

SEMI S25-0319

SAFETY GUIDELINE FOR HYDROGEN PEROXIDE STORAGE AND HANDLING SYSTEMS

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NOTICE: Paragraphs entitled ‘NOTE:’ are not an official part of this Standard or Safety Guideline and are not intended to modify or supersede the official Standard or Safety Guideline. These have been supplied by the global technical committee to enhance the usage of the Standard or Safety Guideline.

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1 Purpose

1.1 The purpose of this Safety Guideline is to set out the minimum safety and health criteria to be applied to equipment and systems for storage and handling of hydrogen peroxide in the semiconductor and flat panel display industries.

2 Scope

2.1 This Safety Guideline addresses concentrations of hydrogen peroxide (H₂O₂) commonly used in the semiconductor and FPD industries (i.e., concentrations below 40% w/w).

NOTE 1: While the guidance given is applicable to higher concentrations of hydrogen peroxide, there are particular hazards associated with concentrations above 44%. These hazards are discussed only briefly, in § 7.4.

2.2 This Safety Guideline is focused on the storage, handling, transfer, and distribution of hydrogen peroxide within the semiconductor or flat panel display facility.

NOTE 2: While this Safety Guideline is not intended to address the internal distribution of hydrogen peroxide within semiconductor manufacturing equipment the General Principles outlined in § 7 can also be useful for semiconductor manufacturing equipment designers.

NOTE 3: The list of section numbers and their titles that were shown in ¶ 2.3 in previous revisions of SEMI S25 are relocated in front of the main part of the document in the Table of Contents.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 This Document is not intended to impart requirements on any party.

3.2 This Safety Guideline does not address issues of transportation of hydrogen peroxide.

NOTE 4: These issues are generally well covered by the various national and international transport regulations.

3.3 This Safety Guideline does not directly address process applications involving hydrogen peroxide (e.g., use of hydrogen peroxide in formulation of chemical mechanical polishing slurries), as these are often proprietary.

NOTE 5: The general principles of this Safety Guideline can be used by end users to carry out a risk assessment of their own particular process applications.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI S2 — Environmental, Health, and Safety Guideline for Semiconductor Manufacturing Equipment

SEMI S10 — Safety Guideline for Risk Assessment and Risk Evaluation Process

4.2 CEFIC Guidelines¹

CEFIC Guidelines for Bulk Storage of H₂O₂

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 *ECTFE* — ethylene-chlorotrifluoroethylene copolymer

5.1.2 *ETFE* — ethylene tetrafluoroethylene

5.1.3 *FEP* — fluorinated ethylene propylene

5.1.4 *HDPE* — high density polyethylene

¹ European Chemical Industry Council, Avenue E. van Nieuwenhuysse 4 - 1160 Brussels, Belgium; <http://www.cefic.org>

5.1.5 *ISO* — International Organization for Standardization

5.1.6 *PE* — polyethylene

5.1.7 *PFA* — perfluoroalkoxy

5.1.8 *PP* — polypropylene

5.1.9 *ppb* — parts per billion

5.1.10 *ppt* — parts per trillion

5.1.11 *PTFE* — polytetrafluoroethylene

5.1.12 *PVDF* — polyvinylidene fluoride

5.1.13 *SOP* — standard operating procedure

5.1.14 *SS* — stainless steel

5.1.15 *VLSI* — very large scale integration (refers to microchips containing in the hundreds of thousands of transistors).

5.1.16 *w/w* — weight for weight; when referring to concentration of hydrogen peroxide.

5.2 Definitions

5.2.1 *colloid* — a substance comprised of a dispersed phase and a continuous phase. It differs from a solution in that the dispersed phase is comprised of particles larger than molecules. Each phase can be a gas, liquid, or solid; except that gas in gas colloids do not form because neither component remains aggregated.

5.2.2 *exothermic reaction* — a chemical process in which heat is released.

5.2.3 *ISO container* — a container, usually more than 5000 liters in capacity, for storing chemicals that is able to be transported directly and designed in compliance with criteria from the International Standards Organization.

5.2.4 *photochemical decomposition* — chemical reaction, caused by light, in which the material is decomposed into other materials.

5.2.5 *stabilizers* — chemicals used to help maintain physical and chemical properties of a material during processing and service life.

5.2.6 *standard operating procedure (SOP)* — an established procedure to be followed in carrying out a given operation or in a given situation.

5.2.7 *spontaneous combustion* — the ignition of material due to a heat producing (exothermic) chemical reaction within the material itself without exposure to an external source of ignition.

6 Safety Philosophy

6.1 The order of precedence for resolving identified hazards should be as follows:

6.1.1 *Design to Eliminate Hazards* — From the initial concept phase, the designer should design to eliminate hazards, if the hazards present unacceptable risk and the elimination of the hazards is consistent with the performance of the intended function.

NOTE 6: It is recommended that designers continue to work to reduce risk in installation, testing, commissioning, operation, maintenance, service and decommissioning.

6.1.2 *Incorporate Safety Devices* — If hazards in the design present unacceptable risk, then that risk should be reduced to an acceptable level by the incorporation of fixed or automatic features of the design. These are commonly called ‘engineering controls.’ It is recommended that provisions be made for periodic functional checks of safety devices, when applicable.

6.1.3 Safety devices should be compatible with cleanliness requirements, otherwise other methods of protection should be chosen.

6.1.4 *Provide Warning Devices* — If design or safety devices do not effectively eliminate identified hazards or adequately reduce associated risk, a means should be used to detect the condition of increased risk and to produce a warning signal to alert personnel of this condition.

6.1.5 *Provide Hazard Alert Labels* — Where it is impractical to eliminate hazards through design selection or adequately reduce the associated risk with safety or warning devices, hazard alert labels should be provided to identify and warn against hazards.

6.1.6 *Develop Administrative Procedures and Training* — Where hazards are not eliminated through design selection or adequately controlled with safety or warning devices or hazard alert labels, procedures and training should be used. It should be ensured that such procedures and training are capable of reducing risk to an acceptable level. Procedures may include the use of personal protective equipment.

6.1.7 A combination of these approaches may be needed.

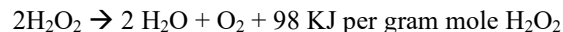
NOTE 7: Safety philosophy is in line with SEMI S2 and risk assessment can be based on SEMI S10.

7 General Principles

7.1 Hazards Associated with Hydrogen Peroxide

7.1.1 Decomposition (leading to vapor release and possible over-pressure)

Hydrogen peroxide decomposes to water and oxygen represented as:



Decomposition can occur under various conditions which are identified in §§ 7.1.3 and 7.1.4.

7.1.2 Because semiconductor grade hydrogen peroxide has to meet the most demanding specifications in terms of metal ion levels of all wet process chemicals, much of the hydrogen peroxide used in microelectronics manufacturing is unstabilized (i.e., no chemical stabilizer has been added to it). In this case the stability of the product comes from its purity level, because if no impurity is present which can catalyze decomposition the product is stable for transport and storage. However, unstabilized peroxide is more sensitive to potential contamination and therefore not normally used for industrial applications other than microelectronics manufacturing.

7.1.3 Homogeneous Decomposition

7.1.3.1 The decomposition rate of hydrogen peroxide to water and oxygen is normally very low. However, if the hydrogen peroxide becomes contaminated, for example with salts of metals such as iron, copper, chromium, vanadium, tungsten, molybdenum, silver or metals from the platinum group, then fast decomposition to water and oxygen may follow. The increased rate of decomposition in this case is described as homogeneous decomposition. Fast decomposition can be caused by relatively low levels of contaminants. This decomposition is a catalytic reaction in which the metallic ions are successively oxidized and reduced. This explains why it is possible for small amounts of catalyst to cause extensive decomposition of hydrogen peroxide. In addition, the effect of pH on the rate of decomposition of contaminated hydrogen peroxide is considerable; any increase in pH value will result in an increased rate of decomposition.

7.1.4 Heterogeneous Decomposition

7.1.4.1 Decomposition may also occur if the hydrogen peroxide is brought into contact with insoluble solids. This is known as heterogeneous decomposition. Hydrogen peroxide will decompose to some extent on any surface even at ambient temperature, although the rate varies enormously with the nature and condition of the surface. For example; the rate of decomposition on a silver surface is more than 100 times faster than, for example, on polyethylene. Some of the solids which catalyze the decomposition of hydrogen peroxide include heavy metals and noble metals as well as their hydroxides and oxides.

7.1.4.2 Heterogeneous decomposition catalysts are most active when their specific surface is large as with, for example, colloids and powdered metals. In addition even 'compatible' materials of construction can cause accelerated decomposition if the surface is of inadequate quality or has not been properly prepared. As an example, stabilized hydrogen peroxide can be stored in stainless steel tanks but the metal should first undergo a special treatment of pickling and passivation.

7.1.5 Effect of pH

7.1.5.1 Hydrogen peroxide is slightly acidic in nature. In alkaline solution, the rate of decomposition increases rapidly as the pH is increased.

7.1.6 *Effect of Light*

7.1.6.1 Light can cause photochemical decomposition of hydrogen peroxide and the absorption of radiation by hydrogen peroxide solutions occurs over a wide continuous spectrum. Hydrogen peroxide solutions should not be exposed for long periods to light, especially direct unfiltered sunlight or UV radiation.

7.1.7 *Effect of Heat*

7.1.7.1 The decomposition of hydrogen peroxide is exothermic. In addition to self-heating as a result of decomposition, the effect of temperature rises caused by outside sources of heat should be considered. For purely physical-chemical reasons, the rate of the decomposition reaction in solution (homogeneous) will increase 2 to 3 times for every 10°C increase in temperature, and the rate of the surface decomposition (heterogeneous) will increase 1 to 2 times per 10°C. The effect of increased contamination from dissolution of the surface will make the situation worse.

7.1.8 *Effects of Decomposition*

7.1.8.1 *Pressure Build-Up*

7.1.8.1.1 Even at low concentrations, hydrogen peroxide will decompose slowly but continuously into water and oxygen. This rate is very low when hydrogen peroxide is stored in suitable materials and is kept free from contaminants.

7.1.8.1.2 If oxygen pressure is not relieved, then a very high pressure may build up (31% hydrogen peroxide, if fully decomposed, will release approximately one hundred times its' own volume of steam and oxygen). For this reason hydrogen peroxide pipe-work should be designed so that pressure cannot be accumulated leading possibly to a pipe failure (from hydrogen peroxide trapped between two valves, for example). For ball valves or plug valves, a release bore is needed to ensure no peroxide can be trapped behind the ball or plug sealing.

7.1.8.1.3 Special care is also strongly recommended when filtering hydrogen peroxide (see § 13). The decomposition of peroxide may be accelerated by particulate matter accumulated on the filter membrane (heterogeneous decomposition catalysis), therefore any filter housings should also have an appropriate pressure relief. Preventive replacement of the filter element is advised if the continuous formation of oxygen bubbles is observed from a filter even if the filtration is still working well.

7.1.8.2 *Heat Release and Self-Heating*

7.1.8.2.1 The decomposition of hydrogen peroxide is exothermic and the rate of decomposition increases with increasing temperature. If the heat of decomposition is not removed with at least the same rate at which it is developed (by spontaneous heat loss to the surroundings or by deliberate cooling), then the temperature will rise and the rate of decomposition will increase. This can lead to a self-accelerating decomposition which, in the case of badly contaminated solutions (e.g., from a major in-liner failure of lined metal storage or transport tanks), may culminate in a rapid decomposition or 'boil off.'

7.1.9 *Spontaneous Combustion of Organic Substances*

7.1.9.1 Hydrogen peroxide can cause spontaneous combustion if it comes in contact with many different organic materials including cloth, paper, and wood.

7.1.10 *Loss of Containment (leading to possible fire, environmental and health hazards)*

7.1.10.1 Hydrogen peroxide should be handled with care so that no product is spilled during unloading or transfer. If spillage does occur, it should be diluted with water and cleaned up thoroughly, ensuring that all cleaning equipment is well rinsed after use.

7.1.10.2 Hydrogen peroxide should be kept in its original container. Handling and transferring should be done only with approved dedicated equipment made of compatible material (see § 10). Once hydrogen peroxide has been drawn from a storage container, it should not be returned since it may have become contaminated and could cause the decomposition of the contents of the entire container. Recirculation of the hydrogen peroxide in a loop system designed for that purpose is acceptable provided that there is no metal contamination within the system (for instance, from metal parts in contact with the solution in the loop).

7.1.11 Hydrogen peroxide should be kept away from heat sources because, as with most chemical reactions, the decomposition rate increases with temperature.

7.1.12 Hydrogen peroxide should not be contaminated during storage and handling, and contact with incompatible surfaces should be avoided. Although strict contamination control is mandatory in microelectronics manufacturing, scrupulous cleanliness is also vital with hydrogen peroxide for safety reasons.

7.2 Access Control

7.2.1 Hydrogen peroxide should be handled by only trained personnel who are well aware of its hazards and the necessary safety precautions. Thus it is important to limit the access to hydrogen peroxide installations.

7.3 Alarm Systems

7.3.1 Features of bulk hydrogen peroxide storage should include level indicator and temperature indicator alarms. A standard set-up uses alarm settings for temperature level as well as for rate of temperature change. Alarm switches and thermometers should be suitable for use with hydrogen peroxide (see § 13).

7.3.2 Storage tanks may also be fitted with a dilution connection and an optional mixing device. In the event of a decomposition situation it is best practice to use clean water to dilute the peroxide to a very low concentration which eliminates any further hazard. Please note, the use of deionized water with low metal and organic content is recommended for unstabilized hydrogen peroxide emergency dilution because a less pure water quality might introduce further contamination, accelerating further the decomposition of the product.

7.4 Scenarios not Addressed in this Safety Guideline

7.4.1 Explosive Characteristics

7.4.1.1 Hydrogen peroxide solutions less than 70% w/w are not, in themselves, explosive. Hydrogen peroxide solutions used in microelectronics manufacturing are mostly limited to 30% to 35% w/w concentrations so this Safety Guideline does not provide more detailed information about this subject.

7.4.1.2 However, explosions may occur under certain conditions when hydrogen peroxide, especially of more than 44% w/w content is mixed with organic compounds to form a single phase, emulsion or suspension. The most important factors which govern whether or not an explosion occurs are:

- the concentration of hydrogen peroxide, water and organic material present,
- the nature of the organic material,
- the presence of an initiation source, and
- the temperature of the mixture.

7.4.1.3 This hazard exists when using hydrogen peroxide even at less than 44% initial concentration, if there is a potential for the concentration to subsequently increase (e.g., by water evaporation). In addition, hydrogen peroxide reacts with certain organic compounds to form organic peroxides which may, themselves, have explosive properties. Explosions may also occur if hydrogen peroxide is brought into contact with certain incompatible inorganic materials such as powerful reducing or oxidizing agents.

7.4.1.4 Decomposition of hydrogen peroxide can also lead to oxygen enrichment of the atmosphere above it. Under certain conditions (e.g., in the presence of flammable liquids or flammable gases) this can lead to a high risk of fires or even vapor phase explosions.

7.4.2 External Fire

7.4.2.1 Hydrogen peroxide is not combustible and so this scenario is not part of this Standard. However, it should be remembered that oxygen generated by decomposition of hydrogen peroxide may accelerate the burning of combustible materials. Also, heating of containers of hydrogen peroxide by their exposure to external fire is likely to result in accelerated decomposition.

8 Education and Training

8.1 All operators handling hydrogen peroxide should be informed of the hazards and risks involved. These can result from skin contact, eye contact, inhalation or ingestion as follows: