

**RECOMMENDED MATERIALS AND PRACTICES FOR
USE WITH CRYOGENIC PROPELLANTS**

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Revised

FOREWORD

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.

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I. RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH CRYOGENIC PROPELLANTS

- A Compilation from the Literature with Annotated Bibliography -

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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, hygienic 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
Ground Support Systems for Missiles and Space Vehicles

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

Journals

Cryogenics - An International Journal of Low Temperature Engineering and Research

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

Cryogenic Data Book

Compatibility of Rocket Propellants with Materials of Construction

Metals and Alloys for Cryogenic Application - A Review

Manuals

The Handling and Storage of Liquid Propellants
Liquid Propellant Manual
Manual for Handling Missile Propellants

Miscellaneous Papers

Cryogenic Piping System Design Considerations
Design of Cryogenic Storage Tanks for Industrial Applications
Safe Handling of Cryogenic Fluids
The Storage and Handling of Cryogenic Liquids

Miscellaneous Reports

Sparking Characteristics and Safety Hazards of Metallic Materials
Fire-Hazard Properties of Flammable Liquids, Gases, and Volatile Solids
Review of Fire and Explosion Hazards of Flight Vehicle Combustibles

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)

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.

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.

ADVANCES IN CRYOGENIC ENGINEERING - Timmerhaus, K. D. (Editor) - Advances in Cryogenic Engineering Vols. 1-9, Plenum Press, New York (1960-64)

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 Sys-

tems, (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.

CRYOGENICS - AN INTERNATIONAL JOURNAL OF LOW TEMPERATURE ENGINEERING AND RESEARCH - Mendelsohn, 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.

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, (L₂₉₃-LT) L₂₉₃, and the linear expansion coefficient, dL/L₂₉₃dT, of thirty elements, forty-five alloys, twenty-two other inorganic substances and twenty plastics and elastomers in the temperature range, 0 to 300°K.

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.

METALS AND ALLOYS FOR CRYOGENIC APPLICATION - A REVIEW - Kendall, E. G. - Aerospace Corp., ElSegundo, 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.

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. ASTIA 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.

THE HANDLING AND STORAGE OF LIQUID PROPELLANTS - Liquid Propellant Information Agency, Defense Research and Engineering, Wash., D. C. (March 1961) 248 pp.

This manual is being published for information; it is intended that it can be used 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) ASTIA 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.

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.

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 O₂, N₂, A, CH₄, F₂, H₂, 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.

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).

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.

II. RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH LIQUID OXYGEN

- A Compilation from the Literature with Annotated Bibliography -

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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 Ohmstead 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 contrac-

tors, 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 meantime 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-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.

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. ASTIA 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.

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 ASTIA 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.

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/ft² 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.

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 ASTIA 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.

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.

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 accentuated. Included in this article are properties of liquid and gaseous oxygen, materials compatibility with oxygen, flammability and ignition characteristics, etc.

PRECAUTIONS AND SAFE PRACTICES FOR HANDLING LIQUEFIED ATMOSPHERIC 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.

OXYGEN PLANT SAFETY PRINCIPLES - McKinely, 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.

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.

PHYSICAL PROPERTIES OF LIQUID OXYGEN

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 solid and dP/dT of fusion line by the Clapeyron equation.

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

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)

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	0.0406	4, 5		
		Liquid	0.0392	a		
		Vapor	0.00000336	4		
Normal Boiling Values	Temperature (T _b), °K		90.180	b		
	Density, mole/cc	Liquid	0.0357	4, 6, 7		
		Vapor	0.000140	4		
Critical Values	Temperature, °K		154.77	2, 3		
	Pressure, mm Hg		38109	2, 3		
	Density, mols/cc		0.013	3		
One Liter Liquid (NBT) Equivalents	Weight, kg		1.14	1, 4, 6, 7		
	Volume of Gas, liters	NBT	255	4, 6, 7		
		NTP	861	2, 4, 6, 7		
Equivalent Volumes of Gas per Volume of Liquid (NBT)		NBT	255	4, 6, 7		
		NTP	861	2, 4, 6, 7		
Heat of Fusion, Cal/mole		TP	106.3	4, 8		
Heat of Vaporization, Cal/mole		NBT	1630	4		
Specific Heat Cal/mole-°K	C _s	Solid	TP	11.1	4, 8	
		Liquid	NBT	13.0	4, 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	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	
		Vapor	NBT	0.00001930	13	
		Gas	NTP	0.00006277	13	
Viscosity μ Gm/cm-sec		Liquid	NBT	0.00190	14, 15	
		Vapor	NBT	0.0000692	16, 17	
		Gas	NTP	0.0002033	2	

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	81.0	4, 5		
		Liquid	78.2	a		
		Vapor	0.000670 ^b	4		
Normal Boiling Values	Temperature (T _b), °F		-297.35	2, 3		
	Density, lb/ft ³	Liquid	71.2	4, 6, 7		
		Vapor	0.279	4		
Critical Values	Temperature, °F		-181.08	2, 3		
	Pressure, psia		736.90	2, 3		
	Density, lb/ft ³		27	3		
One Gallon Liquid (NBT) Equivalents	Weight, lb		9.52	1, 4, 6, 7		
	Volume of gas, ft ³	NBT	34.1	4, 6, 7		
		NTP	115	2, 4, 6, 7		
Equivalent Volumes of Gas per Volume of Liquid (NBT)			NBT	255	4, 6, 7	
			NTP	861	2, 4, 6, 7	
Heat of Fusion, Btu/lb			TP	5.976	4, 8	
Heat of Vaporization, Btu/lb			NBT	91.63	4	
Specific Heat Btu/lb-°F	C _s	Solid	TP	0.346	4, 8	
		Liquid	NBT	0.405	4, 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	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	
		Vapor	NBT	0.004666	13	
		Gas	NTP	0.01517	13	
Viscosity μ Centipoise		Liquid	NBT	0.190	14, 15	
		Vapor	NBT	0.00692	16, 17	
		Gas	NTP	0.02033	2	

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III. RECOMMENDED MATERIALS AND PRACTICES FOR USE WITH LIQUID HYDROGEN

- A Compilation from the Literature with Annotated Bibliography -

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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 deflagration 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.

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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 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.

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.

CRYOGENIC HYDROGEN - Pratt and Whitney Aircraft Div., United Aircraft Corporation, Booklet S-132 (Feb. 1960).

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 "new" and promising fuel. Sections of the booklet deal with preparation, storage, handling, physical and thermodynamic properties of hydrogen.

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.

SAFETY IN THE USE OF LIQUID HYDROGEN - Chelton, D. B. - Publication arrangements in progress. (To be a chapter in a book on The Technology and Uses of Liquid Hydrogen, Pergamon Press, London) 5-11-62 6 fig 3 tab 17 ref.

Safety in systems using liquid hydrogen is a subject of considerable present-day importance. Reducing or eliminating the potential safety hazards involved requires a basic understanding of the physical and chemical properties of hydrogen and the application of known safety technology. These factors are reviewed and recommendations are given for safety criteria. Comparisons are made with propane and methane to assist in establishing the relative hazard. Consideration is given in the use of liquid hydrogen on a large scale and on a laboratory scale.

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.

STORAGE, TRANSPORT, AND TRANSFER OF LIQUID HYDROGEN - Jacobs, R. B. - Publication arrangements in progress. (To be a chapter in a book on The Technology and Uses of Liquid Hydrogen, Pergamon Press, London) 7-19-62 23 fig 4 tab 45 ref.

This work presents information useful to designers and users of equipment for the storage, transport, and transfer of liquid hydrogen. The topics discussed are, in general, confined to those which are unique to cryogenic equipment; those concepts and techniques which are used in connection with equipment that operates at normal temperatures are not discussed. The chapter is divided into three sections: Thermal Insulation, Containers, and Transfer Systems. The discussion of thermal insulation includes information for non-insulated equipment, for non-vacuum insulated equipment, and for vacuum insulated equipment. Examples of other areas that are discussed include instrumentation, cool-down requirements, pressurization, valves, pumps, and fluid mechanical design.

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.

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.

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