight chance that the burn may develop beyond the erythema stage, the tissue beneath and around the affected area should be infiltrated with 10% calcium gluconate. This precipitates the fluorine as inert calcium fluoride.

Fluorine burns of the eye require immediate, copious and prolonged irrigation with tepid tap water. Subsequent treatment should be directed by an opthalmologist and consists in the application of pontociane for the relief of pain, mydriatics, and the removal of any necrotic tissue in the cornea.

Under no conditions should the first aid treatment consist of the application of oil or ointments to either the skin or eye.

The effect of chronic long term exposure to gaseoue fluorine may cause chronic pulmonary damage and deposition of fluoride in bones and teeth. Tests at Edwards AFB in which volunteers were subjected to concentrations of about 25 ppm for a period of even less than a minute showed the exposed person has a sore throat and minor chest pains for a period of six hours. Emergency tolerance limits (ETL) for fluorine are dependent on exposure time. The following tabulated values are for seldom or non-occupational frequency of exposure such as is likely to be encountered in rocket operations

Exposure Time in Minutes	ETL in ppmv
10	3
30	2
60	1

0.5 ppmv is the ETL for repeated exposure. 0.1 ppmv/8 hour day has been accepted for occupational exposure ETL.

The inhalation of flood concentrations of fluorine would probably cause asphyxia by mechanism of laryngeal and bronchiole spasm, and later by bronchiole obstruction and pulmonary edema. Exposure to high concentrations of fluorine would also be accompanied by gastrointestinal symptoms and irritation of the eyes, throat and skin; but these symptoms would be secondary in importance to lung damage.

1.1.3 First Aid and Self Aid - Treatment of fluorine burns is specific and highly efficient and is discussed in the previous section. In the event of exposure of persons to concentrations of fluorine vapor exceeding the hygenic standards, remove the patients from the contaminated atmosphere and keep them as quiet as possible. If breathing stops, apply artificial respiration and get medical attention as soon as possible. If there is evidence of air hunger, oxygen therapy should be instituted. Administration of the gas under slightly increased pressure may force more oxygen past the stenosed bronchiole tubes, and an increased oxygen tension in the alveoli will result in more efficient transfer of oxygen to the blood. If the patient does not succumb to anoxemia within a few hours, complete recovery can be expected and residual conditions should be treated symptomatically.

1.2 Fire

1.2.1 General - Fluorine is the most powerful chemical oxidizing agent known; it reacts with practically all organic and inorganic substances. The few exceptions are the inert gases, metal fluorides in their highest valence state, and a few (catalyst and adulterant free) completely fluorinated organic compounds. Even the latter may burn in a fluorine atmosphere if contaminated with a combustible material or if subjected to high flow velocities of fluorine. The heats of reaction are always high and most reactions take place with ignition.

1.2.2 Control - The reaction of fuels with liquid fluorine is frequently so rapid that no attempt can be made to extinguish them. After consumption or dissipation of the fluorine in the fluorine-fed fire, extinguishing methods appropriate to the nature of the resultant fire may be used. Small spills of fluorine may be handled by remote application of water fog to promote smooth rapid combustion of the fluorine. Areas surrounding large spills should be evacuated until the fluorine has evaporated.

1.3 Explosion

1.3.1 General - Fluorine itself is insensitive to explosive decomposition; however, explosive reactions may result in the action of fluorine on most materials. While fluorine "explosions" are not at detonation velocities the reaction of fluorine with other material is in some cases sufficiently violent that it may cause slight overpressures even in unconfined areas. In confined spaces such as tanks, lines, etc. the reaction of fluorine with some foreign material (e.g. condensed water) will initiate the reaction of fluorine with the transfer or storage container resulting in pressure ruptures and subsequent fires or secondary explosions. The hypergolicity of fluorine precludes the formation of detonable liquid mixtures, but explosive vapor mixtures may be formed with combustibles which can explode spontaneously.

Explosions may occur when liquid fluorine is trapped in a closed system and refrigeration is not maintained. Liquid fluorine trapped between valves, can cause violent rupture of the pipe or tube on warming. This condition is not unique with fluorine but it exists with all cryogenics.

1.3.2 Prevention - Any equipment to be used for fluorine service should be thoroughly cleaned, degreased and dried, then treated with increasing concentrations of fluorine gas so that any impurities may be reacted without the simultaneous ignition of the equipment.

2. SAFETY MEASURES

2.1 General - Although fluorine is the most reactive element and recognized as a very dangerous material, it can be handled without undue hazard if proper precautions are taken. It is important for the safe handling of fluorine that in addition to the safety measures given below and in subsequent sections that common sense safety precautions necessary for the handling of any toxic or reactive material should not be overlooked. All operations involving the handling of fluorine shall be performed by persons working in a group. Trained supervision of all potentially hazardous activities involving fluorine is essential.

The hand covering used should protect against fluorine and also allow free movement of the fingers. Clean neoprene gloves should be worn when handling equipment which contains, or has recently contained, fluorine. This precaution affords protection against inadvertent exposure to "puffs" of fluorine gas (but it is not to be considered as an absolute protection against the impingement by high concentration and high velocity fluorine gas or liquid); it also provides protection against hydrofluoric acid which may be formed when escaping fluorine reacts with moisture in the air and which may coat valve handles and other similar equipment.

Boots of any of the approved protective materials are not manufactured commercially. A neoprene overboot should be selected which is designed to be worn over regular safety footwear and high enough to fit comfortably under the legs of protective trousers.

Protective clothing covered by Specification MIL-S-12527 (QMC) suit protective, acid and fuel resistant, can be used. Neoprene jackets and trousers, designed to allow quick removal are recommended. Full hoods should be worn.

Gas masks and cartridge respirators shall not be relied upon for protection against fluorine. Approved self-contained breathing apparatus with full face mask shall be used for respiratory protection against fluorine.

2.2 Personnel Education - The following subjects shall be explained thoroughly to all personnel concerned with the handling, transfer, and storage of fluorine:

(a) Nature and properties of fluorine, with emphasis on its toxicity.

(b) Approved materials which are compatible with fluorine.

(c) Proper equipment and its operation.

(d) Use and care of protective equipment and clothing.

(e) Safety, self-aid, and first-aid instructions.

2.3 Personal Protection - The principal personal hazards associated with the handling of fluorine are as follows:

(a) Inhalation of vapor.

(b) Exposure of the body to the liquid or vapor.

(c) Fire.

No materials are known at present that will provide complete protection. Impermeable gloves, boots, and body protection shall be worn when handling fluorine. All such protection clothing shall be designed and used in such a manner that it can be shed easily and quickly.

3. TRANSFER AND STORAGE

3.1 General - Liquid fluorine must be stored in containers (either fixed or mobile) of approved design, materials, and construction.

Storage, transfer, and test areas must be kept neat and free from combustibles. These areas must be inspected frequently.

In designing a reliable fluorine system the greatest emphasis is placed on three factors:

(a) Achieving an absolutely leak proof system.

(b) Avoiding irregularities in the flow passages such as crevices and lap joints, weld slag, rough or oxidized surfaces.

(c) Taking extreme care in the assembly, cleaning, passivation, and in the prevention of contamination.

The success of this procedure has been demonstrated by many successful operations of liquid fluorine at the NASA Lewis Research Center. It should be mentioned here that much of the material presented in this section was derived from the paper "Some Problems in using Fluorine in Rocket Systems" by H. W. Schmidt and E. A. Rothenberg, as presented in O.S.U. Special Report No. 12 entitled PROCEEDINGS OF THE PROPELLANT THERMODYNAMICS AND HANDLING CONFERENCE - this is referenced in the General Bibliography of the present document. For a comprehensive, much expanded treatment of the subject of fluorine, the reader is referred to NASA SP-3037, HANDLING AND USE OF FLUORINE AND FLUORINE-OXYGEN MIXTURES IN ROCKET SYSTEMS by H. W. Schmidt - a report which was in press at the time of this writing and is referenced in the fluorine bibliography following this section.

3.2 Materials - Partially oxidized material can be fully oxidized simply by exposure to an oxidizing atmosphere of suitable temperature. This is particularly true with fluorine since fluorine has the highest oxidation potential of all the elements. Ordinary oxides may be considered to be in a state of less than maximum oxidation because fluorine is capable of replacing the oxygen atoms with sufficient heat release to maintain combustion. Most metallic oxides react with fluorine at temperatures less than -250°C (-419°F). Even fire brick (Al_2O_3 - SiO_2) will burn in fluorine. The reaction of fluorocarbon polymers with fluorine is another example of a reaction of a higher state of oxidation. Polytetrafluoroethylene ($-CF_2-CF_2-$), for example, is a saturated fluorocarbon chain but fluorine is capable of breaking the carbon bond reacting the carbon to a higher degree of saturation forming carbon tetrafluoride. The reaction may be initiated from an unreacting system by increasing the temperature.

A pressure increase will also initiate reaction with fluorine. Several non-metallic materials were tested under the static conditions for compatibility with both liquid and gaseous fluorine at atmospheric pressure and at 1500 psig respectively. In a majority of the tests on which no reaction occurred at atmospheric pressure, reaction was initiated by the pressure increase.

Metallic materials with a high thermal conductivity resist ignition with fluorine more readily than materials with low conductivity. Combustion with fluorine will not occur if the heat of reaction can be dissipated from the point of ignition fast enough to maintain less than the combustion temperature for the material involved.

Fluorocarbon materials undergo two types of reaction with the fluorine--a slow reaction in which the material slowly reacts forming fluoride at the surface at a relatively low temperature, and a fast combustion reaction. The type of reaction is generally determined by the ability or the capacity of material adjacent to the reacting zone to dissipate the heat of reaction at a rate equal to or greater than the rate in which the heat is produced. Fluorocarbon O-rings or valve stem packings closely surrounded by metal slowly react away if the gaseous fluorine is able to leak past them. However, active combustion is generally prevented because of the high thermal conductivity of the system surrounding the O-ring or packing.

Fluorine will react with the surface of nearly all solid materials. If the material is spontaneously combustible, reaction will continue until the fluorine or the material is depleted. If the material is not spontaneously combustible, like most metals, surface reaction simply forms a fluoride film on the surface. This film, if sufficiently tenacious, is considered generally to be an aid in preventing fluorine attack on fluorine systems. If, however, the surface area exposed to fluorine is very large in proportion to the mass, for example, a fine mesh screen or finely divided material such as powdered metal or spun glass, the surface reaction will initiate combustion and the material becomes spontaneously reactive.

Many fluorine system failures occur during flow conditions, although the flow condition itself has not been established as the direct cause of failure in most cases. In one test at NASA Lewis, polytetrafluoroethylene (Teflon) was exposed statically to liquid fluorine at 1500 psi without reaction. The same material when subjected to flow conditions at 50 psi reacted violently. The fact that Teflon withstood static exposure to liquid fluorine and yet failed in the dynamic test is of particular interest. Metals form a protective fluoride surface film when exposed to fluorine. Teflon, on the other hand, tends to react with fluorine to break down the polymer and form unsaturated low molecular weight fluorocarbons. These fluorocarbons would not adhere to the surface and therefore would be of no value as protective films. It is also possible, of course, that the surface impurity could act as a reaction initiator although this should be independent of kinetic or static conditions.

In the experience at NASA Lewis in fluorine system failures, combustion reaction was initiated with fluorine and its containing system. The section in which failure occurred was usually consumed which destroyed the evidence so that the exact cause could not be determined. However, high pressure flow of liquid fluorine was most frequently involved and the compatibility of materials was suspected. A series of compatibility tests with liquid fluorine were conducted in an effort to isolate the cause of burnouts. Flow tests were run at pressures up to 1500 psi. Fluorine was cycled to the test sections by means of an appropriate control value in pressures up to 1500 psi. The materials tested were Monel, stainless steel, nickel, brass, and aluminum. Pinhole orifices were used to simulate leaks for determining erosion tendencies. Fluorine was impinged against flat-ended plugs at velocities over 350 ft. per sec. and sharpedged wedges were used to study turbulence and the effect of sharp edges in fluorine flow. Liquid fluorine at 1500 psi was released suddenly into one-quarter inch stainless steel and aluminum tubing containing gaseous fluorine at ambient temperatures without adverse effect on the system. No metal erosion or appreciable chemical attack occurred on any of the metal specimens used and tested. Pressure, flow rate, Reynolds number, or system configuration had no effect on the test. After the entire preparation and operating procedure was reviewed it was concluded that the primary cause of burnouts in fluorine systems was not associated with the selection of materials or configuration of system components, but rather must be due to system contamination. Contamination includes all foreign material, organic or inorganic that is not fully fluorinated. Use of extreme care in assembly, together with astringent cleaning procedures to obtain meticulously clean systems resulted in a marked reduction in system failures.

A secondary cause of "burnouts" may be attributed to mechanical failure of the containing system which may allow the fluorine to come into contact with reactable material. For example, a flange leak may allow fluorine to contact moisture or dirt on the outside of the flow line which may initiate combustion with the type material.

Most metal materials of construction are resistant to fluorine attack if the conditions of exposure are not too severe. In many cases, this resistance is enhanced by the fluoride film that forms on or in the surface of the material from initial reaction. Materials more subject to fluorine and hydrogen fluoride corrosion accumulate relatively heavy fluoride coatings during prolonged use. Iron is such a material and is used mostly in gaseous fluorine systems at low pressures in moderate ambient temperatures. The advantage is low cost; the disadvantage is flow restriction and clogging from accumulated solids which necessitates more frequent maintenance. Fluoride coatings are sometimes very brittle, sometimes porous and powdery. The more resistant materials such as nickel and stainless steel rarely exhibit visible surface films from fluorine exposures. The permeability of the fluoride coating, which varies with the material, is one of the controlling factors in the corrosion rate. Those metals with greatest resistivity to fluorine attack are least dependent on the fluoride film for protection. For example, nickel is nearly passive to liquid fluorine, and may be exposed to severe dynamic conditions without prior surface passivation. Other commonly used materials with excellent resistivity to fluorine are Monel, Inconel, 300 series stainless steel, brass, copper, and aluminum.

There are no non-metals that are known to be entirely resistant to reaction with liquid fluorine. One reference reports that the ceramic material mullite was not visibly affected by the liquid fluorine, but it is reasonable to assume that if enough heat was generated to melt or burn most metals, the fluorine could attack the ceramic material.

Fluorine reacts with organic, aqueous, or siliceous materials otherwise considered inert, as well as with oxidizable materials. Therefore, silicants and standard petroleum-based lubricants are not usable. There are no reliable lubricants for fluorine service.

3.3 Equipment - Liquid fluorine handling equipment shall be degreased by washing with approved grease-removing solvents before being used. Passivation is recommended as a final treatment prior to liquid exposure. Equipment taken out of service for maintenance or modification shall be inspected and cleaned before returned to service. The tanks for storage of liquid fluorine are usually constructed with three horizontal concentric shells; an outer shell, an intermediate shell and an inner shell. As dictated by the user, the shells can be constructed of either Monel, aluminum, or stainless steel. The inner shell will contain liquid fluorine; the intermediate shell will contain liquid nitrogen; and the outer shell an insulating material of low thermal conductivity such as Santocel or perlite provided there is no concern of potential fluorine leakage into the insulating annulus. In the event there is a probability that fluorine may seep into the insulated space, it is recommended that a vacuum only, or a high vacuum plus a metallic radiation shield, be utilized. The primary objective in fluorine tank fabrication is to achieve a smooth crevice free interior; seam welds which have flux and slag inclusions, pockets or bubbles, and oxidized surface flaking are considered particularly hazardous, and this type of contaminant is capable of reacting and combusting with fluorine. The higher the state of purity of the container, its surface and even the fluorine itself, the less possible it is for reaction to occur. It follows that pressurizing gases must be free of moisture or other contaminants.

3.3.1 Containers - Liquid fluorine may be stored in either fixed or mobile tanks of approved design and materials. Storage and shipping containers designed for non-cryogenic fluids shall not be used in this service. Storage tanks shall be tested in accordance with the provisions of applicable ASME, ASTM, or ICC specifications for pressure vessels. Containers for shipment, storage and transfer of liquid fluorine shall be fabricated in accordance with the physical and structural requirements dictated by the use for which they are intended.

3.3.2 Lines and Fittings - For lines and fittings the objective again must be a leakproof plainly designed system free of contamination. A reliable way to join fluorine flow lines is to arc weld them in an inert helium atmosphere (Heliarc process) using a V-notch butt weld; for removable sections, the use of concentrically serrated flanges bolted together against an annealed soft aluminum gasket is acceptable. Bolt tension should be checked frequently, especially after several extreme temperature cycles.

Compression fittings and threaded connections have been used successfully for high pressure fluorine systems in lines less than 3/4 in. diameter, but for 3/4 in. or above they are not considered a reliable joint for liquid fluorine service. Compression fittings above 3/4 in. are more difficult to seat properly than the smaller sizes, thereby increasing the possibility of high pressure leaks. Also they tend to fail more readily from high pressure by tubing pulling out of the fittings.

The threaded type connections should be avoided but have been used successfully when the threaded portion has been silver soldered in place or better if both ends of the threaded section have been welded or brazed; this prevents fluorine from getting into the spaces between the threads where cleaning is difficult.

3.3.3 Valves - Many of the standard globe, plug or needle valves can be adapted for gaseous fluorine by using Teflon valve stem packings. In most cases, liquid fluorine requires that diaphragm- or bellows-sealed valves be used to prevent liquid from contacting the seal material. Because of the extremely low temperatures of liquid fluorine systems, standard valves packed with Teflon or Kel-F are unsuitable although some reliability can be achieved by using a valve on an extension 10 to 12 inches long; vertically mounted valve-bonnet extensions reduce the possibility of liquid fluorine contacting the stem packing since the heat transfer into the valve maintains a gas pocket in the area of the packing. This provides higher packing temperatures, thus preventing leaks that may cause spontaneous ignition.

Hand-operated valves should be equipped with valve stem extension through a suitable barrier for the protection of the operator. This type of operation should be limited to low pressure ($<$500 psi) gaseous systems.

For high pressure liquid fluorine systems, remotely operated diaphragm- or bellows-type valves are preferred. Excellent results have been obtained with valve plugs of Monel or stainless steel and seats of nickel, brass, copper, or aluminum. Valves should be completely disassembled for thorough cleaning prior to use and while the valve is apart for cleaning it is good practice to mate the valve plug in its respective seat for perfect seating. Valve actuators may be either hydraulic or pneumatic.

3.3.4 Pumps and Hoses - The requirement for flexible tubing for liquid fluorine use is that it be all metal. Bellows-section or diaphragm flexer units are designed for a minimum of stress and strain of the required motion and should be adequate for most requirements. Difficulty could be expected if excessive surface flexing causes cracks, flaking or leaks in the tubing or if the design prevents suitable cleaning.

In the event a pump is utilized in a transfer operation, extreme caution should be exercised on the design of the shaft seal. Depending on the use, the seal should be designed to prevent fluorine leakage entirely, or to control the leakage and its path so as to prevent it from mixing or associating with other incompatible elements of the pump.

3.4 Transfer Procedures - Transfer of liquid fluorine is generally accomplished by pressurization with helium or by evaporation of the liquid. It is essential that all of the equipment, lines, and fittings be leak-tight, dry and thoroughly cleansed of all foreign material prior to use.

Because of the fact that fluorine is the most powerful oxidizing agent known, reacting with practically all organic and inorganic substances - exceptions being the inert gases, metal fluorides in the highest valence state, and a few (catalyst and adulterant free) completely fluorinated organic compounds - limited information can be provided here regarding transfer methods and techniques. The necessary procedures for transferring to and from storage containers and various items of equipment shall be based on specific component design features and specific requirements of each test, experiment, or application. All operating personnel shall have complete and thorough instruction prior to any transfer operation.

USE CAUTION --- DOUBLE-CHECK EVERY OPERATION

3.5 Spills, Leaks and Decontamination - All areas containing fluorine under pressure shall be inspected for leaks at suitable intervals. Do not move leaking fluorine cylinders. A leak in the cylinder wall is usually caused by an impurity in the cylinder and is often associated with a pressure rise which may cause the cylinder to rupture. When a valve is found to be leaking, no attempt should be made to tighten the valve or the packing nut. Evacuate the area.

Repair all leaks only after venting the fluorine. The use of filter paper moistened with potassium - iodide solution or moist starch-potassium iodide paper is a very sensitive means of detecting fluorine (down to about 25 ppm). The odor of fluorine is so strong that very low concentrations can be detected, but this is not a safe or reliable method of detecting lethal quantities.

Ammonium hydroxide (aqua ammonia) in a plastic squirt bottle should be used as a rapid qualitative test. This method is used for the detection and location of small gas leaks; the chemical smoke produced is very visible.

Small amounts of fluorine may be disposed of by slow venting. It may also be disposed of by a fluorine-hydrocarbon-air burner, scrubber, and stack. Possibly the safest disposal method is that in which fluorine is converted to unreactive and nontoxic carbon tetrafluoride by passing it through charcoal.

In the event that liquid fluorine is spilled, the contaminated area can be neutralized with sodium carbonate. The dry powder can be sprayed on to the spill area from a fluidized system similar in principle to that of dry chemical fire extinguishers. If major spillages occur in areas where formation of hydrofluoric acid liquid and vapor pose no undue danger, water in the form of a fine mist or fog is recommended. A major portion of the fluorine will be converted to hot, light gaseous products which rise vertically and diffuse quickly into the atmosphere.

3.6 Cleaning Procedures - Equipment is to be cleaned in accordance with the provisions of Appendix A.

BIBLIOGRAPHY

DESIGN HANDBOOK FOR LIQUID FLUORINE GROUND HANDLING EQUIPMENT (Second Edition) - Aerojet-General Corp., AFRPL-TR-65-133 (Aug. 1965) Contr. AF 04(611)-10541, 484 pp 126 fig 72 tab 265 ref - DDC AD 468 216.

This handbook is a compilation of available design data and methods of operation representing present technical experience levels as applied to fluorine. In addition, it includes design and operational data for liquid helium, liquid oxygen and liquid nitrogen systems in those areas likely to be of use to a designer of a liquid fluorine facility.

The handbook also contains considerable design information to assist the designer in scaling up current sizes of fluorine and cryogenic systems to meet the designer's specific requirements.

Because no exact system requirements are specified, no optimum system is selected, though several fluorine systems are discussed. Both advantages and disadvantages of the various components are discussed to enable the designer to choose the best system for his particular needs. Bases for comparison include cost, availability, length of operation, fluorine loss and location.

THE PROPERTIES AND HANDLING OF FLUORINE - Air Products & Chemicals, Inc., ASD-TDR-62-273 (Oct. 1963) Contr. AF 33(616)-6515, 131 pp 11 fig 57 tab 187 ref - DDC AD 423 751.

This report presents data on properties of fluorine, methods of analysis, safe-handling procedures, compatibility of materials of construction with fluorine, corrosion rates of metals, and bibliography of pertinent references.

FLUORINE (Product Information Technical Bulletins) - General Chemical Division, Allied Chemical and Dye Corporation, New York.

Information from "the nation's primary supplier of fluorine, in both gaseous and liquid forms for commercial and research applications" on the storage, handling, safety, and material compatibility of fluorine.

BIBLIOGRAPHY OF FLUORINE - Briggs, C. (Ed.), Martin Company, Denver, Colo. (July 1, 1961) 12 pp DDC AD 293 821.

This compilation includes titles of approximately 142 documents related to the use of fluorine in liquid rocket engines. Covered in this listing are books, reports, journals, and magazines prior to, and including, the year 1961.

BIBLIOGRAPHY OF FLUORINE AND FLUORINE-OXYGEN OXIDIZERS FOR SPACE APPLICATIONS - Cabaniss, J. H. - NASA TM X-53149 (Oct. 1964) 76 pp 353 ref.

The bibliography references approximately 350 reports on fluorine and fluorine-oxygen mixtures (FLOX). In the introduction, current government contracts pertaining to FLOX and fluorine are listed. The bibliography includes separate sections dealing with material compatibility; handling, storage, disposal, and safety considerations; physical and chemical properties; propellant oxidizer studies; vehicle component design studies; and miscellaneous reports.

A LITERATURE SURVEY OF THE CORROSION OF METAL ALLOYS IN LIQUID AND GASEOUS FLUORINE - Cabaniss, J. H. and Williamson, J. G. - NASA-George C. Marshall Space Flight Center, Huntsville, Ala. - Internal Report MTP-P & VE-M-63-21 (Dec. 31, 1963).

A literature survey on the corrosive nature of both liquid and gaseous fluorine is presented. This paper contains general information regarding: (1) chemical reaction of fluorine with various metallic materials; (2) conditions under which these materials can be used with fluorine; (3) results of corrosion tests that have been conducted on various materials over the range of -320°F (-196°C) to 1300°F (704°C).

FLUORINE PROPULSION TECHNOLOGY - Flanagan, J. R. and Stephenson, F. W., Jr. - AIAA Second Annual Meeting, July 26-29, 1965, AIAA Paper No. 65-536.

This paper presents a review of the technological investigations that have been conducted to advance the state-of-the-art of fluorine propulsion. It also reports the key accomplish-

ments in the current technological investigations and discusses the role that fluorine may play in our future space program.

HANDLING FLUORINE AND FLUORINE COMPOUNDS - The International Nickel Company, Inc., New York.

A general information document concerning fluorine and fluorine compounds.

EXPERIMENTAL EVALUATION OF LIQUID FLUORINE SYSTEM COMPONENTS - DeWitt, R. L. and Schmidt, H. W. - NASA-Lewis Research Center, Cleveland, Ohio - NASA Tech. Note D-1727 (June 1963).

The investigation reported here was undertaken primarily to design, develop, and test prototype flight hardware to be used in systems for the safe ground-to-vehicle transfer of liquid fluorine and secondarily to test the capability of liquid fluorine with the materials and fabrication techniques used in construction of the hardware. The prototype hardware consisted of a "quick-disconnect" coupling and a valve, which were designed and fabricated at the Lewis Research Center, and a commercially procured rotating-vane flowmeter.

FRICTION, WEAR, AND DYNAMIC SEAL STUDIES IN LIQUID FLUORINE AND LIQUID OXYGEN - Hady, W. F., Allen, G. P., Sliney, H. E., and Johnson, R. L. - NASA-Lewis Research Center, Cleveland, Ohio - NASA Tech. Note D-2453 (Aug. 1964) 15 pp.

Friction and wear of four material combinations were determined running submerged in liquid oxygen and in liquid fluorine. Results of these studies and two face contact seals run submerged in liquid fluorine indicated that Al_2O_3 sliding against either a fused fluoride film on Al_2O_3 or a nickel-bonded TiC cermet are acceptable material combinations for fluorine seal applications. The presence of a fluoride film, either as an applied fused coating (CaF_2 + LiF + NiF_2) or as a film formed during sliding (NiF_2 on a nickel-bonded TiC cermet or possibly AlF_3 on Al_2O_3) in liquid fluorine was beneficial in reducing friction and wear of the Al_2O_3 riders.

HANDLING LIQUID FLUORINE IN ROCKET APPLICATIONS- Kimball, A. R., *Advances in Cryogenic Engineering* 5, 77-84 (Proc. of 1959 Cryogenic Eng. Conf.) Plenum Press, Inc., New York (1960) Paper B-1, 3 fig 1 tab.

Fluorine is extremely attractive as the oxidizer in rocket propulsion systems in view of the 40% performance increase that may be realized by replacing present day operational propellants with a high-energy combination. Development of fluorine propulsion systems has, however, been approached cautiously because of concern expressed in view of its extreme reactivity and toxicity.

In this paper a review is made of the present state-of-the-art (1959) and Bell Aircraft Corporation's findings in the areas of material compatibility, equipment fabrication, operating techniques, instrumentation, and safety when using liquid fluorine.

LIQUID FLUORINE - PRODUCTION AND HANDLING - Neumark, H. R. - Allied Chemical Corporation - Presented at 2nd Missile Liquid Propellant Symposium (Nov. 1964).

A discussion and clarification of some of the problems related to the use of liquid fluorine.

THE COMPATIBILITY OF VARIOUS METALS WITH LIQUID FLUORINE - Kleinberg, S. and Tompkins, J. F. - Air Products, Inc., Allentown, Pa. - ASD-TDR-62-250 Report for Oct. 1960-Oct. 1961 on Finishes and Materials Preservation (Mar. 1962) Contr. AF 33(616)6515, 114 pp 22 fig 19 tab 14 ref.

Studies were made of liquid fluorine and its contaminants, reactions on metal surfaces, fluoride films, and immersion tests of tensile specimens. A method of preparing contaminant-free fluorine and its infrared analysis is discussed.

COMPATIBILITY OF POLYMERIC MATERIALS WITH FLUORINE AND FLUORINE-OXYGEN MIXTURES - Russell, L. M., Schmidt, H. W., and Gordon, L. H. NASA-Lewis Research Center, Cleveland, Ohio - NASA Tech. Note D-3392 (June 1966) 39 pp 17 fig 5 tab 3 ref.

Compatibility tests were performed on a number of polymeric materials with the use of various mixtures of fluorine and oxygen in both gaseous and liquid states. The purpose of these tests was to investigate the feasibility of using fluorine-oxygen mixtures in rocket-propulsion systems containing some nonmetallic materials. The tests were divided into two major areas, static tests and dynamic tests.

In the static tests, a number of test samples were exposed to various FLOX (fluorine-oxygen) mixtures, both gaseous and liquid, at atmospheric pressure and virtually static conditions in order to obtain information on compatibility solely as a function of fluorine concentration. The reactivity of the materials tested with FLOX under static conditions is a function of the concentration of fluorine in the mixture.

In the dynamic tests, selected materials were exposed to fluorine and FLOX at various combinations of concentration and flow velocity. Reactivity profiles were generated for these materials as functions of these two parameters. At any given fluorine concentration, flow velocity was a strongly significant parameter in the reactivity of FLOX with all materials tested. Generally the fluorocarbon polymers, particularly the fully fluorinated, straight-chain polymers were the most compatible with fluorine and with FLOX.

In both static and dynamic tests, a comparison between cryogenic liquid and ambient-temperature gaseous test results indicated that the liquid was the more reactive.

It was concluded that some of the materials tested may be considered for use in rocket systems with fluorine or FLOX under controlled conditions of exposure; however, because of possible variations in quality and because polymers are more sensitive to contamination than metals in a fluorine environment, they should be used with a margin of safety.