NATIONAL BUREAU OF STANDARDS REPORT

4711

A SURVEY OF THE HAZARDS OF
HANDLING LIQUID OXYGEN

by

C. S. McCamy

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services.

Radio Propagation Engineering. Frequency Utilization Research. Tropospheric Propagation Research.

Radio Standards. High Frequency Standards Branch: High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Microwave Standards Branch: Extreme High Frequency and Noise. Microwave Frequency and Spectroscopy. Microwave Circuit Standards.

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0302-10-2604 June 18, 1956 4711

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Interdivision work order No. 03-2651

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1. INTRODUCTION

Proposed increased use of liquid oxygen has prompted the following brief review of the characteristics of this material which determine the hazards involved in its use.

2. LIQUID OXYGEN

At normal atmospheric pressure (760 mm of Hg), liquid oxygen has the following properties (1)*

boiling point	-183.0°C
density	1.14 gm/cm^3
heat capacity	0.394 cal/gm-°C
heat of vaporization	50.9 cal/gm
critical temperature	-118.8°C
critical pressure	49.7 atm
critical density	0.430 gm/cm^3

On passing from the liquid state at the boiling point to the gaseous state at 20°C (both at a pressure of 760 mm Hg), oxygen expands to about 858 times the initial volume. If the material were confined to the initial volume during this increase in temperature, the pressure would increase to about 2440 atmospheres, as calculated by the method of Hirschfelder and co-workers (2) on the basis of the critical constants given above. Consequently, the pressure rupture of liquid oxygen containers is likely if proper venting is not provided.

The properties of most materials are altered considerably when they are cooled from room temperature to the temperature of liquid oxygen (3, 4, 5, 6, 7). This fact must be borne in mind in designing equipment for storage and handling of liquid oxygen. With few exceptions, ferrous alloys are too brittle for use at these temperatures but the following metals are useable at the temperature of liquid oxygen and are listed in order of increasing brittleness (6): pure nickel, monel metal, inconel, copper, aluminum, 18-8 low carbon stainless steel, and annealed brass.

*Numbers in parenthesis correspond to the references at the end of this report.

The differences in thermal coefficients of expansion of materials may give trouble where close dimensional tolerances must be maintained.

Exposure of the flesh to materials at the temperature of liquid oxygen for more than a few seconds can cause tissue damage similar to that produced by severe burns. Protective clothing made of asbestos or degreased chrome leather lined with relatively impermeable materials such as polyvinyl chloride, polyethylene, or neoprene has been recommended (5,7).

Violent boiling and splashing usually occurs if liquid oxygen is poured into a wide mouthed container at or above room temperature or if any warm object is placed in contact with the liquid.

3. LIQUID OXYGEN WITH OTHER MATERIALS

The oxygen concentration, in weight per unit of volume, of 98% pure liquid oxygen is about 4000 times that in dry air at 20°C and 760 mm Hg, therefore oxidation reactions, once initiated, proceed at very high rates in the presence of the liquid. Though it might seem that such a cold liquid would extinguish a burning match, the actual effect of such a combination is deflagration of nearly explosive violence (4). Finely divided charcoal saturated with liquid oxygen may comprise an explosive similar in many respects to 40 - percent nitroglycerine dynamite and this combination is used as an industrial explosive (8, 9, 10). Other materials that have been used in this way are wood pulp, cotton, lampblack, carbon black, various chars, hydrocarbons, metal powders, sulfur, and coal dust (10). Mixtures of any of these materials and liquid oxygen detonate so readily that it seems likely that an intimate mixture of liquid oxygen and almost any combustible material might detonate under certain conditions. The following incident illustrates this point. A leak developed in a pipe joint in a liquid oxygen line and the liquid flowed onto an asphalt-paved surface directly below. When a workman attempting to repair the leak struck the joint, the impact was transmitted by the joint to the pavement below and the pavement detonated. Among the materials considered particularly hazardous in the presence of liquid oxygen are sulfur, hydrocarbons, alcohols, ethers, fuels of all kinds, oils, greases, waxes, tars, asphalt, starches, sugars, soaps, powdered metals, wood, cork, paper, textiles, rope, paints, and some plastics (3, 4, 5, 8, 9, 10, 11, 12, 13, 14). Since

liquid oxygen is denser than water and most liquid petroleum products, it will sink in such materials and boil violently, producing an intimate mixture. Porous materials may retain a large concentration of gaseous oxygen long after the liquid has vaporized. It appears that the hazard represented by a small sample of a given material when soaked in liquid oxygen does not differ appreciably between samples soaked 24 hours and those immersed for 2 or 3 minutes (14). Thermal insulating materials for use around oxygen containers must be chosen with due regard for the conditions which would result from a leak. Inorganic materials such as glass wool or magnesium carbonate may be used if they contain no flammable additives. Ordinarily, to avoid the flammability hazard of paint, pipe lines carrying liquid oxygen are not painted.

4. GASEOUS OXYGEN

In the gaseous state, at 0°C and 760 mm Hg, oxygen has a density of 1.429 g/ℓ. Oxygen constitutes about 21% by volume or about 23% by weight of the earth's normal atmosphere at sea level. Wherever liquid oxygen is handled or stored, the continual release of gas is required to maintain normal pressure. Besides the precautions necessary to prevent the pressure rupture of containers, it is necessary to provide sufficient ventilation to prevent excessive concentration of gaseous oxygen in confined spaces. In general, combustible materials burn violently in an atmosphere of oxygen. Glowing or smoldering materials, including metals, burst into flame or brilliant candescence when introduced into oxygen. Mixtures of flammable vapors or dusts with gaseous oxygen may be explosive (10).

Although the human body can tolerate rather wide variations in the oxygen concentration in the atmosphere, prolonged exposure to an atmosphere containing 80 percent or more of oxygen can induce a pneumonia (15).

5. IGNITION

The prevention of ignition is a matter of greatest importance wherever liquid oxygen is handled.

Friction in itself may be regarded as a possible source of ignition where oxygen is in contact with combustibles (10). An incident is reported in which liquid oxygen had been spilled on a gravelled surface and detonation occurred, presumably in asphalt beneath the gravel, when a man walked across the gravelled surface.

A large number of materials may be placed in liquid oxygen for a few minutes and detonated by impact (14).

On the basis of two experiments with a vegetable base fiberboard in an adiabatic furnace at the National Bureau of Standards, it appears that the rate of self-heating was not greatly affected by increased oxygen concentration in the atmosphere at temperatures below 200°C but the change in rate with respect to temperature was somewhat increased. Above 200°C the rate of self heating was considerably higher in the enriched atmosphere than it was in air. Materials containing unsaturated hydrocarbons should be considered particularly hazardous in this respect. It appears that heaters and steam lines which would not otherwise be considered potentially hazardous heat sources might become so in the presence of an oxygen-rich atmosphere.

The lower dilution limit of flammability of combustible gases is generally very little different in oxygen than in air (16).

Tests have shown that the liquid-oxygen explosives in use in industry were rather insensitive to ordinary electrostatic discharges and that the discharge energy required to constitute a hazard was considerably greater than would ordinarily be encountered, except where lightning or electric power line sparking are involved (10).

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THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the front cover.

Reports and Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers and reports. Reports are issued to the sponsoring agency of a particular project or program. Published papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three monthly periodicals, available from the Government Printing Office: The Journal of Research, which presents complete papers reporting technical investigations; the Technical News Bulletin, which presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions, which provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: The Applied Mathematics Series, Circulars, Handbooks, Building Materials and Structures Reports, and Miscellaneous Publications.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.25) and its Supplement ($0.75), available from the Superintendent of Documents, Government Printing Office. Inquiries regarding the Bureau's reports and publications should be addressed to the Office of Scientific Publications, National Bureau of Standards, Washington 25, D. C.

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