PCS INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY

Health and Safety Guide No. 105

METHANOL

HEALTH AND SAFETY GUIDE



UNITED NATIONS ENVIRONMENT PROGRAMME



INTERNATIONAL LABOUR ORGANISATION



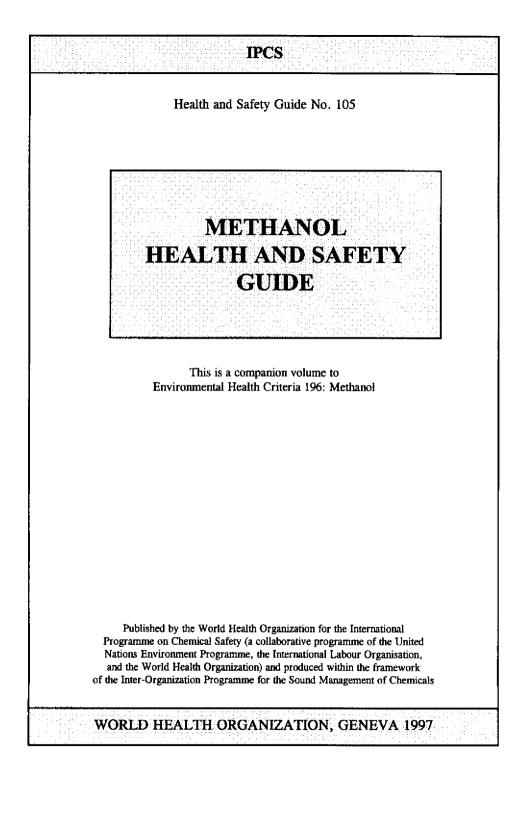
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INTRODUCTION

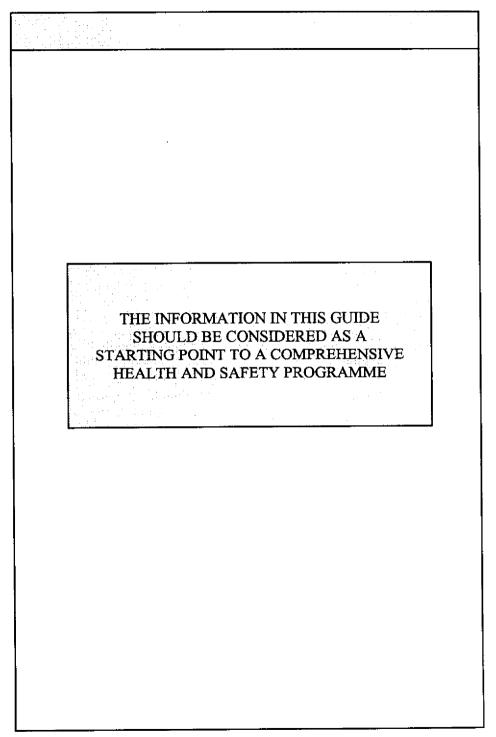
The Environmental Health Criteria (EHC) monographs produced by the International Programme on Chemical Safety include an assessment of the effects on the environment and on human health of exposure to a chemical or combination of chemicals, or physical or biological agents. They also provide guidelines for setting exposure limits.

The purpose of a Health and Safety Guide is to facilitate the application of these guidelines in national chemical safety programmes. The first three sections of a Health and Safety Guide highlight the relevant technical information in the corresponding EHC. Section 4 includes advice on preventive and protective measures and emergency action; health workers should be thoroughly familiar with the medical information to ensure that they can act efficiently in an emergency. Within the Guide is a Summary of Chemical Safety Information which should be readily available, and should be clearly explained, to all who could come into contact with the chemical. The section on regulatory information has been extracted from the legal file of the International Register of Potentially Toxic Chemicals (IRPTC) and from other United Nations sources.

The target readership includes occupational health services, those in ministries, governmental agencies, industry, and trade unions who are involved in the safe use of chemicals and the avoidance of environmental health hazards, and those wanting more information on this topic. An attempt has been made to use only terms that will be familiar to the intended user. However, sections 1 and 2 inevitably contain some technical terms. A bibliography has been included for readers who require further background information.

Revision of the information in this Guide will take place in due course, and the eventual aim is to use standardized terminology. Comments on any difficulties encountered in using the Guide would be very helpful and should be addressed to:

> The Director International Programme on Chemical Safety World Health Organization 1211 Geneva 27 Switzerland



1. PRODUCT IDENTITY AND USES

1.1 Identity

Common name:	methanol
Chemical formula:	CH₃OH
Chemical structure:	H H-C-OH H
Relative molecular mass:	32.04
Common synonyms:	methyl alcohol; methyl carbinol; carbinol; wood alcohol; wood spirits; wood naphtha; Columbian spirits; Manhattan spirits
Abbreviations:	None
CAS registry number:	67-56-1
RTECS number:	PC 1400000
United Nations number:	1230
EC number:	603-001-00-X
Conversion factors:	1 ppm = 1.31 mg/m ³ ; 1 mg/m ³ = 0.763 ppm at 25 °C and 101.4 kPa (760 mmHg)

1.2 Physical and chemical properties

Methanol is a colourless, polar, volatile, flammable liquid with a mild alcoholic odour when pure. It decomposes on heating producing carbon monoxide and formaldehyde. Methanol reacts violently with oxidizing materials such as perchlorates, chromium trioxide, bromine, sodium hypochlorite, chlorine and hydrogen peroxide resulting in fire and explosive mixtures.

PRODUCT IDENTITY AND USES

Methanol mixes well with air, easily forming explosive mixtures. It is miscible with water, alcohols, esters, ketones and most organic solvents and forms many azeotropic mixtures.

Methanol for laboratory use is available in various purity grades for fine chemicals: 1) "synthesis" quality corresponding to normal commercial methanol; 2) certified analytical quality and 3) extremely pure quality for semiconductor manufacture. In addition to laboratory grades, commercial methanol is generally classified according to ASTM purity grades A and AA. The composition of methanol varies according to synthesis conditions. In addition to water, typical impurities include acetone, acetaldehyde, ethanol and higher alcohols, methyl formate and higher esters.

1.2.1 Physical properties

Melting point (°C)	-97.8
Boiling point (°C)	64.7
Refractive index n ²⁰	1.3284
Solubility in water	miscible
Relative density (d 20/4)	0.7915
Relative vapour density	1.1
(air = 1)	
Vapour pressure (kPa at 20 °C)	12.3
Ignition temperature (°C)	470
Explosive limits in air	lower 5.5
(% by volume)	upper 44
T1 1 1 (0.0)	
Flash-point (°C)	
(open cup)	15.60
• · · ·	15.60 12.20

1.3 Analytical methods

For the analysis of production batches of methanol, comparative ultraviolet spectroscopy has proved to be a convenient rapid test method. Further tests for establishing the quality of methanol include measurements of boiling point range, permanganate number, turbidity colour index and acid number. More comprehensive tests include water determination according to the Karl Fischer method and gas chromatographic determination of by-products of synthesis. The most important standardized test methods for methanol are: ASTM D1078, boiling range; ASTM D1209, colour index; ASTM D1353, dry residue; ASTM D1363, permanganate number; ASTM D1364, water content; ASTM D1612, acetone content; ASTM D1613, acid content; and ASTM D941, density.

1.4 **Production and uses**

Modern industrial-scale methanol production is based exclusively on the catalytic conversion of pressurized synthesis gas (hydrogen, carbon monoxide and carbon dioxide) in the presence of metallic heterogenous catalysts. All carbonaceous materials such as coal, coke, natural gas, petroleum and fractions obtained from petroleum (asphalt, gasoline and gaseous compounds) can be employed as starting material for synthesis gas production.

The required synthesis pressure is dependent upon the activity of the particular metallic catalyst employed with copper-containing zinc oxidealumina catalysts, the most effective employed with low pressure processes (50-100 atm) in modern methanol plants. Methanol is purified by distillation.

Prior to 1930, the earliest important source of methanol (wood alcohol) was the dry distillation of wood at about 350 °C.

Approximately 70% of the methanol produced worldwide is used in chemical synthesis. The products, in order of importance, are: methyl tertiary-butyl ether (MTBE), formaldehyde, acetic acid, methyl methacrylate and dimethyl terephthalate.

Methanol is widely used as an industrial and laboratory solvent for extracting, washing, drying and recrystallization.

Methanol is present in a broad variety of commercial and consumer products, including paints, varnishes, shellacs, antifreeze and gasoline deicers, windshield washer fluids, cleansing solutions, mixed solvents in duplicating machines, and hobby glues and adhesives. Only a small proportion of methanol is currently used for energy production. There is a potential for its use as an oxygenate for alternative fuel or in fuel blends with gasolines.

2.1 Human exposure to methanol

Methanol occurs naturally. It is a natural constituent in blood, urine, saliva and expired air. Mean blood methanol levels of about 0.73 mg/litre in unexposed individuals have been reported. A mean level of 0.25 μ g methanol/litre is expired by unexposed humans. The two most important sources of background body burdens of methanol (and its metabolite formate) are diet and metabolic processes.

Methanol is available in the diet principally from fresh citrus fruits and juices, vegetables, fermented beverages and diet foods (principally soft drinks) containing the artificial sweetener aspartame (which on hydrolysis yields 10% by weight of the molecule to free methanol that is available for absorption).

The general population may be exposed to methanol principally from air emissions from miscellaneous industrial and domestic solvent use, methanol production, end-product manufacturing and bulk storage and handling losses. General population exposures through air are currently typically 10 000 times lower than occupational limits.

Occupational exposure to methanol via inhalation is generally low but may be greater in less controlled conditions. Accidental or intentional ingestion of methanol-containing products occurs less frequently and is associated with high morbidity and mortality.

2.2 Uptake, metabolism and excretion

Methanol is readily absorbed by inhalation, ingestion and dermal exposure and is rapidly distributed to tissues according to the distribution of body water. A small amount of methanol is excreted unchanged by the lungs and kidneys.

Metabolism of methanol occurs in a three-step process initially involving oxidation to formaldehyde by hepatic alcohol dehydrogenase, which is a saturable rate-limiting process. In the second step, formaldehyde is oxidized by aldehyde dehydrogenase to formic acid or formate depending on

the pH. In the third step, formic acid is detoxified by a folate-dependent pathway to carbon dioxide. Elimination of methanol from the blood appears to be slow in all species, especially when compared to ethanol. In humans, urinary methanol concentrations have been found to be proportional to the concentration of methanol in blood.

Formate clearance from the blood of exposed primates is at least 50% slower than for rodents.

2.3 Effects on organisms in the environment

Methanol is readily degraded in the environment by photooxidation and by biodegradation processes. Many genera and strains of microorganisms are capable of using methanol as a growth substrate. Methanol is readily degradable under both aerobic and anaerobic conditions in a broad spectrum of environmental media including fresh and salt water, sediments and soils, ground water, aquifer material and industrial wastewater.

Methanol is a normal growth substrate for many soil microorganisms, which are capable of completely degrading methanol to carbon dioxide and water.

 LC_{50} values in aquatic organisms range from 1300 to 15 900 mg/litre for invertebrates (48- and 96-h exposures), and 13 000 to 29 000 mg/litre for fish (96-h exposure).

 LC_{50} values in aquatic organisms range from 1300 to 15 900 mg/litre for invertebrates (48-h and 96-h exposures), and 13 000 to 29 000 mg/litre for fish (96-h exposures).

Methanol is of low toxicity to aquatic and terrestrial organisms and effects due to environmental exposure to methanol are unlikely to be observed, except in the case of spillage.

2.4 Effects on laboratory animals and in vitro test systems

Methanol has a low acute toxicity to non-primate animals. The LD_{50} values after oral exposure in the rat, mouse, rabbit and dog range from 6200 to 13 000 mg/kg and the MLD value is 2000-7000 mg/kg for the monkey.

Methanol causes profound species-specific toxicity, dependent on the extent to which formate accumulates in the body following methanol exposure. Sensitive primate species develop increased blood formate concentrations following methanol exposure while resistant rodents, rabbits and dogs do not.

Exposure of non-primate laboratory mammals to high methanol doses results in CNS depression. Toxic effects found in methanol-exposed primates include metabolic acidosis and ocular toxicity, effects not normally found in methanol-exposed lower animals.

Monkeys exposed by inhalation to up to 6550 mg/m^3 (5000 ppm) methanol 6 h/day, 5 days/week for 4 weeks, showed no treatment-related effects. Twenty repeated exposures to 6550 mg/m^3 failed to elicit optic effects in exposed monkeys.

The inhalation of methanol by pregnant rodents throughout the period of embryogenesis induces a wide range of concentration-dependent teratogenic and embryolethal effects.

Negative findings have been reported in studies investigating the ability of methanol to produce gene mutations in bacteria (*Salmonella typhimurium and E.coli*) and yeast (*Saccharomyces pombe*). It induces chromosomal malsegragation in *Aspergillus nidulans*.

Methanol does not induce sister chromatid exchanges in Chinese hamster cells *in vitro* but caused significant increases in mutation frequencies in L5178Y mouse lymphoma cells. Administration by inhalation does not induce chromosomal damage in mice, but there is some evidence that oral or intraperitoneal administration does.

There are no adequate studies to assess carcinogenicity.

2.5 Effects on humans

Methanol is irritating to the eyes, skin and respiratory tract. A broad range of ocular effects have been associated with longer-term occupational

exposure to lower levels of methanol. Acute oral and inhalation exposures and, to a lesser extent, percutaneous absorption of high concentrations of methanol have resulted in central nervous system depression, blindness, coma and death.

Repeated or prolonged contact of methanol with skin may result in dermatitis. Liquid methanol defats the skin. It is also an effective extracting solvent and may damage the skin permeability barrier.

Nearly all the information on methanol toxicity in humans relates to the consequences of acute rather than chronic exposure and the vast majority of poisonings result from the consumption of adulterated beverages or methanol-containing products. Although oral ingestion is the most frequent route of poisoning, in severe and exceptional conditions inhalation of methanol vapour and percutaneous absorption of methanolic liquids are also effective in producing acute toxic syndrome characterized by metabolic acidosis, central nervous system depression, blindness, coma and death.

The severity of the metabolic acidosis is variable and may not correlate well with the amount of methanol ingested. The variability of the toxic dose is a prominent feature in methanol toxicity.

The symptoms of methanol poisoning, which may not appear for 12 to 24 h, include visual disturbances, nausea, abdominal and muscle pain, dizziness, weakness and disturbances of consciousness ranging from coma to clonic seizures.

The lethal dose of methanol for humans is not known for certain, but is reported to range from 0.3 to 1 g/kg. Autopsies from victims of lethal methanol poisoning reveal retinal and optic nerve degeneration and gross pathology in the visceral organs, lungs and central nervous system, involving a variety of oedematous, haemorrhagic and degenerative changes.

Visual disturbances of several types (blurring, constriction of the visual field, changes in colour perception and temporary or permanent blindness) have been reported in workers exposed to methanol air levels in excess of occupational exposure limits.

No epidemiological data are available to evaluate the carcinogenicity of methanol for humans. Folate-deficient individuals might be at greater risk of methanol toxicity compared to normal individuals. Human populations that are potentially at risk of folate deficiency include pregnant women, the elderly, alcoholics, individuals with poor quality diets and individuals on certain medication.

3. CONCLUSIONS

The general population may be exposed to very low levels of methanol due to emissions in air from its production, end-uses, storage and handling, and the broad range of methanol-containing products.

Occupational exposure may occur during the production of methanol and its storage and handling, as well as in end-use product synthesis. Although the individual responses of humans to methanol may vary considerably, industrial exposures are not considered hazardous if concentrations are maintained within prescribed occupational exposure limits.

Methanol occurs naturally and is present in the diet. It can be absorbed rapidly by the inhalation, oral and dermal routes and distributed in the body, but it is only slowly metabolized to formate (which is believed to be the cause of visual damage) and then excreted. Methanol is rapidly degraded in the environment with no evidence of bioaccumulation. The available data do not indicate that there are any significant effects in the environment.

4. HUMAN HEALTH HAZARDS, PREVENTION AND PROTECTION, EMERGENCY ACTION

4.1 Human health hazards, prevention and protection, first aid

Methanol vapour and solutions are irritating to the skin and eyes. Prolonged or repetitive skin contact can cause dryness, cracking and dermatitis.

Methanol is well absorbed by the inhalation, oral and percutaneous routes and can cause metabolic acidosis and damage to the central nervous system, optic nerve, retina and liver. The onset of symptoms may be delayed following exposure (see Summary of Chemical Safety Information, section 6).

4.2 Information for physicians

Full information on the diagnosis and treatment of methanol poisoning is contained in the IPCS Poisons Information Monograph No. 335.

Thorough and vigorous washing of the skin with water will minimize systemic absorption following skin contamination. Gastric decontamination should be considered if the patient is seen relatively early (e.g., within one hour after ingestion).

Following ingestion, effects may be delayed and it is important to keep the patient under observation. The treatment of poisoning is based upon the use of ethanol as antidote, haemodialysis and correction of acidosis (by bicarbonate administration). It is recommended to contact urgently the nearest poisons information centre.

4.3 Health surveillance advice

Control of exposure by containment and good working conditions and hygiene is most important.

A complete medical and occupational pre-employment history should be taken and a physical examination performed with particular attention to the skin, eyes, liver and kidneys. Pre-existing skin disease and a history of alcoholism require a decision as to fitness for employment.

HUMAN HEALTH HAZARDS, PREVENTION AND PROTECTION, EMERGENCY ACTION

Because the recognized toxic effects of methanol include retinal toxicity, optic atrophy and blindness, pre-existing eye disease and folic acid deficiency should be identified and used as a baseline for future health assessments.

Subsequent medical examination should be on a regular basis, and should also be performed in the event of excessive exposure, splashes in the eye or for any employee who develops ocular symptoms while working with methanol.

4.4 Explosion and fire hazards

4.4.1 Explosion hazards

Methanol vapour/air mixtures are explosive. Violent reactions of methanol can occur with oxidizing agents (see section 1.2).

4.4.2 Fire hazards

Methanol is highly flammable and burns with an invisible or light blue flame. Methanol may be ignited by heat, sparks or flames and vapour may travel to a source of ignition and flash back.

4.4.3 Prevention

There should be no ignition sources such as open flames, sparks or smoking in the vicinity of methanol storage or use. Contact of methanol with oxidants should be avoided. Methanol must be used and stored in cool closed systems with adequate ventilation and explosion-proof electrical equipment and lighting.

4.4.4 Fire-extinguishing agents

Small fires can be fought with dry chemical, carbon dioxide, water spray, alcohol-resistant foam or, if these are not available, by dilution with plenty of water.

HUMAN HEALTH HAZARDS, PREVENTION AND PROTECTION, EMERGENCY ACTION

Large fires can be attacked with water spray, fog or alcohol-resistant foam.

Water spray should be used to cool down containers in fire area.

4.5 Storage

Methanol should be stored in clean containers made from either mild steel, stainless steel, high density polyethylene or vulcanized natural rubber. Unsuitable container materials include zinc, aluminium, magnesium, magnesium alloys, lead, tin, titanium, plasticised PVC, polystyrene or polymethyl-methacrylate. Storage tanks should be constructed with an internal floating roof and an inert gas pad to minimize vapour emissions.

Methanol should be stored in well-ventilated areas away from direct sunlight and moisture. It should not be stored with oxidizing materials such as perchlorates, chromium trioxide, bromine, sodium hypochlorite, chlorine or hydrogen peroxide, owing to fire and explosive dangers.

Because of the flammability of methanol, storage tanks should be enclosed by a dike and protected by a foam-type (either carbon dioxide or dry chemical) fire-extinguishing system.

4.6 Transport

All shipping containers (tank cars, tank trucks, barges, drums and barrels) should be of carbon steel and in a clean and dry condition prior to loading.

Air pressure should never be used to load or unload methanol. Pumping is preferred but inert gas should be used when pressure loading or unloading.

In case of an accident involving tank trucks or transport carrying drums or barrels of methanol, the vehicle should be immediately stopped, and all sources of ignition rapidly removed. In case of spillage or fire, methods advised in sections 4.7 and 4.4, respectively, should be used.

HUMAN HEALTH HAZARDS, PREVENTION AND PROTECTION, EMERGENCY ACTION

4.7 Spillage and disposal

Evacuate danger area, collect leaking liquid in sealable containers, or dike far ahead of liquid spill for later disposal. Flush spilled liquids with copious amounts of water and prevent direct access of run-off to water courses.

For relatively small spillages (about 25 litres), the liquid may be absorbed onto sand or vermiculite and transferred into suitable containers. The site of the spillage should be washed thoroughly with water.

Protective wear, appropriate to the degree of spillage, should be worn, and personnel allowed to enter the hazard area only when necessary. Extra personal protection can be achieved by using complete protective clothing, including self-contained breathing apparatus.

5. HAZARDS FOR THE ENVIRONMENT AND THEIR PREVENTION

Methanol does not pose a significant hazard for aquatic or terrestrial life, except in the case of a spillage. Contamination of soil, water and the atmosphere can be avoided by proper methods of storage, handling, transport and waste disposal.

6. SUMMARY OF CHEMICAL SAFETY INFORMATION

This summary should be easily available to all health workers concerned with, and users of methanol. It should be displayed at or near entrances to areas where there is potential exposure to methanol, and on processing equipment and containers. The summary should be translated into the appropriate language(s). All persons potentially exposed to the chemical should also have the instructions in the summary clearly explained.

The National Occupational Exposure Limit, the address and telephone number of the nearest Poison Information Centre, and local trade names should be added to the summary.

	SUMMARY OF CHEMICAL SAFETY INFORMATION	RMATION
	METHANOL CH ₃ OH	
PHYSICAL PROPERTIES		OTHER CHARACTERISTICS
Relative molecular mass Melting point (°C) Boiling point (°C) (760 mmHg) Flash point (closed up) (°C) Ignition temperature (°C) Relative density (20°C) Relative vapour density Vapour pressure (kPa at 20 °C)	32.04 -97.8 64.7 12.2 470 0.792 1.1 12.3	Flammable liquid; slight alcoholic odour when pure; crude material may have a repulsive pungent odour; burns with non- luminous blue flame; miscible with water, ethanol, ether, benzene, ketones and most other organic solvents
HAZARDS/SYMPTOMS	PREVENTION AND PROTECTION	FIRST AID
SKIN: Vapour and solutions are irritant; irritation, redness	Wear protective gloves and protective clothing	Remove contaminated clothing immediately, wash contaminated skin thoroughly with clear running water and refer for medical attention
EYES: irritation, redness, pain	Ensure vapour concentrations are below occupational exposure limits; wear chemical safety goggles; use face visor when handling solutions	Rinse eyes with plenty of water for at least 15 min, then obtain medical advice

INGESTION AND SYSTEMIC ABSORPTION BY OTHER ROUTES: Possibility of delayed CNS, optic nerve, retina and liver damage	Do not eat, drink or smoke during work	Do not induce vomiting; obtain medical attention immediately; the possibility of alcohol administration should be considered
SPILLAGE	STORAGE	FIRE AND EXPLOSION
SOLUTIONS: Evacuate danger area, collect leaking liquid in sealable containers, wash away spilled liquid with plenty of water	Store in cool, fireproof area separated from strong oxidants	
WASTE DISPOSAL		LABELLING
Collect in sealable containers		United Nations Hazard Class; 3 Subsidiary risks; 6.1 Packing group; 11

7. CURRENT REGULATIONS, GUIDELINES AND STANDARDS

7.1 Exposure limit values

Some exposure limit values are given in the accompanying table.

7.2 Labelling, packaging and transport

- UN: UN Hazard Class: 3 UN Subsidiary Risks: 6.1 UN Packing Group: 11
- EU: The European Union legislation requires labelling as a dangerous substance, using the designated symbols.

The following standard risk phrases should be used:

F symbol, T symbol R: 11-23/25 S: 2-7-16-24

Exposure Limit Values	it Values	REN REGIEAT	CURRENT RECULATIONS, GUIDELINES AND STANDARDS	NDARDS	
Medium	Specification	Country/organization	Exposure limit description	Value (mg/m ³)	Effective date
AIR	Occupational	Australia	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (Skin absorption)	260 310	
		Belgium	Time-weighted average (TWA) (Skin absorption) Short-term exposure limit (STEL) (skin absorption)	262 328	
		Czech Republic	Time-weighted average (TWA) Short-term exposure limit (STEL)	100 500	
		Denmark	Time-weighted average (TWA) (skin absorption)	260	1988
		Finland	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL)	260 325	
		France	Time-weighted average (TWA) Short-term exposure limit (STEL)	260 1300	1982-1989

Medium	Specification	Country/organization	Exposure limit description	Value (mg/m ³)	Effective date
		Germany	Time-weighted average (TWA) (skin absorption)	260	1990
		Hungary	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	50 100	
		Ireland	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	262 328	
		Italy	Time-weighted average limit (STEL) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	262 328	
		Japan	Time-weighted average (TWA) (skin absorption)	260	
		Luxembourg	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	262 328	
		-			

L	Medium	Specification	Country/organization	Exposure limit description	Value (mg/m³)	Effective date
<u> </u>			Netherlands	Time-weighted average (TWA)	260	1989
			Poland	Time-weighted average (TWA)	001	
			Portugal	Time-weighted average (TWA)	262	
				(skin absorption) Short-term exposure limit (STEL) (skin absorption)	328	
			Spain	Time-weighted average (TWA)	262	
78				(skin aosorption) Short-term exposure limit (STEL) (skin absorption)	328	
			Sweden	Time-weighted average (TWA)	250	
				(skin absorption) Short-term exposure limit (STEL) (skin absorption)	350	
			Switzerland	Time-weighted average (TWA)	260	
				(skin absorption) Short-term exposure limit (STEL) (skin absorption)	520	
			United	Time-weighted average (TWA)	260	1990
			Ninguon	(skin ausorphum) Short-term exposure limit (STEL) (skin absorption)	310	

Medium	Specification	Country/organization	Exposure limit description	Value (mg/m³)	Effective date
20		USA (ACGIH)	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	262 328	-989- 1990
		USA (NIOSH/OSHA)	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	260 310	
4.		Former USSR	Time-weighted average (TWA) (skin absorption) Short-term exposure limit (STEL) (skin absorption)	Ś	

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