#### The Safe Use of Chemicals at Work

# Cyanide



## A Good Practice Guide

Cyanide is a term which is used to describe a group of compounds containing carbon (C) and nitrogen (N) atoms. Cyanide is a chemical that acts very rapidly and is a potentially deadly poison prohibiting our bodies from using life-sustaining oxygen.

Low levels of cyanide are present in certain foods and plants such as almonds, spinach and cassava. Certain pits and seeds of common fruits and flowers such as apricots, apples, peaches and many members of the rose family may have certain chemicals which get metabolized to cyanide. The parts of such fruits which we normally eat however contain even much lower amounts of these chemicals. Only chronic or massive ingestion of any of these plants or pits can lead to serious cyanide poisoning.

Cyanides are also found in cigarette smoke, in vehicle exhaust and formed by incomplete combustion of all nitrogen-containing substances (such as plastics including polyurethane and polyacrylnitrile, as well as wool, rubber and silk).

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## **Properties of Cyanide**

Cyanide can be found in various chemical forms and these can vary according to temperature and other conditions.

Hydrogen cyanide for instance is a colourless or pale blue liquid at room temperature but turns into a colourless gas at high temperatures. Hydrogen cyanide is less dense than air and disperses rapidly and it is also miscible in water and soluble in ethanol. Sodium cyanide and



potassium cyanide are white powders. All these are said to have a "bitter almond" smell which is usually smelled easily by most people. However, the absence of this odour does not exclude cyanide being present because some people [20%-40%] are genetically unable to sense the bitter almond smell. As a result, reliance on the sense of smell should not be used as a warning signal.

Other chemicals called cyanogens can generate cyanides. Cyanogen chloride is a colourless gas or liquid with a boiling point of 13°C with a pungent, irritating odour. Cyanogen chloride vapour is heavier than air and therefore it may accumulate in low-lying areas.

## Uses of Cyanide

Cyanide is used in various processes and workplaces. These include:

- Mining of gold and silver as it helps to dissolve these metals and their ores;
- Electroplating as it is used to stabilize the metal ions in the electrolyte solution before their deposition;
- Fumigation as a method of pest control used particularly to destroy pests and vermin in buildings and ships;
- Welding and metal work;
- Waste water treatment;
- Food additive as it forms very stable complexes with iron, forming ferrocyanides which are used in the food industry;
- Photography and blueprints;
- Medical uses which include sodium nitroprusside which is a cyanide compound used to measure urine ketone bodies in diabetic patients. Also used in vascular research and in emergency situations to rapidly decrease the blood pressure in humans;
- Manufacture of textiles, paper, synthetic fibres and plastics;
- Case-hardening in the iron and steel industry;
- Laboratory analysis of cyanide compounds.

### **Types of Cyanide**

**Acrylonitrile** (vinyl cyanide, cyanoethylene, propene nitrile) - A colourless to pale yellow, volatile, flammable liquid, with a faintly pungent odour whose vapours can easily form explosive mixtures with air, liquid found in surface coatings and adhesives. It is used in the manufacture of resins, synthetic rubbers plastics and acrylic fibres. It is also used as a chemical intermediate in the synthesis of antioxidants, pharmaceuticals, pesticides, dyes, surface-active agents and in the production of adiponitrile, acrylamide and carbon fibre. It was previously also used as a fumigant.

**Calcium cyanamide** (nitrolim, calcium carbimide, cyanamide) - a blackishgrey, shiny powder used in agriculture as a fertilizer, herbicide, pesticide and a defoliant for cotton plants. It is also used in steel hardening and as a desulphurizer in the iron and steel industry. In industry, calcium cyanamide is used for the manufacture of calcium cyanide and dicyandiamide, the raw material for melamine.

**Cyanogen, cyanogen bromide and cyanogen chloride** are used in organic syntheses. Cyanogen is also a fumigant and a fuel gas for welding and cutting heat-resistant metals. It is a rocket or missile propellant in mixtures with ozone or fluorine; and it may also be present in blast furnace emissions. Cyanogen bromide is utilized in textile treatment, as a fumigant and pesticide, and in gold extraction processes. Cyanogen chloride serves as a warning agent in fumigant gases.

**Hydrogen cyanide** finds use in the manufacture of synthetic fibres and plastics, in metal polishes, electroplating solutions, metallurgical and photographic processes, and in the production of cyanide salts. It is a combustion by-product of burning plastics, wool and many other natural and synthetic products.

**Sodium cyanide** and **potassium cyanide** are used in electroplating, steel hardening, extraction of gold and silver from ores, and in the manufacture of dyes and pigments. In addition, sodium cyanide functions as a depressant in the froth flotation separation of ores.

**Potassium ferricyanide** (red prussiate of potash) is used in photography and in blueprints, metal tempering, electroplating and pigments. Potassium ferrocyanide (yellow prussiate of potash) is used in the tempering of steel and in process engraving. It is employed in the manufacture of pigments and as a chemical reagent.

**Ammonium thiocyanate** is used in the match and photography industries and for double-dyeing fabrics and improving the strength of silks weighted with tin salts. It is a stabilizer for glues, a tracer in oil fields, and an ingredient in pesticides and liquid rocket propellants. Calcium cyanide, malononitrile, acetone cyanohydrin (2-hydroxy-2methylproprionitrile) and cyanamide are other useful compounds in the metal, plastics, rubber and chemical industries. Calcium cyanide and malononitrile are leaching agents for gold. In addition, calcium cyanide is used as a fumigant, a pesticide, a stabilizer for cement, and in the manufacture of stainless steel. Acetone cyanohydrin is a complexing agent for metal refining and separation, and cyanamide is used in metal cleaners, the refining of ores and the production of synthetic rubber.

Potassium cyanate serves as a chemical intermediate and as a weed killer.

Some of the more important organic **nitriles** in industrial use include acryonitrile (vinyl cyanamide, cyanethylene, propene nitrile), acetonitrile, (methyl cyanamide, ethanenitrile, cyanomethane), ethylene cyanohydrin, proprionitrile (ethyl cyanide), lactonitrile, glycolonitrile (formaldehyde cyanohydrin, hydroxyacetonitrile, hydroxy-methylcyanide, methylene cyanohydrin), 2-methyl-lactonitrile, and adiponitrile.

Source: Encyclopaedia of Occupational Health and Safety, International Labour Organisation, 2012.



#### Exposure to Cyanide

One may be exposed to low levels of cyanides from food, drinking water, breathing air or touching soil that contains cyanide. Consuming foods that contain cyanide may cause negative health effects. However breathing cyanide gas, particularly when the area is not properly ventilated, causes the most harm as this leads to fast absorption and circulation around the body.

Fatal exposures to cyanides only result from accidents or intentional acts such as terrorism attacks.

Smoking cigarettes is one of the major sources of cyanide exposure for people who do not work in cyanide-related industries. Cyanide is naturally found in tobacco, and smokers can have more than 2.5 times the mean whole blood cyanide level of non-smokers, though this is generally not enough to cause poisoning.

#### How Cyanide Works

The extent of poisoning caused by cyanide depends on a number of factors mainly the amount of cyanide the person is exposed to, the way of exposure and the length of time that person was exposed.

After exposure, cyanide quickly enters the bloodstream. The body handles different amounts of cyanide in a different way.

In **small doses**, cyanide in the body is usually converted into thiocyanate, which is less harmful and is then excreted into urine. It might also combine with another chemical to form vitamin B12, which helps maintain healthy nerve and red blood cells. In large doses however, the body's ability to change cyanide into thiocyanate is overwhelmed.

Large doses of cyanide prevent cells from using oxygen and eventually these cells die. The heart, respiratory system and central nervous system are most susceptible to cyanide poisoning.

Acute exposure can cause death by asphyxia whether cyanide was inhaled, swallowed or absorbed through the skin.



## Signs and Symptoms of Cyanide Exposure

Abrupt onset of profound toxic effects shortly after exposure is an important characteristic of cyanide poisoning.

When a person is exposed to a **small amount** of cyanide whether this is inhaled, swallowed or absorbed through the skin, some or all of the following signs and symptoms may result within minutes:

- Dizziness
- Headache
- Palpitations
- Nausea and vomiting
- Rapid breathing
- Rapid heart rate
- Restlessness and anxiety
- Weakness

In cases of **moderate** toxicity there may be brief episodes of loss of consciousness, convulsions, vomiting and hypotension. Exposure to a **large amount** of cyanide may cause these other health effects as well:

- Lung injury including pulmonary oedema (excessive fluid in the lungs)
- Respiratory failure leading to death
- Slow heart rate

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- Cardiovascular collapse
- Deep coma
- Fixed unreactive pupils
- Myocardial ischaemia (reduced blood flow to the heart, preventing it from receiving enough oxygen)
- Cardiac arrhythmias (heart beat which is irregular, either too fast or too low).

## It is important to note however that showing these signs and symptoms does not necessarily mean exposure to cyanide.

**Chronic exposure** (over a long period of time) to cyanides at levels too low to produce such serious symptoms may cause a variety of problems. The *International Labour Organisation* notes that "Among fumigators, mild cyanide poisoning has been recognized as the cause of symptoms of oxygen starvation, headache, rapid heart rate, and nausea, all of which were completely reversed when the exposure ceased.

Chronic systemic cyanide poisoning may occur, but is rarely recognized because of the gradual onset of the disability, and symptoms which are consistent with other diagnoses. It has been suggested that excessive thiocyanate in extracellular fluids might explain chronic illness due to cyanide, since the symptoms reported are similar to those found when thiocyanate is used as a drug. Symptoms of chronic disease have been reported in electroplaters and silver polishers after several years of exposure. The most prominent were motor weakness of arms and legs, headaches and thyroid diseases; these findings have also been reported as complications of thiocyanate therapy." (ILO, 1972).

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What can you do if you think you have been exposed to cyanide?

If you think that you have been exposed to cyanide, you should move away from the area where cyanide gas might have been released, remove your clothing, wash your entire body very rapidly with soap and water and get medical help right away.

The Centers for Disease Control and Prevention give the following advice:

Quickly move away from the area where you think you were exposed. If the release was indoors, go outdoors.

If you are near a release of cyanide, emergency coordinators may tell you to either evacuate the area or to "shelter in place." To "shelter in place" means to remain indoors to avoid being exposed to the chemical. While indoors, shut and lock all doors and windows, turn off air conditioners, fans and heaters, and close fireplace dampers.

Quickly remove any clothing that may have cyanide on it. If possible, clothing that is normally removed over the head (like t-shirts and sweaters) should be cut off the body to prevent additional contact with the agent.

- Place your clothing inside a plastic bag and seal the bag tightly. Put it into another bag.
- Do not handle the plastic bag, and wait for instructions on proper disposal.
- Disposing of your clothing in a sealed bag helps protect you and other people from additional exposure.
- Store the bagged clothing in a secure location away from people, especially children.

Quickly wash any cyanide from your skin with large amounts of soap and water, and flush your eyes with large amounts of water.

- Remove and throw away contact lenses even if they are not the disposable type.
- Wash eyeglasses with soap and water before wearing.
- Wash jewellery thoroughly with soap and water before putting it back on. If it cannot be washed, dispose of it in the bag where you would have placed your clothes.
- Do not use bleach to remove cyanide from your skin.

# If needed, seek medical attention right away by phoning 112 and explain the situation.

- Primary responders should wear appropriate personal protective equipment (PPE).
- Responders should not enter a contaminated area without PPE and self-contained breathing apparatus.
- If the patient has not been decontaminated, secondary carers must wear appropriate PPE for chemical exposure to avoid contaminating themselves. The area should be well ventilated.

Decontamination should be carried out in a well-ventilated area, preferably with its own ventilation system. Contaminated clothing should be removed, double-bagged, sealed and stored safely. Any open wounds should be decontaminated first and avoiding contamination of unexposed skin. Any particulate matter adherent to skin should be removed and the patient washed with soap and water under low pressure for at least 10-15 minutes. Particular attention should be paid to mucous membranes, moist areas such as skin folds, fingernails and ears.

### How Cyanide Poisoning is Treated

Cyanide poisoning is treated with particular antidotes and other care in hospital. These antidotes should ideally be given as soon as possible following exposure. Hence it is very important that when one calls for medical help, information about the cyanide exposure is given on the phone to alert the emergency team coming to assist you.

Clinicians should treat suspected cases of cyanide poisoning accordingly and not wait for laboratory results confirmations.

The most important thing though is for the victim to seek medical help immediately.

#### **Antidotes for Cyanide Poisoning**

The European guidance document (EMEA/CPMP/1255/03) "on the use of medicinal products for the treatment of patients exposed to terrorist attack with chemical agents" summarizes properties of the different cyanide antidotes, which can be categorized into 3 groups:

**1.** Complexation agents that act by direct binding of the cyanide ions. These are considered as the preferred antidotes. Two products are available:

- **Dicobalt edetate** which is an efficient complexation antidote to cyanide; but its use should be restricted to cases when the diagnosis of cyanide poisoning is certain and only for severe poisoning, since it is potentially toxic particularly in the absence of cyanide poisoning due to the presence in the formulation of free cobalt ions.

- **Hydroxocobalamin**, in the formulation of hydroxocobalamin 5-g vial powder, is considered to be the best choice antidote, if available, as it is experimentally well documented with clear advantages in situations such as fires with concomitant exposure to agents that reduce oxygen transport, such as carbon monoxide. Vitamin B12, or hydroxocobalamin, detoxifies cyanide and forms cyanocobalamin, which is excreted through the kidneys.

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Hydroxocobalamin is an appealing cyanide antidote because it is relatively safe, does not compromise the blood's oxygen-carrying capacity, and, unlike the nitrites or sodium thiosulfate, does not produce hypotension. These features make hydroxocobalamin an ideal agent for empiric use in patients with smoke inhalation who are suspected to have cyanide toxicity.

Hydroxocobalamin is approved by the US Food and Drug Administration and the Committee for Medicinal Products for Human Use (CHMP) of the European Medicines Agency.

**2. Sulfur supplying agents** which act by promoting conversion of cyanide to thiocyanate, thusenhancing the physiological cyanide detoxification process:

- **Thiosulphate** is the main product in this class; it should be considered together with the other cyanide antidotes in sequential treatment (but should not be administered as a mixture at the same time as hydroxocobalamin), as it is a rather slow acting agent.

**3.** Methaemoglobin inducers which act by complexation of cyanide to methaemoglobin:

- Sodium nitrite is an example of an agent belonging to this class.

Sodium nitrite and sodium thiosulfate may be used in combination. Sodium nitrite is rapidly effective but can cause life-threatening toxicity, whereas sodium thiosulfate has a somewhat delayed effect but is far safer. Sodium nitrite should not be used in patients with smoke inhalation unless their carboxyhemoglobin concentration is very low (< 10%).

Due to the risk of excessive methaemoglobinemia, sodium nitrite, and sodium thiosulfate should be used in case of non-availability of hydroxocobalamin or dicobalt edetate.



## Health and Safety Measures

As stated in **Legal Notice 36 of 2003**, it is the duty of the employer or selfemployed person to ensure that a risk assessment is carried out by a competent person.

The risk assessment must be a suitable, sufficient and systematic assessment and include all the occupational health and safety hazards which may be present at the place of work and the resultant risks involved concerning all aspects of the work activity.

When chemical agents such as cyanides are present at the workplace, the employer shall assess any health and safety risk that the workers may be exposed to arising from the use of chemical agents as stated in **Legal Notice 227 of 2003**.

The following points need to be taken into consideration:

- a) The hazardous properties of the cyanides;
- b) Information on health and safety provided by the supplier which must include the relevant Material Safety Data Sheet;
- c) The level, type, duration and frequency of exposure;
- d) The circumstances of the work which includes the amount of cyanides involved;
- e) Occupational exposure limit values or biological limit values;
- f) The effect of preventive and control measures which have been or will be taken;
- g) If available, conclusions to be drawn from any health surveillance already undertaken.

## **Hierarchy of Prevention**

The following recommendations are being made by the Occupational Health and Safety Authority, to all users of Cyanides, who are strongly advised to review their particular situation and mode of usage, and to make the necessary changes in the light of these recommendations. They shall be constructed as the minimum requirements for all workplaces where cyanides are used.

#### **Elimination and Substitution**

The first priority of an employer is to ensure the prevention of exposure of employees to cyanide. This can be brought about by a) changing the method of work b) altering the process to remove the production of hazardous by-product or waste product c) if cyanide is used intentionally – a cyanide-free material which is non hazardous can be used instead such as replacing copper cyanide with copper pyrophosphate in electroplating.

An employer must prevent the exposure of employees to cyanide or else if this cannot take place, exposure has to be adequately controlled.

#### **Engineering Controls**

Due attention should be given to the adequacy of ventilation in the work area. The extract ventilation should be capable of handling any released HCN gas promptly.

• A scrubbing system should be considered in conjunction with local exhaust ventilation to reduce any potential exposure to cyanide fumes, mists and gases.

• Air monitoring should be done to measure the concentration of cyanide in the surrounding air. Further information about air monitoring can be obtained from the competent person appointed by the employer to assist in the measures required to safeguard occupational health and safety.

#### Administrative Controls

Workers must be given the relevant information, training and instructions with regards to any potential hazards and risks which are associated with working with cyanide, such as about the safe use, handling and storage of cyanide, the proper use and maintenance of PPE and any emergency procedures in workplaces.

Only workers who have been adequately trained on the risks and on the safe handling of cyanides should be allowed to work with these chemicals. Entry to all areas where cyanides are in use shall be limited to these persons only.

Because of the low permissible exposure level for hydrogen cyanide, complete segregation and enclosure of the process is recommended.

All cyanide salt containers should be properly labelled and kept tightly closed and stored away from acids at all times.

Warning signs should be affixed near entrances to areas containing HCN, or where emergencies may occur.

All cyanide salt containers must be locked in a secure cabinet or store when not in use. Access to such storage areas should be limited to a person, who by reasons of training or experience could be considered a responsible person. This same person shall keep written records of stock levels.

A cyanide antidote kit is to be kept closed at all times where the cyanide is being used. The kit must be easily recognisable and accessible. Training of all workers in its administration in case of emergency should also be ensured.

#### **Personal Protective Equipment**

In case of residual exposure, where the workers are still exposed to a particular chemical after all possible measures were taken, for example in cases where the skin can be exposed (either to solution, powder, or pellets of cyanide salts or to HCN in gaseous form), personal protective clothing (PPE), including impervious hand protection should be provided and used. This is always the last resort, however if such situations arise, the use of PPE must be enforced.

Impervious gloves must be worn, when handling cyanides. Protective apron, rubber boots, face shields and goggles must be worn, if there is a chance of one being splashed with cyanides.

Appropriate respiratory equipment for the concentration of cyanide gas, dust or air.

In case of an accident where a worker is poisoned by cyanide, speed is of utmost importance, and first aid should be administered as soon as possible by a trained First Aider. If smoke inhalation is the cause of the cyanide exposure the worker should be extracted as quickly as possible. Any contaminated clothing should be removed and skin is washed. The poisoned worker must either be immediately transported to a hospital accompanied by the antidote kit, or else a request must be made to have an ambulance sent to the site with an accompanying doctor. One should protect oneself and the victim from further exposure during decontamination and treatment. It is the responsibility of the employer to ensure that the cyanide antidote kit is replaced before the expiry date.

#### **Health Surveillance**

Medical surveillance should be made available to all workers who are exposed to hydrogen cyanide at **potentially hazardous levels**.

An initial medical examination should take place prior to commencing work. This should consist of a complete history and physical examination to establish whether the exposed individual is at increased risk. Examination and relevant investigations of the cardiovascular, nervous, and upper respiratory systems should be carried out. Periodic medical examinations should be carried out annually.

#### Vulnerable Groups

As stated in Subsidiary Legislation 424.10, young persons are prohibited from being employed where they may be exposed to acute toxic chemicals such as cyanides. Pregnant and lactating women should also avoid exposure, as an unborn child is especially vulnerable from exposure to cyanides especially in the early weeks (Subsidiary Legislation 424.11).



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EMEA/CPMP Guidance Document on the Use of Medicinal Products for the Treatment of Patients Exposed to Terrorist Attacks with Chemical Agents. http://www.ema.europa.eu/docs/en\_GB/document\_library/Other/2010/01/WC500059884.pdf (accessed Feb 24, 2016).

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#### **Legal Notices**

<u>General Provisions for health and safety at work places regulations</u>, Subsidiary Legislation 424.18.

Protection of the health and safety of workers from the risks related to chemical agents at work regulations, Subsidiary Legislation 424.24.

Protection of young workers at work places regulations, Subsidiary Legislation 424.10.

Protection of maternity at work places regulations, Subsidiary Legislation 424.11.



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