

# Safety Advice.

## 13 – Handling of Hydrogen.



### 1. Introduction

For the safe handling of hydrogen, it is important to know its properties and the necessary safety measures. This Safety Advice describes the properties that are relevant to its safety, and provides practical hints for working safely with this gas. It supplements, but does not replace, any national or international regulations.

### 2. Properties

#### 2.1. Physical Properties

Hydrogen is the lightest of all gases (density 84 g/m<sup>3</sup> at a temperature of 15 °C and 1 bar). That is why escaping hydrogen will immediately rise upwards and accumulate under ceilings or similar areas.

Hydrogen is either stored in gaseous form in cylinders or tanks at ambient temperature under high pressure (up to 300 bar), or it is stored or transported almost pressureless in the form of cryogenic liquid hydrogen in isolated receptacles. A pressure release of hydrogen at normal temperature results – unlike with other gases – in a slight rise in temperature. The temperature rises from 20 to 25 °C when the pressure falls from 175 to 1 bar. This rise in temperature is not sufficient to cause the escaping hydrogen to ignite on its own, since the ignition temperature lies by 600 °C.

Liquid Hydrogen (LH<sub>2</sub>) is a very light liquid (density 70 g/litre at a temperature of –253 °C). LH<sub>2</sub> evaporates very quickly at normal temperature, creating about 845 litres of gaseous hydrogen out of 1 litre LH<sub>2</sub>. Immediately after evaporation the gaseous hydrogen is still very cold and has approximately the same weight as air. That is the reason that it spreads out almost horizontally. However, it does warm up

very fast. Its density is continually reduced and it then spreads upwards.

At the temperature of liquid hydrogen all liquids and gases – except for helium – are solid. That is why all other substances have to be kept away from LH<sub>2</sub> installations. A mixture of solid air and LH<sub>2</sub> would have explosive characteristics.

The low temperature of the liquid hydrogen causes the atmospheric air to condense on the outside of installation parts that haven't been insulated. Through the partial evaporation of nitrogen the liquid air could become enriched with oxygen and when coming into contact with combustible substances, act as a fire agent.



Flammable substance warning

#### 2.2. Chemical Properties

Hydrogen when combined with air or oxygen and then ignited will burn to water. Hydrogen can also react with other oxidising agents, i. e. chlorine or laughing gas. When hydrogen is combined with an oxidising agent and then ignited, the burning process can be explosive. If this process takes place in a closed room, a rapid pressure rise, which can be very destructive, can take place because of the generated heat.

The concentration levels at which hydrogen can react with air under normal pressure and normal temperature are, compared with other combustible gases, very wide spread (the lower explosion limit being – LEL – 4 vol.-%; the upper explosion limit being – UEL – 75,6 vol.-%). Hydrogen/air mixtures are ignited through ignition sources containing very little energy. The least amount of energy needed to ignite hydrogen is 0,019 mJ which is only 1/10 of that of propane. For instance particles of rust, which have been transported by a fast flowing jet of hydrogen can develop an igniting spark through electrostatic charge or by hitting an object. Because it is difficult to recognize or prove this ignition source, hydrogen has been unjustly thought to be able to ignite itself.

A hydrogen flame is very pale and cannot be seen in bright daylight. Other indications must be used, for example a piece of paper into the suspected area.

Of course liquid hydrogen has the same chemical properties as gaseous hydrogen. However, the ability to react with oxygen is slightly reduced because of the low temperature.

#### 2.3. Corrosion, Materials

Hydrogen is noncorrosive. At normal temperature the usual metallic materials – steel, copper, brass, aluminium – are suitable for hydrogen.

Some types of steel can be damaged by hydrogen under certain circumstances, for instance when production flaws (crackings, embeddings) are present. That is why the materials used in hydrogen installations have to be chosen by experts, who are familiar with the specific operating conditions. Apart from metallic materials, rubber

and plastics can also be used for hydrogen installations.

Hydrogen is a very “flexible” gas. The tiny molecules can find their way into materials or tight fissures, that would be impermeable for other gases. Cast materials should not be used for hydrogen, because their porosity could be the cause for leaks.

Because of its low temperature, liquid hydrogen can cause embrittlement in rubber, plastics and carbon steel. Because of this the ductility of these materials can be greatly reduced. That is why these materials are not suitable for use in LH<sub>2</sub>-installations.



## 2.4. Physiological Effects / Environmental Protection

Hydrogen is a colourless, odourless and tasteless gas and therefore cannot be perceived with the human senses.

Hydrogen is not poisonous. When inhaled in large concentrations it will cause suffocation. People should not be allowed in such an atmosphere because of the explosion danger. For this reason respiratory protection is not relevant when working with hydrogen. Cryogenic hydrogen in liquid or gaseous form (just evaporated) can cause cryogenic burns when brought into contact with the skin. The same applies when the skin gets into contact with any uninsulated pipe or equipment containing liquid hydrogen. Please also note Linde Safety Advice 1 “Handling of cryogenic liquefied gases”.

Hydrogen does not impose a danger to the environment. It doesn't harm the ozone layer and doesn't contribute to the greenhouse effect. The combustion exhaust gas of hydrogen is water and not carbon dioxide or soot.

## 2.5. Characteristics of Gas Mixtures Containing Hydrogen

Gas mixtures do not become separated under the influence of gravity. When for instance, a mixture of hydrogen / argon escapes into a room, hydrogen doesn't accumulate under the ceiling and argon

doesn't accumulate on the ground. The mixture moves upwards as a whole, when it is lighter than air, and downwards when it is heavier than air. While doing so it continually blends itself into the air. Mixtures of hydrogen with helium or nitrogen are always lighter than air. Hydrogen / argon-mixtures up to 71 vol.-% argon are lighter than air and with a higher argon content heavier than air.

Hydrogen/inert gas-mixtures are combustible when their hydrogen content is above certain levels. The corresponding values are standardised in ISO 10156. It is specified that hydrogen/nitrogen mixtures with more than 5,7 vol. % H<sub>2</sub> and hydrogen/helium - respectively hydrogen / argon-mixtures with more than 2.9 vol. % H<sub>2</sub> are combustible. The quoted values are theoretical values and are “on the safe side” and are to be used to classify a gas-mixture according to the regulations. The actual threshold combustibility values, that have been identified in experiments lie by a somewhat higher hydrogen content in the hydrogen/inertgas-mixture.

## 3. Safety Measures

### 3.1. How to avoid explosive atmospheres in rooms and outdoors

It is possible to avoid the build-up of an explosive atmosphere in areas surrounding hydrogen installations by:

- building hydrogen plants in well ventilated areas,
- making certain that hydrogen plants are leakproof and stay that way.



Hydrogen installations should when possible be set up outside, so that leaking hydrogen can escape into the atmosphere without danger. If this is not possible, at least the hydrogen storage container should be installed outside. Exhaust lines from safety valves or vacuum pumps, have to lead outside. Exhaust openings are not to be located under ledges, under openings in buildings or in the vicinity of an air-intake area. Exhaust openings should be marked clearly so that in case of hot work in the vicinity, everyone is aware of the necessary precautions that have to take.

Hydrogen supply lines should have a shut off valve when entering an indoors area. At indoors hydrogen installations blind flanges or nuts have to cover unused connections, in order to avoid gas release into the room.

Rooms with hydrogen installations shall have an effective natural or effective ventilation. The hydrogen content in the room can be controlled through a warning system (explosimeter).

Special attention should be given to very small rooms as for instance to the housing of gas-mixing installations and hydrogen measuring apparatus. Parts in such housing containing hydrogen have to be definitely leakproof, for instance by using permanent pipe connections. The housing is to be equipped with ventilation openings so that hydrogen can escape.

Pipe connections in hydrogen installations should, whenever possible, be permanently welded or hard soldered because this ensures long lasting leakproofness. This recommendation is especially true for hydrogen pipes running under the ground or in not easily accessible areas as for instance in a channel.

When pipes that can be detached are connected with screwed flanges or tube fittings, the most leakproof types are to be used. In pipe connections that are screwed together, compression fittings should be favoured. Leak checking in hydrogen installations should first be done with a nonflammable gas, such as nitrogen or helium. Only after the evident leaks have been repaired, a second leakcheck should be done using hydrogen at working pressure.

A hydrogen installation with known leaks is not safe. The installation has to be depressurized, purged and repaired.

### 3.2. How to avoid ignition causing sources in rooms and outside

The hydrogen plant and installation including surrounding areas shall be classified

for the risk of explosive atmosphere, see DIN EN 1127-1, DIN EN 60079-10 or other relevant regulations. The classification gives guidance on the needed precautions to avoid ignition. Nevertheless the following general advice should be considered:

- Electrical equipment is not to be used or else be installed in an explosion proof version.
- Working with fire (welding, cutting, soldering, grinding) is only allowed if the endangered area is free of hydrogen. This should be checked with an explosimeter, under no circumstances with an open flame. When performing work with fire it is important to keep in mind, that welding and grinding sparks can fly as far as 10 m from the place of origin.
- Assembly work is not allowed when hydrogen is escaping, because even when using spark free tools, there is still a risk of an ignition.

### 3.3. How to avoid explosive mixtures in hydrogen installations

It is not acceptable to have an explosive mixture in a hydrogen installation. These mixtures are easily ignitable, for instance through frictional heat when operating a valve or through rust particles that have been transported (see paragraph 2). Even the heating up of the gas that has been caused by the pressure shock of fast flowing hydrogen into an air filled section of the installation can cause an ignition.

Air and Oxygen have to be kept away from hydrogen installations. This is possible if the installation has no connection to air or oxygen containing systems. If such connections exist, for instance in welding equipment that operates with hydrogen and oxygen, non return valves have to be

installed to ensure that it is not possible for one of the gases to enter into the other feedline.

Hydrogen compressors should be fitted with low suction pressure alarm to ensure and oxygen alarm to ensure that an explosive hydrogen / air mixture cannot be created.

If hydrogen is to be combined with air or oxygen for special technical process, it is only to be done under closely supervised prerequisites – maintenance of the right concentration and permissible pressure and the absence of spark sources.

Before hydrogen installations are put into operation, air has to be removed, for instance through vacuum pumping or purging. The safest method is purging with nitrogen, if an oxygen content of under 1 vol.-% in the installation is reached. If combustible argon / hydrogen-mixtures or forming gases (nitrogen/hydrogen-mixture) are used for soldering of containers, the air also has to be removed through purging in order to prevent an explosion in the container. (Because of technical welding reasons – prevention of annealing colour – the oxygen content has to be quite a bit below the above mentioned content). Also when shutting off, a hydrogen installation has to be made hydrogen gas free through vacuum pumping or purging. The hydrogen content has to be reduced to 1 vol.-%, before the installation is opened. If, when shutting off the installation, parts of it remain under pressure, the hydrogen has to carefully be cut off from the part that is under pressure, for instance through a double block with a bleed valve in-between, disconnection, etc.. In all purging processes it is important to remember, that purging gas will go the way of least resi-

stance. Therefore special attention should be paid to dead ends. It can be necessary to see whether all valves have actually assumed their necessary control position. (Valves that appear to be open, don't always permit passage and valves that are closed are not always leakproof.)



Explosive atmosphere warning

### 3.4. How to react when hydrogen is escaping, or when there is a hydrogen fire

If hydrogen is leaking unintentionally, the gas supply has to be cut off by closing the necessary controls. It shouldn't be attempted to repair the leak while hydrogen is escaping, because of the danger of an ignition. If a large amount of hydrogen has been escaping into the room, there is an acute danger of an explosion. Personnel have to leave the room which then has to be thoroughly ventilated. In order to prove the effectiveness of the ventilation, a measuring check should be carried out.

If the hydrogen escape has caught fire, it can be extinguished by shutting down the hydrogen supply lines. If this is not successful, do not attempt to extinguish the fire in rooms with extinguishing agents because the continued flow of hydrogen would present an explosion risk. In such a case, one has to let the fire burn until the hydrogen is burnt up and the fire burns out on its own. It may be necessary to cool areas with water that could be endangered by the fire (i. e. gas cylinders). When the burning process is almost over, the affected installation should be purged with nitrogen to assure that there is no flashback into the interior.

### 3.5. Safe handling of hydrogen cylinders

National regulations contain different requirements on handling of gas cylinders. The following should also be noted when handling hydrogen cylinders and bundles: Cylinder and bundle valves are only to be opened when the pressure reducer with undamaged sealings has been carefully connected. The points of connection should be checked to ensure they don't leak. Cylinder and bundle valves are to be closed when not in use in order to prevent gas leakage from leaking connections.



If a cylinder or bundle valve is leaking or when hydrogen escape cannot be stopped by closing the valve, the hydrogen container has to be transported outside where it is to be emptied. Repairs on hydrogen cylinders or bundles, including the valves, are only to be carried through by the gas supplier.

### 3.6. How to avoid abuse

Hydrogen is not to be used for the filling of toy balloons because of the danger of an explosion.

Hydrogen should also not be used as carrier for pneumatic energy, for instance for spray painting or for similar processes.

Hydrogen should not purposely be inhaled in large dosages. The suffocating effect can already begin after inhaling one deep breath.

### 4. Final remarks

Hydrogen can be used for many purposes. Our gas specialists will be pleased to inform you on how to use it safely and effectively.



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