Care with Cryogenics.
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This document is designed to be used in conjunction with BOC’s publications: “Controlling the Risks of Oxygen” or “Controlling Risks of Inert Gases” and is an overview of the hazards and precautions to be taken when handling low temperature liquefied gases.

People with a special responsibility for safety or who are engaged in teaching or training others in the use of low temperature liquefied gases should refer to more comprehensive materials available from EIGA at www.eiga.org.

Introduction.

There are a number of potential hazards when using gases that are liquefied by cooling them to low temperatures. These may be referred to as “CRYOGENIC” liquids. The gases covered in this document and their physical properties are detailed in the table below. All the gases are non-flammable, although liquid oxygen is an oxidant and can promote vigorous combustion of many materials.

<table>
<thead>
<tr>
<th>Property</th>
<th>Oxygen (O₂)</th>
<th>Nitrogen (N₂)</th>
<th>Argon (Ar)</th>
<th>Helium (He)</th>
<th>Carbon dioxide (CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>32</td>
<td>28</td>
<td>40</td>
<td>4</td>
<td>44</td>
</tr>
<tr>
<td>Colour of gas</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Colour of liquid</td>
<td>Light Blue</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Normal boiling point (°C)</td>
<td>-183</td>
<td>-196</td>
<td>-186</td>
<td>-269</td>
<td>-78.5 (sublimes)</td>
</tr>
<tr>
<td>Ratio of volume gas (measured at 15°C and Patm) to volume of liquid (measured at Tb and Patm)</td>
<td>842</td>
<td>682</td>
<td>822</td>
<td>758</td>
<td>845 (solid)</td>
</tr>
<tr>
<td>Relative density of gas at Patm (Air = 1)</td>
<td>1.105@25°C</td>
<td>0.967@25°C</td>
<td>1.380@0°C</td>
<td>0.138@0°C</td>
<td>1.48@25°C</td>
</tr>
<tr>
<td>Liquid density at Tb and Patm (kg/m³)</td>
<td>1142</td>
<td>808</td>
<td>125</td>
<td>1564 (solid)</td>
<td></td>
</tr>
<tr>
<td>Latent heat of evaporation at Tb (kJ/kg)</td>
<td>213</td>
<td>199</td>
<td>163</td>
<td>573 (sublimation)</td>
<td></td>
</tr>
</tbody>
</table>
Low temperature hazards.
Cold burns, frostbite and hypothermia.

Cold burns and frostbite
Because of the low temperature of liquefied atmospheric gases, the liquid, cold vapour or gas can produce damage to the skin similar to heat burns. Unprotected parts of the skin coming into contact with uninsulated items of cold equipment may also become stuck to them and the flesh may be torn on removal.

Cold vapours or gases from liquefied atmospheric gases may cause frostbite, given prolonged or severe exposure of unprotected parts. A symptom that usually gives warning of freezing is local pain, however sometimes no pain is felt or it is short lived. Frozen tissues are painless and appear waxy, with a pale yellowish colour. Thawing of the frozen tissue can cause intense pain. Shock may also occur.

Treatment of cold burns
The immediate treatment is to loosen any clothing that may restrict blood circulation and seek hospital attention for all but the most superficial injuries. Do not try to remove clothing that is frozen to skin. Do not apply direct heat to the affected parts, but if possible place the affected parts in tepid water until the skin is released.

Cryogenic systems must therefore be designed with adequate pressure relief on storage vessels and anywhere where liquid may be trapped, such as pipework between valves.

Overpressurisation
When vaporised into gas, all of these liquefied gases increase many hundreds of times in volume. This results in a large pressure increase if the volume change is restricted. The normal inmate of heat through the insulated walls of the storage vessels and pipework into the cryogenic liquid raises its temperature and hence, with time, the pressure rises due to the generation of gas.

Contact with cold surfaces
Where possible, insulate all exposed cold surfaces using suitably approved materials.

Splashes and spillages
→ Use suitable PPE
→ Use approved manual handling equipment when moving vessels containing cryogenic liquids
→ Report all leaks immediately

Prolonged exposure to low temperature environments
→ Use suitable insulating PPE
→ Minimise time of exposure

Inadequate design/incorrect choice of materials
→ Only use competent system designers
→ Only use approved materials
→ Conduct regular planned preventative maintenance
→ Do not exceed the flow rate specified for the equipment

Liquid argon cannot condense air from the atmosphere.

Embrittlement
The most significant consideration when selecting equipment and materials for low temperature use is that of possible brittle fracture. Carbon steel is extremely brittle at the cryogenic temperatures of liquid nitrogen, argon and oxygen. (Certain types of carbon steel can be used with cryogenic carbon dioxide because it is relatively warm in comparison to liquid nitrogen, argon and oxygen.) Metals used in any equipment should satisfy the impact test requirements of the design code being used.

If there is a change in the use of a plant from its original design, it may result in the liquid usage rate exceeding the capacity of the vaporising equipment. This can cause cryogenic liquid to reach parts of the equipment that were not originally intended for low temperature conditions, increasing the risk of potential brittle fracture.

Liquid air condensation
Whilst nitrogen and helium appear to be safe from the risk of combustion because they are inert, these liquids are cold enough at normal boiling points to condense air from the atmosphere. This condensed air contains higher oxygen content than normal air, increasing the risk of combustion. It is therefore essential that the vessel is properly insulated. It is also recommended to exclude combustible insulating materials from liquid nitrogen and helium systems and installations.

Dense cold vapour
Due to the relatively high density of the cold vapour of the liquids, the gases may collect and persist in areas which may not be immediately recognisable as confined spaces, posing an oxygen deficiency or enrichment hazard. Manholes, trenches, basements, drainage systems, underground service ducts and any low lying, poorly ventilated areas may pose such a hazard and entry into these areas should be controlled by a Permit to Work.
Preventative measures.

Information and training

All people who work with low temperature liquefied gases or systems using such gases should be given adequate training on the risks of asphyxiation, fire hazards, cold burns, frostbite and hypothermia. Special attention should be drawn to the insidious nature of the risks due to the rapidity of the effects, coupled with the fact that an operator may be completely unaware that a hazardous condition has developed.

Protective clothing

Protective clothing is only intended to protect the wearer handling cold equipment from accidental contact with liquefied atmospheric gases or parts in contact with it. Non-absorbent leather gloves should always be worn when handling anything that is, or has been recently, in contact with cryogenic liquids. The gloves should be a loose fit so that they can easily be removed if liquid should splash onto or into them. Gauntlet gloves are not recommended because liquid can easily splash into the wide cuff.

It is essential that clothing is kept free of oil and grease where oxygen is in use.

If clothing becomes contaminated with liquefied atmospheric gases or their vapour, the wearer should ventilate it for a minimum of five minutes whilst walking around in a well-ventilated area. The risk with contamination by liquid oxygen is of rapid burning of the material, even when started via a tiny ignition source (a spark or a piece of burning tobacco).

Therefore, in these circumstances it is essential to ventilate clothing for at least 15 minutes (or replace it) and to keep away from any such source of ignition.

Woven materials are best avoided, but if they are used for protective clothing, it is essential to ensure that they do not become saturated with cold liquid.

Goggles or a facemask should be used to protect the eyes and face when carrying out operations where spraying or splashing of liquid may occur. Overalls or similar clothing should be worn. These should be without open pockets or turn-ups where liquid could collect. Trousers should be worn outside boots for the same reason.

A person whose clothing catches fire should be deluged with water from a shower, hose or series of fire buckets and moved into the fresh air as soon as possible. It is very dangerous to attempt to rescue a person catching fire in an oxygen-enriched atmosphere, as the rescuer is likely to catch fire as well. (In some cases it may be possible to enter such a space if the rescuer is totally deluged with water and protected by constant water hosing).

Because of its low boiling point and latent heat of evaporation, liquid helium is supplied in specifically designed dewars which must be handled with care at all times. In particular, liquid helium dewars should not be filled with other liquids whose higher specific gravity might result in failure of the suspension system.

This liquid can only be transferred in vacuum insulated lines and equipment. Even some types of steels which are satisfactory at liquid nitrogen temperature, become brittle when in contact with liquid helium.

Liquid helium.

Any receiving equipment or dewars which have been precooled with liquid nitrogen must be clearly identified and subsequently purged with pure helium gas prior to transfer to liquid helium service. Liquid helium can solidify all other known gases and liquids.

The oxygen enrichment hazard, due to condensation of the air is much more significant than with liquid nitrogen. All equipment which may be at liquid helium temperatures must be kept clean to the same standards as liquid oxygen installations.

Dewars.

Safe working procedures must be developed and adhered to for the use of dewars, including their transportation within and around the premises. Special safety procedures are necessary when carrying filled dewars in lifts. Only use dewars that are correctly and clearly labelled. Always ensure that adequate ventilation is provided in areas where dewars are filled, used or stored.

Adequate emergency procedures must be in place in the event of a liquid spillage, cold burn or suspected asphyxiation. Ice plugs can form in the neck of dewars and can be ejected at high velocity due to pressure build up. Avoid them by ensuring that protective caps are always used and that dewars are fully emptied before being taken out of use or put into storage.

Refer to BCGA (British Compressed Gases Association) CP30 for further guidance.
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