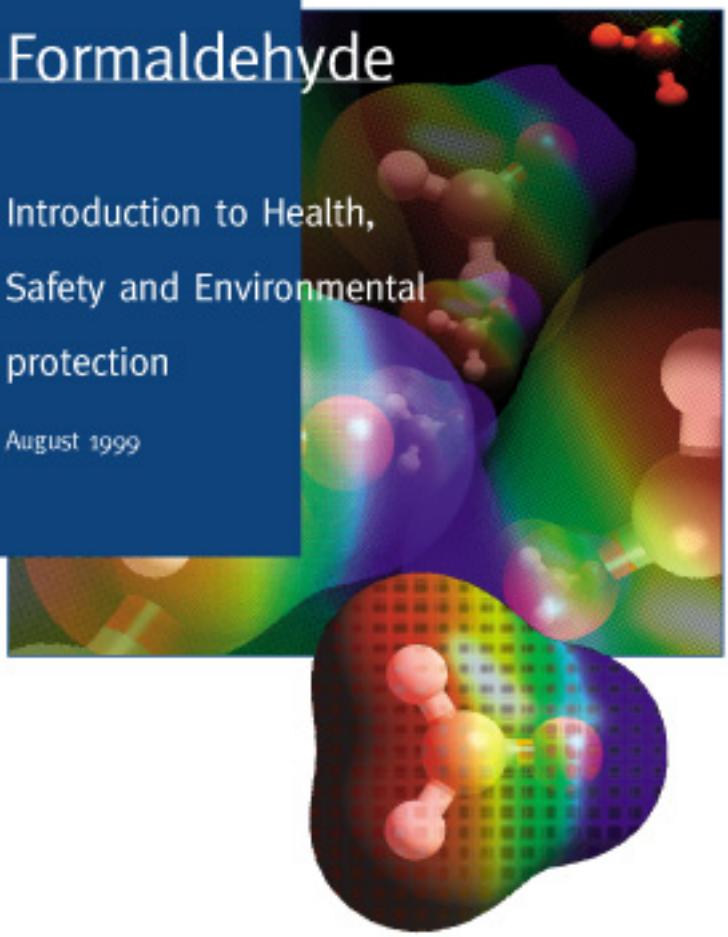
Formaldehyde

Introduction to Health, Safety and Environmental protection

August 1999



Introduction

Formaldehyde is an important organic base chemical, usually delivered in aqueous solutions in various concentrations. It is used as feedstock for the manufacture of numerous products. Because of this great variety of applications it is impossible to imagine life today without products made from formaldehyde. All these products - which can be either a 100% polymer of formaldehyde or a reaction product together with other chemicals - can be encountered in furniture, stuffing for upholstery, household products, white fabrics, kitchen articles, sporting articles, shoes, paints and coatings, lubricants, hydraulic fluids, foam rubber, insulating, automotive industry, foundry industry, textile industry, paper industry, pharmaceuticals, surfactants, prostheses, disinfectants and many more products besides.

Although formaldehyde is produced via a chemical process from methanol it is found in nature as a metabolite for plants, animals and even human beings. Formaldehyde is also formed in nature by photooxidation of organic substances and by incomplete combustion of organic substances (exhaust from engines, power plants and cigarette smoke).

Formaldehyde was discovered in 1859 and can therefore be considered as a well-known and extensively examined chemical substance. There are a great number of studies reporting about the toxicity of formaldehyde, however up till now none of the imputations have been proven. Because formaldehyde has been known for so many years and is a substance thoroughly investigated and examined by a great number of experts, people have learnt to handle it with the necessary care. The fact that formaldehyde has a strong irritating odour even in very low concentrations works out well but means that it can be considered as a chemical with self- warning potential. This prevents human beings from staying in any environment where formaldehyde is present in higher concentrations. Toxicological reports suppose that this built-in threshold is beyond concentrations where formaldehyde is potentially (possibly) harmful.

Products which are manufactured from formaldehyde and their uses:

Resins are products used for: adhesives, bonding agents, glues, paint and coatings, insulating materials, sealing materials. Resins are mostly reaction products from formaldehyde with phenol, urea, melamine, furfuryl alcohol, resorcinol. Typical applications of those resins are chip-board, particle-boards, plywood and laminates made from either paper or veneer as decorative finish, in the rubber and tyre industry as a bonding and tackifying agent and in the foundry industry for making cores and moulds.

Polyurethanes are products used for: foams used in stuffing and insulation, synthetic leather, engineering plastics used as for instance in the automotive industry i.e. dashboards, upholstery, bumpers as well as in shoes and clothing etc.

Polyoxymethlene: a 100 % polymer used as an engineering plastic for ski bindings, toothed wheels, prosthesis and other comparable strong- wear applications, kitchen articles, gasholders for lighters, automotive industry, shoes etc. etc.

Paints and Coatings Polyols made from formaldehyde play a major role in water-soluble systems.

Hydraulic fluids and Lubricants are polyol esters with outstanding performances that are widely used in aircraft and the space industry.

Pharmaceuticals, Food and Feed via intermediates for many products as for instance provitamin B3 and building block for enzymes.

Chelating agents (EDTA, NTA etc.) are products having a strong interaction with metal ions by means of binding / deactivating them where they can have a detrimental influence or selective extraction as for instance precious metals. These characteristics are used in agricultural products, detergents, soaps, cleaners, food industry, mining industry, metal plating, pulp and paper, textiles etc. etc.

1. HAZARDS

1.1. Health hazards:

Formaldehyde is a colourless gas with a pungent, suffocating odour. Trade forms are aqueous solutions and solids (paraformaldehyde) with the same distinctive odour. Its aqueous solutions are clear liquids. Most people can smell formaldehyde at concentrations of about 0,5 ppm (1 ppm = 1,2 mg/ m^3 at 25 °C), so the odour provides a warning before significant concentrations are present.

The occupational health hazards of formaldehyde are mainly related to its irritant effects. It is irritant on inhalation, direct contact with skin or eyes and on ingestion.

Formaldehyde is also classified as a carcinogenic hazard. Two separate classifications have been published:

1. International Agency for Research on Cancer (IARC) has classified formaldehyde as 2A (probably carcinogenic to humans). The latest review on this was done in 1995. IARC is a non-regulatory body.

2. In the EU countries formaldehyde is classified according to the Dangerous Substances Directive as a category 3 (C3) carcinogen leading to a risk phrase R 40 (Limited evidence of a carcinogenic effect). This is the weakest class of carcinogenic hazard.

Both of the above classifications are based on animal studies which show nasal cancer at high doses, although there is doubt about the relevance of this data to humans. A large number of human studies have provided no convincing evidence that formaldehyde produces cancer in man. However, exposure at the workplace has to be kept as low as reasonably practicable. Compliance with workplace occupational limit values should minimise the risk to health from inhalation of formaldehyde.

1.1.1. Inhalation:

Formaldehyde vapour irritates the respiratory system. Individual sensitivity varies broadly, but irritancy can occur below 1 to 2 ppm (1 ppm = 1,2 mg/m^3 at 25°C). Immediate strong discomfort is caused at a level of 10 ppm. Disorientation is possible.

1.1.2. Skin contact:

Formaldehyde solution is a moderate skin irritant and a repeated contact can cause hardening and cracking of skin. This may give rise to dermatitis. In addition there is a potential for skin sensitisation (allergy).

1.1.3. Eye contact:

Formaldehyde solution is a severe eye irritant. If it comes into contact with eyes, it may lead to permanent eye damage. Exposure to vapour or formaldehyde containing dust may cause inflammation of the eyelids.

1.1.4. Ingestion:

The swallowing of formaldehyde solution causes immediate irritation of the mouth, throat and stomach, resulting in nausea and vomiting. In extreme cases severe abdominal pain is experienced, possibly followed by loss of consciousness.(by collapse)

NOTE:
Always consult current Safety Data Sheets before handling formaldehyde.

1.2. Fire/ explosion hazards:

Formaldehyde and formaldehyde solutions release vapours which form explosive mixtures with air and can be ignited by various sources of ignition. (eg sparks, flames, hot surfaces etc.). Under normal working conditions the fire hazard of formaldehyde solutions is minimal, but increases with higher methanol content.

1.3. Other hazards:

Formaldehyde is a very reactive chemical and should not accidentally be brought into contact with some other substances, for example oxidising chemicals, hydrochloric acid etc.

2. PERSONAL PROTECTIVE EQUIPMENT (PPE)

Whenever possible, engineering control methods should be designed so that personal protective equipment is not generally needed and is only used as a last resort, for instance in an emergency situation.
The extent of protection varies according to circumstances or level of risk. These are best determined by the risk assessment referred to earlier. Training plays a key role in successful personal protection. Consider the following topics for training:

- the reason for using PPE and the circumstances when it is required
- the principles of operation and use of the PPE
- the limitations of PPE
- workplace arrangements for issuing, cleaning, storage, etc
- procedure for reporting defects and replacement of PPE.

2.1. Respiratory protection:

In cases where the occupational exposure level is potentially exceeded, a full face mask or hood type filter is recommended (full mask against eye irritation and splashes). In severe conditions, especially if oxygen deficiency is expected, a self-contained breathing apparatus is needed. In case it is necessary to escape from an emergency situation a respirator with an organic vapour filter is recommended.

2.2. Hand protection:

Formaldehyde reacts with skin protein to cause hardening and cracking of the skin. Therefore suitable gloves such as butyl rubber, neoprene, PVC or polyethylene should be worn.

2.3. Eye protection:

In contact with the eyes, severe burns will occur. Safety goggles or acid goggles or facial protection with glasses should be worn.

2.4. Skin protection:

When large amounts of formaldehyde are handled, (loading, unloading, filling drums) non liquid penetrable clothing should be worn.

2.5. Occupational Exposure limit (OEL):

The OEL depends on national regulations.

Occupational Exposure Limits in selected countries in parts per million (ppm):
(March 1999)

Country	8 hours	short term
Germany	0,5	0,5
Netherlands	1,0	2,0
Belgium	-	0,3
France	0,5	1,0
Sweden	0,5	1,0
Denmark	0,3	0,3
UK	2,0	2,0
Italy	0,3	
Spain	0,3	

3. FIRST AID

3.1. If vapour is inhaled:

Move to fresh air and keep person at rest. Give oxygen or artificial respiration if needed. Seek medical advice after significant exposure.

3.2. If splashed onto skin:

Remove all contaminated clothes and shoes. Wash off immediately with plenty of water. In severe cases seek medical advice.

3.3. If splashed onto clothing:

Immediately remove the contaminated clothing. In case of loss of consciousness, place patient in recovery position and transport accordingly. Apply artificial respiration if necessary. First-aiders should pay attention to their own safety. In severe cases seek medical advice.

3.4. If splashed into eyes:

Rinse thoroughly with plenty of water for at least 10-15 minutes. Seek medical advice.

3.5. If swallowed:

Immediately give plenty of water (if available, give activated carbon slurry). Do not induce vomiting. Seek medical advice.

4. ENVIRONMENTAL ASPECTS

4.1. Formaldehyde in the environment:

Formaldehyde is naturally present everywhere in our environment. The biggest source is methane, released from biodegradation of biomass and transformed by photo oxidation via formaldehyde to carbon dioxide. Natural life processes as well as human metabolism produce and degrade formaldehyde.
Main man-made sources of formaldehyde into ambient air are various combustion processes, as well as mobile (vehicles) and stationary sources (e.g. combustion plants). For indoor air main formaldehyde sources are smoking cooking using gas, construction materials and textiles.

4.1.1. In air:

In the air formaldehyde is degraded rapidly to carbon dioxide by photo-oxidation. Half-life in daylight has been determined to be few hours.
Typical background levels of formaldehyde in remote areas are below 1 ppb (parts per billion). In urban areas annual average levels between 5 and 10 ppb have been reported. During unfavourable weather conditions in big cities levels may rise above 100 ppb. Levels in indoor air vary widely. Figures from 50 ppb up to 1000 ppb (=1 ppm) have been reported. (Nowadays formaldehyde-based resins - used in the manufacture of wood panels - can be produced that emit less than 50 ppb of formaldehyde per cubic metre of indoor air).

4.1.2. In water and soil:

Formaldehyde is rapidly biodegraded in water and in soil. It does not bio-accumulate. High concentrations of formaldehyde are toxic to living organisms. This characteristic is utilised in numerous applications where formaldehyde is used as a sterilising or disinfecting agent.

5. CONTROL OF OCCUPATIONAL EXPOSURE:

Workplaces where formaldehyde solutions are handled are subject to various regulations. The detailed requirements in these regulations do vary from one country to another. Always examine and comply with the legislation in force in your country. Provisions described in this paper refer to the European Union level.

The following elements are typical for a good control of occupational exposure:

1. Assess workplace risks. This is a step- by- step process including collection of data on substances and working practices, evaluating exposures, assessing risks and deciding on ways needed to control risks. Detailed guidance on how to perform workplace risk assessment can be obtained from national authorities.

2. If risks cannot be eliminated, control them to minimise exposure. Ways to do this depend on the situation (if in order of priority: engineering solutions, working procedures, ventilation, personal protective equipment).

3, Maintenance is necessary to keep equipment in good working order. Ensure proper occupational safety measures during maintenance operations.

4. Training and information to understand workplace risks and precautions is always necessary when handling hazardous chemicals. All persons should be properly trained to perform their functions and also to act in foreseeable incidents.

5. Monitor exposure at the workplace to ensure consistency with occupational limit values or your internal standards. This should be done by competent persons.

6. Health surveillance may be needed for persons who may be exposed. Legislation varies greatly, but qualified occupational health staff always have to be used.

6. PHYSICAL/CHEMICAL PROPERTIES:

Pure monomer formaldehyde is a gas and as such is not commercially available. It condenses on chilling to a liquid with a boiling point of –19°C and freezes to a solid at –118°C. Both gas and liquid polymerise rapidly at low temperatures.

Table 1: Physical data

	Gas	Aqueous solution
CAS Nr.		50-00-0
Formaldehyde (wt %)	100	Up to 55
Molecular weight	30,03	
Melting point (°C)	-118	+4 to –4, (depends on methanol content)
Boiling point (°C)	-19,5	99,5 (50 wt% solution)
Vapour density (air=1)	1,075	1,04
Viscosity (mPas)		1,82 (60°C), 50% solution
Density		See tables 3 and 4
Methanol concentration (wt %)		maximum 3%
Ignition temp. (°C)	430	
Flash point (°C)		55-85, (depends on methanol content)
Conductivity (µS)		12-35, (depends on formic acid content)
Explosive limits (v% CH_2O in air)	7-72	Vapour is flammable
Vapour pressure (mbar) (partial press. of formaldehyde)		See table 2

Table 2: Vapour pressure of formaldehyde, 50% aqueous solution

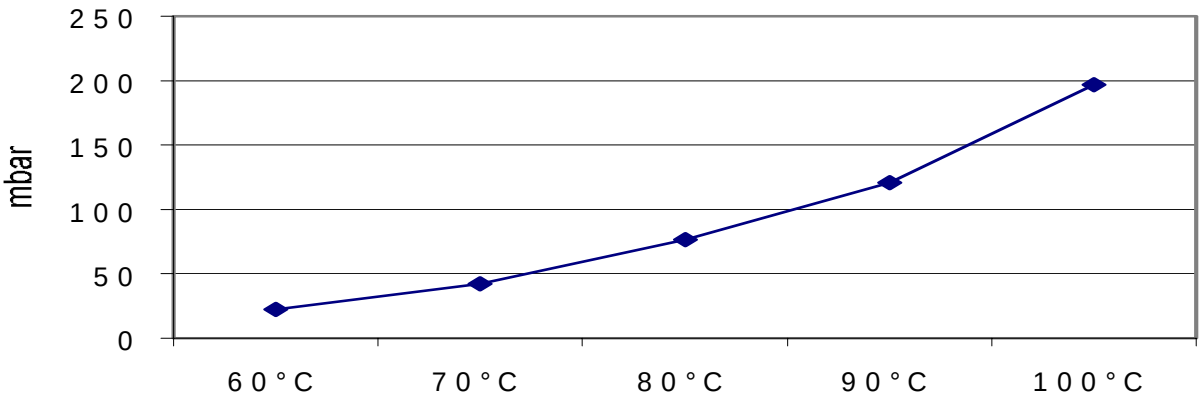


Table 3: Density of formaldehyde solution with 1% methanol

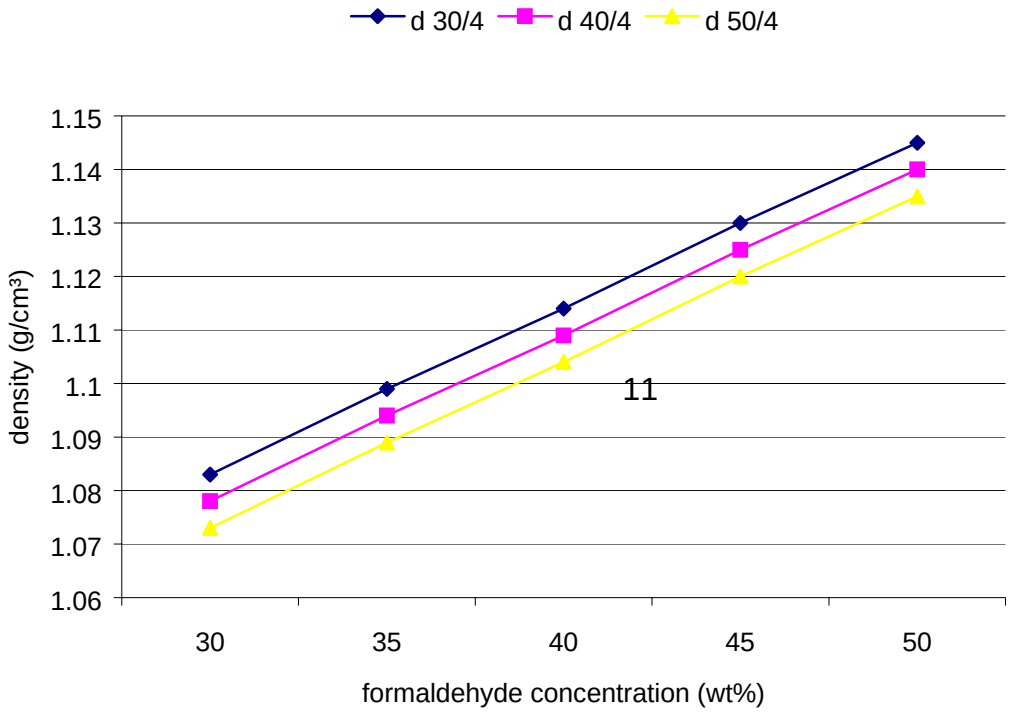
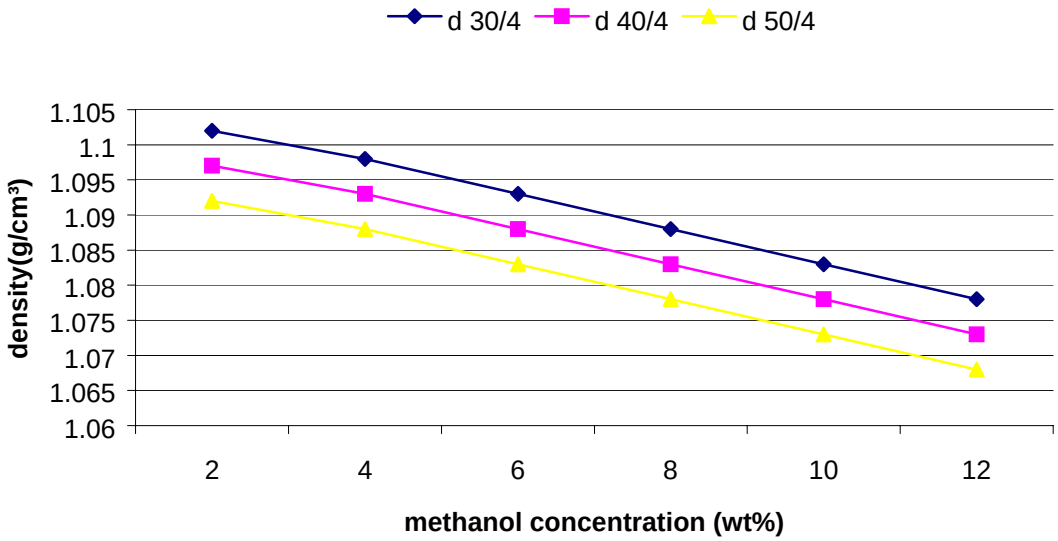


Table 4: Density of 37% formaldehyde solution with wt% methanol

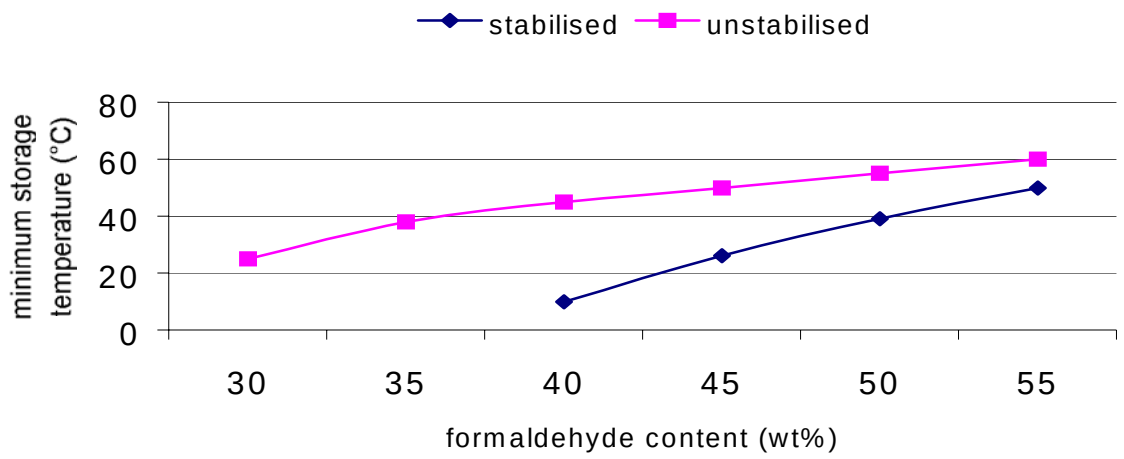


7. STORAGE:

Formaldehyde solutions should be stored in insulated tanks, ideally using 316 stainless steel for tanks, pipelines and valves. Aluminium, glass and poly-ethylene containers can also be used. Materials to be avoided are mild steel, zinc alloys, aluminium copper and brass.

Storage temperature:
The optimum storage temperature for any given solution depends upon the relative concentrations of formaldehyde and methanol according to table 5.

Table 5: Minimum storage temperature for several formaldehyde concentrations, methanol content less than 1 wt% (unstabilised or stabilised with organic stabilisers).



The storage temperatures are dependent on the Methanol concentrations of the formaldehyde solution. A mixture with 8 wt% methanol decreases the minimum storage temperature compared to unstabilised solution by about 15°C. Up to 12 wt% methanol the effect is practically linear.

7.1. Reactions during storage and production:

When formaldehyde solutions are stored it is likely that the following reactions occur:

1. Polymerisation (formation of paraformaldehyde):

Lowering the temperature of formaldehyde solutions increases the possibility of polymer formation. To minimise this formation it is necessary to store solutions above the minimum storage temperatures. Addition of organic stabilisers helps to decrease the minimum storage temperature and therefore the polymer formation.

2. Formic acid formation is accelerated by high temperature storage conditions according to the Cannizzaro reaction:

$$2\ CH_2O + H_2O \Rightarrow CH_3OH + HCOOH$$

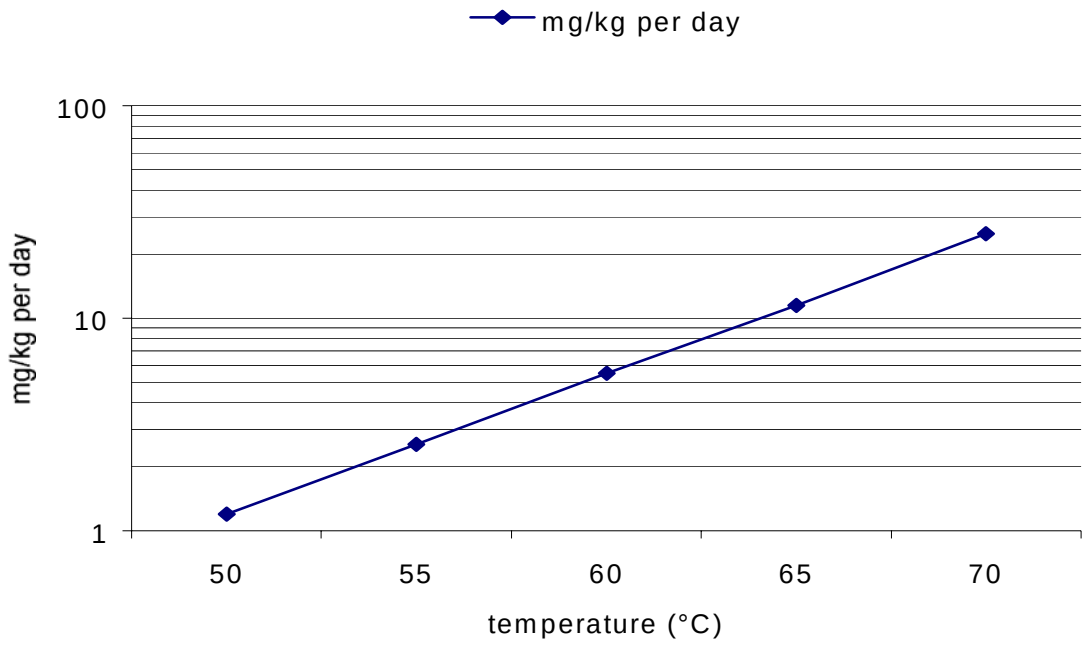
3. Formic acid formation by oxidation:

$$2\ CH_2O + O_2 \Rightarrow 2\ HCOOH$$

4. Formation of methylal by reaction between formaldehyde and methanol according to :

$$CH_2O + 2\ CH_3OH \Rightarrow CH_2(OCH_3)_2 + H_2O$$

Table 6: Approximate formation of formic acid in formaldehyde solutions 55 wt%



7.2. Flash point:

The flash point of aqueous formaldehyde depends on methanol concentration. Under certain methanol content and storage temperature conditions the product can fall into the flammable category. For details ask your supplier.
Out: Walker, Joseph Frederic, 1903 – Formaldehyde
ISBN 0-88275-218-9 American Chemical Society

Flash Points of commercial Formaldehyde Solutions

Formaldehyde	**Methanol**	**Flash Points**	
Content (Wt. %)	**Content** (Wt. %)	**ºC**	**ºF**
37.2	0.5	85	185
37.2	4.1	75	167
37.1	8.0	67	152
37.2	10.1	64	147
37.1	11.9	56	133
37.5	14.0	56	132

Physical Properties of Typical Aqueous Commercial Formaldehyde Solutions

CH^2O content %	37	37	37	45	50
CH^3OH content %	1	5	10	1	1
Flash point, °F (Closed Cup)	185	171	147	177	175

7.3. Paraformaldehyde formation:

Depending on concentrations, temperature and stabilisers it is likely that paraformaldehyde precipitation can occur.
To avoid the precipitation of paraformaldehyde it is advised to keep to the minimum storage temperatures given in table 5.

7.4. Drum storage and drum handling:

Drums should be stored at a temperature sufficiently high to avoid precipitation of paraformaldehyde, in a well-ventilated place and kept away from oxidising substances and ignition sources.

Suitable protective clothing, especially safety goggles and footwear, should be worn when drums of formaldehyde are handled.

Drums used for formaldehyde should be properly cleaned before reuse or disposal and should be discarded in a safe way.

7.5. Bulk storage:

The fire hazard with formaldehyde solutions is rather low but at elevated temperatures solutions can form flammable vapours. The vapours have a characteristic pungent odour and are harmful and lachrymatory. When considering a storage and handling installation both of these facts must be given due consideration.

It is advised that the location of any proposed storage installation is discussed and must meet the respective requirements of the local authorities.

Circulation or agitation is advised for formaldehyde solutions having concentrations higher than 37 wt% to avoid paraformaldehyde formation. The movement of the liquid should be as high as to achieve sufficient mixing (flow per hour about 10 % of tank capacity).

7.6. Heating system:

Depending on formaldehyde concentration, heating of the storage tank is advised. For special requirements contact your formaldehyde supplier.

7.7. Scrubber:

To prevent nuisance from formaldehyde vapours removal by scrubbing or incineration is recommended.

7.8. Sampling:

Sampling valves are of the zero volume type. This is to avoid formation of paraformaldehyde. Sampling tubes must be equipped with heat- tracing, depending on the formaldehyde concentration.

7.9. Breather

For ventilation an under- pressure/ over- pressure valve must be used. Depending on the concentration of formaldehyde the valve must be provided with heat tracing. A regular check is necessary to be sure that paraformaldehyde does not cause a blockage.

8. LOADING/UNLOADING

8.1. Tanker loading and unloading:

8.1.1. Rail tankers should be equipped with a load pipe 3 inch kamlock female, a vapour regulator 2 inch kamlock female and an unload- pipe 4 inch kamlock female.

8.1.2. Trucks:
Loading of formaldehyde solution happens through the manhole via a loadingarm or -pipe provided with a cone closing the free space of the manhole. The cone has a connection to suck off the vapours. Unloading takes place via a bayonet- catch 3 inch DIN 28450 and a vapour return pipe 1 inch GK- coupling.

The procedures for off- loading must be agreed between customer and supplier. During the off- loading a member of the receiver's staff must be available and correct safety precautions must be taken.

9. EMERGENCY ACTIONS

9.1. Spillage and waste disposal:

In work areas where spillage may occur, provision should be made for spillage containment, area decontamination and for waste disposal.

Any waste or contaminated spills should be disposed of in accordance with local and statutory requirements using a registered waste disposal contractor. Big spills should be covered with foam, after which the liquid can be sucked up.

9.2. FIRE FIGHTING

9.2.1. Protective equipment:

All personnel engaged in combating a fire involving formaldehyde solutions or paraformaldehyde should wear protective equipment comprising waterproof coat, rubber boots, goggles and helmet. For an indoor fire self-contained breathing apparatus should be worn. In the case of outdoor fires the latter equipment should be available and used if necessary.

9.2.2. Emergency action:

Extinguish and/or shut down all sources of ignition.
Isolate all electrical equipment.
Containers in the vicinity of the fire should be cooled by means of a water-spray.
If outdoors keep upwind.

9.2.3. Extinguishing media:

The use of water sprays is recommended. Alternatively, dry chemical or foam extinguishers suitable for use with alcohol may be used.

9.2.4. Personnel training:

It is essential that all personnel trained in fire fighting should be fully conversant with and skilled in the use of all of the equipment provided.

10. REGULATORY INFORMATION

10.1. Labelling of packages:

In the European Union countries, user labelling must conform with the Dangerous Substances Directive 67/548/EEC. The label must appear in the user's language. Detailed requirements depend on concentration of formaldehyde solution.
Formaldehyde solutions of less than 0,2 wt% concentration are not currently classified as dangerous and therefore no hazard labelling is required.
For higher concentrations labelling is required.

European Community user labelling requirements

Formaldehyde concentration (wt%)	0,2<c<1	1<c<5	5<c<25	c>25
Symbol	Xi	Xn	Xn	T
Hazard	Irritant	Harmful	Harmful	Toxic
Concentration	Not required	Contains ..% of formaldehyde	Contains ..% of formaldehyde	Contains ..% of formaldehyde
Index no.	605-001-00-5	605-001-00-5	605-001-00-5	605-001-00-5
EEC no.	200-001-8	200-001-8	200-001-8	200-001-8
Risk phrases	43	40-43	20/21/22-36/37/38-40-43	23/24/25-34-40-43
Safety phrases	Not required	26-36/37-45-51	26-36/37-45-51	26-36/37-39-45-51
EEC Category	C3	C3	C3	C3

R 20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R 23/24/25	Toxic by inhalation, in contact with skin and if swallowed
R 34	Causes burns
R 40	Limited evidence of a carcinogenic effect
R 43	May cause sensitisation by skin contact
S 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S 36/37	Wear suitable protective clothing and gloves
S 45	In case of accident or if you feel unwell, seek medical advice immediately
S 39	Wear eye protection
S 51	Use in well-ventilated areas only

10.2. Transport regulations:

Road/ Rail transport requirements:

During international road/rail transportation formaldehyde solutions above 25 wt% are classified as Corrosive, ADR class 8, paragraph 63c. Formaldehyde solutions below 25 wt% are not classified as dangerous goods according to international regulations.

Formaldehyde solutions are transported in bulk tankers or rail cars. Labelling for transport is with the ADR Corrosive symbol and an orange placard with numbers 80 (hazard identity number) and 2209 (substance identification number).

In addition, the vehicle has to carry a transport emergency card (Tremcard) in official languages of all countries en route.

10.2.1. Maritime transport requirements:

The labelling of containers for formaldehyde solutions and paraformaldehyde must conform to the requirements of the International Maritime Dangerous Goods (IMDG) Code.

10.2.2. Air transport requirements:

The marking and labelling of containers must conform to the requirements of the International Civil Aviation Organisation (ICAO) document 9284-AN/905 “Technical instructions for the Save Transport of Dangerous Goods by Air”. Certain airlines place restrictions on transport and the current edition of the International Air Traffic Association (IATA) Restricted Articles Regulations should be consulted in conjunction with the above ICAO requirements.