CLH report

Proposal for Harmonised Classification and Labelling

**Based on Regulation (EC) No 1272/2008 (CLP Regulation),
Annex VI, Part 2**

International Chemical Identification:
Formic Acid… %

EC Number: **200-579-1**

CAS Number: **64-18-6**

Index Number: **607-001-00-0**

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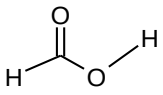
1 IDENTITY OF THE SUBSTANCE

1.1 Name and other identifiers of the substance

Table 1. Substance identity and information related to molecular and structural formula of the substance

Name(s) in the IUPAC nomenclature or other international chemical name(s)	Formic acid
Other names (usual name, trade name, abbreviation)	Carboxylic acid Methanoic acid Ameisensaeure Ameisensäure Aminic acid Formic acid (7CI, 8CI, 9CI) Formira Formisoton Formylic acid Hydrogen carboxylic acid Methanoic acid monomer Myrmicyl Protectol 85 FM
ISO common name (if available and appropriate)	/
EC number (if available and appropriate)	200-579-1
EC name (if available and appropriate)	Formic acid
CAS number (if available)	64-18-6
Other identity code (if available)	/
Molecular formula	CH2O2
Structural formula	
SMILES notation (if available)	O=CO
Molecular weight or molecular weight range	46.03
Information on optical activity and typical ratio of (stereo) isomers (if applicable and appropriate)	Not applicable
Description of the manufacturing process and identity of the source (for UVCB substances only)	Not applicable
Degree of purity (%) (if relevant for the entry in Annex VI)	85 – 99 % aquous solution

1.2 Composition of the substance

Table 2. Constituents (non-confidential information)

Constituent (Name and numerical identifier)	Concentration range (% w/w minimum and maximum in multi-constituent substances)	Current CLH in Annex VI Table 3.1 (CLP)	Current self classification and labelling (CLP)
Formic acid	85 - 99 % aqueous solution	Skin Corr. 1A; H314	Flam. Liq. 3; H226 Metal Corr . H290 Acute Tox. 4 (oral); H302 Acute Tox. 3 (Inhalation - vapour); H331 Skin Corr./Irrit. 1A; H314 Eye Dam./Irrit. 1; H318
Water	1 – 15%	-	-

Table 3. Impurities (non-confidential information) if relevant for the classification of the substance

Impurity (Name and numerical identifier)	Concentration range (% w/w minimum and maximum)	Current CLH in Annex VI Table 3.1 (CLP)	Current self-classification and labelling (CLP)	The impurity contributes to the classification and labelling
N/A				

Table 4. Additives (non-confidential information) if relevant for the classification of the substance

Additive (Name and numerical identifier)	Function	Concentration range (% w/w minimum and maximum)	Current CLH in Annex VI Table 3.1 (CLP)	Current self-classification and labelling (CLP)	The additive contributes to the classification and labelling
N/A					

2 PROPOSED HARMONISED CLASSIFICATION AND LABELLING

2.1 Proposed harmonised classification and labelling according to the CLP criteria

Table 5.

	Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling			Specific Conc. Limits, M-factors	Notes
					Hazard Class and Category Code(s)	Hazard statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	Suppl. Hazard statement Code(s)		
Current Annex VI entry	607-001-00-0	Formic acid … %	200-579-1	64-18-6	Skin Corr. 1A	H314	GHS05 Dgr	H314	-	Skin Corr. 1B; H314: 10% ≤ C < 90% Skin Corr. 1A; H314: C ≥ 90% Skin Irrit. 2; H315: 2% ≤ C < 10% Eye Irrit. 2; H319: 2% ≤ C < 10%	Note B*
Dossier submitters proposal					**Add** Metal Corr.	H290	GHS05	H290	-	C ≥ 85%	
					Add Flam. Liq. 3	H226	GHS02	H226	-	C≥99%	
					Add Acute Tox. 4 (oral)	H302		H302	-		
					Add Acute Tox. 3	H331,	GHS06	H331	EUH071		

					(Inhalation - vapour)						
					Add Eye Dam./Irrit. 1	H318			-	C≥10%	
Resulting Annex VI entry if agreed by RAC and COM	607-001-00-0	Formic acid … %	200-579-1	64-18-6	Metal Corr.	H290	GHS05	H290	-	C ≥ 85%	
					Flam. Liq. 3	H226	GHS02	H226	-	C ≥ 99%	Note B
					Acute Tox. 4 (oral)	H302		H302	-		
					Acute Tox. 3 (Inhalation - vapour)	H331,	GHS06	H331	EUH071		
					Skin Corr./Irrit. 1A	H314	GHS05	H314	-	Skin Corr. 1B; H314: 10% ≤ C < 90% Skin Corr. 1A; H314: C ≥ 90% Skin Irrit. 2; H315: 2% ≤ C < 10% Eye Irrit. 2; H319: 2% ≤ C < 10%	
					Eye Dam./Irrit. 1	H318			-	C≥10%	

** Note B: Some substances (acids, bases, etc.) are placed on the market in aqueous solutions at various concentrations and, therefore, these solutions require different classification and labelling since the hazards vary at different concentrations. In Part 3 entries with Note B have a general designation of the following type: 'nitric acid ? %'. In this case the supplier must state the percentage concentration of the solution on the label. Unless otherwise stated, it is assumed that the percentage concentration is calculated on a weight/weight basis.*

Table 6. Reason for not proposing harmonised classification and status under public consultation

Hazard class	Reason for no classification	Within the scope of public consultation
Explosives	hazard class not assessed in this dossier	No
Flammable gases (including chemically unstable gases)	hazard class not applicable	No
Oxidising gases	hazard class not applicable	No
Gases under pressure	hazard class not applicable	No
Flammable liquids	**harmonised classification proposed**	**Yes**
Flammable solids	hazard class not applicable	No
Self-reactive substances	hazard class not applicable	No
Pyrophoric liquids	hazard class not applicable	No
Pyrophoric solids	hazard class not applicable	No
Self-heating substances	hazard class not applicable	No
Substances which in contact with water emit flammable gases	hazard class not applicable	No
Oxidising liquids	hazard class not applicable	No
Oxidising solids	hazard class not applicable	No
Organic peroxides	hazard class not applicable	No
Corrosive to metals	**harmonised classification proposed**	**Yes**
Acute toxicity via oral route	**harmonised classification proposed**	**Yes**
Acute toxicity via dermal route	hazard class not assessed in this dossier	No
Acute toxicity via inhalation route	**harmonised classification proposed**	**Yes**
Skin corrosion/irritation	Existing harmonised classification	No
Serious eye damage/eye irritation	**harmonised classification proposed**	**Yes**
Respiratory sensitisation	hazard class not assessed in this dossier	No
Skin sensitisation	hazard class not assessed in this dossier	No
Germ cell mutagenicity	hazard class not assessed in this dossier	No
Carcinogenicity	hazard class not assessed in this dossier	No
Reproductive toxicity	hazard class not assessed in this dossier	No
Specific target organ toxicity-single exposure	hazard class not assessed in this dossier	No
Specific target organ toxicity-repeated exposure	hazard class not assessed in this dossier	No
Aspiration hazard	hazard class not assessed in this dossier	No
Hazardous to the aquatic environment	hazard class not assessed in this dossier	No
Hazardous to the ozone layer	hazard class not assessed in this dossier	No

3 HISTORY OF THE PREVIOUS CLASSIFICATION AND LABELLING

Formic acid (CAS n° 64-18-6) was classified as corrosive to the skin with specific concentration ranges under Dir. 67/548/EEC, and this was transferred into CLP Annex VI, GHS classification.

Formic acid is a biocidal active substance and during its evaluation under the Biocidal Product Regulation (BPR, Regulation (EU) 528/2012) it was concluded that the current harmonized classification was no longer up to date. New hazard classes are now proposed in this CLH report, while the previous ones are retained.

4 JUSTIFICATION THAT ACTION IS NEEDED AT COMMUNITY LEVEL

CLH-report was made in the context of Regulation (EU) No 528/2012. Justification is not required if the substance is an active substance used in BP for which normally all hazard classes should be addressed in the CLH report. The proposal addresses only hazard class(es) or differentiation(s) that are not covered by the current entry and thus considered as new proposal. It is considered justified that action is needed at Community level:

- Flammable liquid: change in existing entry due to changes in the criteria (DSD → CLP)
- Corrosive to metals: this hazard class was not part of DSD and is new in CLP
- Acute toxixity: change in existing entry due to changes in the criteria (DSD → CLP)
- Eye damage: a skin corrosive substance is considered to cause also serious eye damage

  Already existing harmonised classification for Skin Corr.1, H314: causes severe skin burns and eye damage

5 IDENTIFIED USES

Identified Use number	Identified Use name
Industrial uses	
11	Industrial manufacture of polymers, resins
12	Polymer processing
14	Industrial use as processing aid
9	Industrial use in Laboratories
4	Use as an Intermediate
5	Uses in Coatings
6	Use in Cleaning Agents
Uses by professional workers	
7	Use in Cleaning Agents

10	Use in Laboratories
13	Polymer processing
15	Use as processing aid
17	Animal nutrition
19	Use as preserving agent

6 DATA SOURCES

See references under chapter 14 of this report

7 PHYSICOCHEMICAL PROPERTIES

Table 7. Summary of physicochemical properties

Property	Value	Reference	Comment (e.g. measured or estimated)
Physical state at 20°C and 101,3 kPa	Liquid	Study no. 07L00084, Dolich, T. (2007)	Organoleptic
Melting/freezing point	4 °C at 1013 hPa	Study no. 07L00084, Dolich, T. (2007)	Measured
Boiling point	100.23 °C at 1013 hPa	Study no. 07L00084, Dolich, T. (2007)	Determination through extrapolation
Relative density	D_4^{20} = 1.2195	Study no. 07L00084, Dolich, T. (2007)	Measured
Vapour pressure	At 20 °C: 42.71 hPa At 25 °C: 54.96 hPa At 50 °C: 170.7 hPa	Study no. 07L00084, Dolich, T. (2007)	Measured
Surface tension	At 20 °C: 71.5 mN/m	Study no. 07L00084, Dolich, T. (2007)	Measured
Water solubility	Completely miscible Corresponding to 1220 g/L (= D_4^{20})	Study no. 02L00109, Drögemüller, A. (2002)	Measured
Partition coefficient n-octanol/water	At pH 5: Log K_{OW} = -1.9 At pH 7: Log K_{OW} = -2.1 At pH 9: Log K_{OW} = -2.3 At 23 ± 1 °C	Study no. 02L00109, Drögemüller, A. (2002)	Measured
Flash point	49.5 °C	Study no. SIK-Nr.07/1018, Bitterlich, S. (2007)	Measured
Flammability	Flammable liquid category 3	/	/
Explosive properties	Not explosive	Gödde, M. (2006)	Expert judgement
Self-ignition temperature	528 °C (corrected according to EN 14522)	Study no. SIK-Nr.07/1018, Bitterlich, S. (2007)	Measured
Oxidising properties	Not oxidising	Gödde, M. (2006)	Expert judgement
Granulometry	N/A	N/A	N/A
Stability in organic solvents and identity of relevant degradation products	Organic solvents not used in the biocidal products	Waived	Waived
Dissociation constant	At 20 °C: pKa = 3.70	Study no. 07L00084, Dolich, T. (2007)	Measured
Viscosity	Dynamic viscosity At 20 °C: 1.80 mPa.s At 40 °C: 1.22 mPa.s	Study no. 07L00084, Dolich, T. (2007)	Measured

Property	Value	Reference	Comment (e.g. measured or estimated)
	Kinematic viscosity At 20 °C: 1.47 mm^2/s At 40 °C: 1.02 mm^2/s		

8 EVALUATION OF PHYSICAL HAZARDS

8.1 Explosives

Hazard class not assessed in this dossier.

8.2 Flammable gases (including chemically unstable gases)

Hazard class is not applicable for this substance.

8.3 Oxidising gases

Hazard class is not applicable for this substance.

8.4 Gases under pressure

Hazard class is not applicable for this substance.

8.5 Flammable liquids

Table 8. Summary table of studies on flammable liquids

Method	Results	Remarks	Reference
EC method A.9	49.5 °C	Closed cup; corrected for atmospheric pressure and rounded to units of 0.5 °C	Study no. SIK-Nr.07/1018, Bitterlich, S. (2007)

Also see § 1.5 of the Confidential Annex I to this CLH report.

8.5.1 Short summary and overall relevance of the provided information on flammable liquids

The flashpoint was experimentally determined according to the closed cup method of German Industrial Standard DIN EN ISO 17376 which is similar to 92/69/EC Annex A.9. The test substance was formic acid with a high purity of 99.48%. The flashpoint is 49.5 °C. The study was performed under GLP.

8.5.2 Comparison with the CLP criteria

Experimental determination as recommended. Result allows to follow decision logic.

Formic acid meets the classification criteria as flammable liquid category 3, as its flash point is ≥ 23 °C and ≤ 60 °C.

8.5.3 Conclusion on classification and labelling for flammable liquids

Formic acid should be classified as Flam. Liq., Cat3, H226.

8.6 Flammable solids

Hazard class is not applicable for this substance.

8.7 Self-reactive substances

Hazard class is not applicable for this substance.

8.8 Pyrophoric liquids

Hazard class is not applicable for this substance.

8.9 Pyrophoric solids

Hazard class is not applicable for this substance.

8.10 Self-heating substances

Hazard class is not applicable for this substance.

8.11 Substances which in contact with water emit flammable gases

Hazard class is not applicable for this substance.

8.12 Oxidising liquids

Hazard class is not applicable for this substance.

8.13 Oxidising solids

Hazard class is not applicable for this substance.

8.14 Organic peroxides

Hazard class is not applicable for this substance.

8.15 Corrosive to metals

Table 9. Summary table of studies on the hazard class corrosive to metals

Method	Results	Remarks	Reference
UN Test C.1 (37.4)	Corrosive to metal	85% solution in water is corrosive to steel Not corrosive to aluminium	Study no 16011907G979 Henke, W. (2016) Study no. 16092902G979 Krebs, F. (2017)

Also see § 1.15 of the Confidential Annex I to this CLH report.

8.15.1 Short summary and overall relevance of the provided information on the hazard class corrosive to metals

Studies performed on the active substance at 85% concentration show a clear corrosion to steel, and are enough to lead to classification for corrosive to metals. The studies performed on the substance at 99.4% concentration show signs of corrosion, but to a level that should normally not lead to classification. However, given the need to classification at 85%, the signs of corrosion at 99.4%, and the need to avoid steel containers at this concentration, it is likely that the weaker corrosion at higher concentration is only due to the lack of water, which leads to a weaker dissociation of the proton from the acid molecule, thus impairing the corrosiveness. The decreased corrosion sign is thus an artefact and both concentration have to be classified as corrosive to metal.

Not compatible material:

- carbon steel

Formic acid is stored and sold in containers made from different types of plastics (BASF , 2005/2006/2007):

- polyethylene (Lupolen, Hostalen, Lucalen)
- copolymer of ethylene and butylacrylate (Lucofin)
- polypropylene (Moplen)
- ethylene propylene diene monomer rubber (EPDM)
- ethylene tetrafluoroethene (ETFE)

8.15.2 Comparison with the CLP criteria

According to CLP guidance , the conclusion corrosive to metals can be reached when the corrosion rate on either steel or aluminium surfaces exceeding 6,25 mm per year at a test temperature of 55 oC when tested on both materials.

This value is exceeded for the formulation at 85%, but not fully reached for the concentration at 99.4%.

8.15.3 Conclusion on classification and labelling for corrosive to metals

Formic acid is to be classified as the available information are conclusive and sufficient for classification.

9 TOXICOKINETICS (ABSORPTION, METABOLISM, DISTRIBUTION AND ELIMINATION)

9.1 Short summary and overall relevance of the provided toxicokinetic information on the proposed classification(s)

Not evaluated

Only new hazards are addressed in this CLH report which are proposed to be added to the existing entry in CLP Annex VI. The evaluation of these hazards (acute oral and inhalation toxicity, serious eye damage) are directly related to the corrosivity of formic acid, i.e. the tissue at the point of contact is affected and toxicokinetics play no role. Therefore, toxicokinetic information was omitted for the sake of clarity.

10 EVALUATION OF HEALTH HAZARDS

10.1 Acute toxicity - oral route

Also see § 3.1 of the Annex I (confidential) to this CLH report.

Table 10. Summary table of animal studies on acute oral toxicity

Method, guideline, deviations if any	**Species, strain, sex, no/group**	**Test substance,**	**Dose levels, duration of exposure**	**Value LD_{50}**	**Reference**
OECD TG 401 Deviations: no GLP: no (not compulsory at the time the study was conducted) Key study Reliability 1	Rat Wistar m+f 5/sex/group	Formic acid Purity 99%	501, 631, 794, 1000 mg/kg bw Single dose **gavage**	730 mg/kg bw (m +f) Males: 863 mg/kg bw Females: 618 mg/kg bw	REACH Registration dossier (Anonymous 1, 1985)
Acute oral toxicity study No GLP No guideline followed	Mouse (strain and sex unspecified)	Formic acid (Purity unknown)	Doses and vehicle not reported **Oral (no more info)**	1100 mg/kg bw	REACH Registration dossier (Anonymous 2, 1969)

Table 11. Summary table of human data on acute oral toxicity

Human case reports on accidental and suicidal *oral* exposure to formic acid are available.

Species Sex, No/group	**Route of exposure**	**Test substance**	**Observations**	**Result**	**Reference**
1 male, 27-year-old Case report	Oral	Formic acid 60%	Suicidal ingestion, 45-90 ml (decalcifying agent). Clinical signs: vomiting, abdominal pain	Corrosion of the gastro-intestinal tract, metabolic acidosis,	Westphal F, *et al.* (2001) Fatal intoxication with a

			Blood: pH 6.86, pCO_2 70.4 mmHg, HCO_3 10.6 mmol/l, base deficit -22 mmol/l, initial serum formate level 370.3 µg/ml, haemolysis Autopsy: ulceration of oesophagus, complete necrosis of gastric mucosa, oedema e necrotic areas in deeper tissue layers of stomach, no perforation, coagulated blood in stomach, necrosis of mucosa duodenum. Post-mortem formate concentrations: 855.4 µg/ml (heart blood) 2712 µg/ml (gastric contents) 1128 µg/ml (hemorrhagic fluid abdominal cavity) 3051 µg/ml (bile) 2664 µg/ml (contents small intestine) 442.7 µg/g (liver) 542.3 µg/g (kidney) Within 30 hours after ingestion: corrosion of the gastro-intestinal tract, metabolic acidosis, haemolysis, massive bleeding, hepatic and renal failure, death.	haemolysis, massive bleeding, hepatic and renal failure, death	decalcifying agent containing formic acid. Int. J. Legal Med. 114, 181-185. BPD ID A6.12.2_01
1 female, 39-year-old Case report	Oral	Formic acid 50%	Suicidal ingestion, 200 ml (descaling product). Clinical signs: severe retrosternal and epigastric pain, dyspnea, cyanotic appearance, vomiting blood (2 h after ingestion) Blood: pH 6.87, pCO_2 46.1 mm Hg, HCO_3 8.6 mmol/l, base deficit of -26.4 mmol/l, haemolysis (20 min after admission to hospital) Initial serum formate level 348 µg/ml (7.6 mmol/l), elimination $T_{1/2}$ 2.5 hours Urine: red Gastroscopy: severe lesions oesophagus and stomach, superficial burns duodenum Complications: severe gastrointestinal bleeding, pneumonia, acute tubular necrosis, adult respiratory distress syndrome, peritonitis, sepsis Death: 6 weeks after ingestion	Local: corrosion and massive bleeding, loss of blood pressure Systemic: Severe metabolic acidosis and haemolysis, renal failure Death	Verstraete AG *et al.* (1989). Formic acid poisoning: Case report and in vitro study of the hemolytic activity. Am J Emerg Med 7, 286-290. BPD ID A6.12.2_02 Summary : BPR: Ann II 8.12.2.02
30 males 23 females 16 to 46 year-old Case report	Oral	Formic acid conc. not known	Suicidal ingestion, ≥ 10 ml, (rubber workers) Major complications: Gastro-intestinal: facial burns, ulcerations of oral and pharyngeal mucosa, abdominal pain, contractures and keloid formation of affected skin, oesophagus stricture (16/53 cases) requiring reparative surgery Respiratory system: inhalation pneumonitis (45 of 53 patients) with cough dyspnea, cyanosis, could proceed to respiratory infection and failure	Local: corrosion and massive bleeding, loss of blood pressure Systemic: Severe metabolic acidosis and haemolysis, renal failure Death	Rajan N *et al.* (1985). Formic acid poisoning with suicidal intent: a report of 53 cases. Postgrad. Med. J. 61, 35-36. BPD ID A6.12.2_03 Summary : BPR: Ann II 8.12.2.03

			Vascular hypotension: 17/53 cases Haemolysis, haematuria within few hours of ingestion, rapidly followed by renal failure in severe cases, within a day in less severe cases, in total 20/53 cases Death: 15/53 patients		
1 male 2 females 35, 56, 66 year-old Case report	Oral	Formic acid 40-55%	Suicidal ingestion, estimated volumes 'one mouthful' to 50-100 ml (descaling product) *35-year-old woman, 40% formic acid, 3 mouthfuls:* massive bleeding, haemolysis, died on d14 after shock and massive haematemesis. Ulcerations throughout oesophagus and stomach, tubular necrosis, early thrombosis of the portal vein *66-year-old woman, 55% formic acid, 55 to 100 ml:* massive bleeding, haemolysis, extensive erosion of oesophagus, stomach, duodenum, died on d5 *56-year-old man, mouthful of 55% formic acid:* died on d11 due to circulatory failure	Local: corrosion and massive bleeding, loss of blood pressure Systemic: Severe metabolic acidosis and haemolysis, renal failure Death	Naik RB *et al.* (1980). Ingestion of formic acid-containing agents - report of three fatal cases. Postgrad. Med. J. 56, 451-456. BPD ID A6.12.2_04 Summary : BPR: Ann II 8.12.2.04
male/female <12 years to adult 45 cases Case report	Oral	Formic acid 44 to 60%	Accidental and suicidal ingestion Estimated doses: < 10 g (children) to 200 g (adults) Children: accidental ingestion of low doses (≤ 10 g), reversible oropharyngeal burns in 9 children, no deaths Adults: suicidal ingestion (34/36 cases), accidental ingestion (2/36) 5-30 g: reversible oropharyngeal burns (16); abdominal pain, vomiting, dyspnea, dysphagia (5); hematemesis, pneumonitis, esophageal strictures (2) 30-45 g: intravascular coagulation, acute renal failure, hematemeses, liver impairment, oesophagal strictures 45-200 g: corrosive perforations of the abdominal viscera and gastrointestinal hemorrhage, acute renal failure dose up to 45g: 28/29 patients survived dose 45g-200g: 14/16 patients died	Local: corrosion and massive bleeding, loss of blood pressure Systemic: Severe metabolic acidosis and haemolysis, renal failure Death	Jefferys DB, and Wiseman HM (1980). Formic acid poisoning. Postgrad. Med. J. 56, 761-763.BPD ID A6.12.2_05
male/female children 183 cases Case report	Oral	Formic acid 87 to 96%	Accidental ingestion: only small quantities Vomiting (10/183 children) and visible caustic lesions in mouth and throat (28/183 cases):	Reversible burns of oesophagus	von Muehlendahl KE *et al.* (1978). Local injuries by accidental ingestion of corrosive substances by children. Arch Toxicol 39, 299-

					314. BPD ID A6.12.2_06 Summary : BPR: Ann II 8.12.2.06
Males and females Age: 29.7-55, mean age 42.8 years 302 cases Retrospective study	Oral, dermal, inhalation	formic acid conc. not known	Suicide Mean (SD) quantity consumed: 110 (78) mL The most common symptoms noted at presentation were: vomiting (78.5 %) abdominal pain (56.3% hematemesis (48.3%) respiratory distress (44 %) haematuria (30.1%) oliguria (24.5%) hypotension (24.5%) melena (22.2%) direct corneal injury (0.007%) Mean (SD) pH of all patients was 7.3 and the bicarbonate concentration was 19.2 (5.1) mEd/L. Leucocytosis was seen in 57.5% of the patients; liver enzymes (GOT, GPT) were elevated above normal values in 62.1% of the patients. The effectivity of medical treatment depends largely on the ingested dose and concentration of FA, the time delay after exposure. Low blood pH and bicarbonate concentration reflect the severity. The mortality rate was 35.4%. Bowel perforation, shock, and tracheoesophageal fistula were associated with 100% mortality. A higher blood pH was less likely to result in mortality. Dysphagia was noted in 154 patients, 98 of whom showed oesophageal stricture on evaluation, requiring repeat endoscopic dilatations after discharge. The prevalence of oesophageal stricture among the 195 patients who survived was 50.2%.	Prognosis depends on the exposure, rapid onset of treatment, proper examination, strict treatment regimen to counteract systemic and local effects. Dose is generally high in suicidal ingestion, resulting in high mortality rate (35%) Survivors show sequels of burns and corrosion in mouth and oesophagus Oesophageal stricture seen in 50% of survivors + dysphagia	Dalus D *et al.* (2013) Formic acid poisoning in a tertiary care center in south India : a 2-year retrospective analysis of clinical profile and predictors of mortality. J Emerg Med, v44 no2, 373-380 Summary: BPR: Ann II 8.12.5.01

10.1.1 Short summary and overall relevance of the provided information on acute oral toxicity

A valid acute oral toxicity rat study is available (male and female Wistar rats, n=5m +5f per dose group) that was conducted according to the OECD TG 401 without deviations (Anonymous 1, 1985).
The animals received single doses of the undiluted test material (Formic acid, 99%) by oral gavage. Dose levels were 501, 631, 794, 1000 mg/kg bw (no control group included). During the 14 day observation period, animals were examined for clinical signs, body weight changes, and mortality. Necropsy was peformed on all animals that died or after sacrifice at the end of the observation period.
Clinical signs were noted 30 minutes after dosing. Symptoms included: unkempt fur, hunched posture, stagger, aggressiveness, dyspnea, sedation and ataxia, lateral and abdominal position, convulsions, bloody noses, blood in urine. At later times hypothermia, body weight loss and pale limbs were additionally noted.

Symptoms subsided and were absent in all animals but one which showed symptoms until the end of the observation period. Both mortality (0, 2, 1, 4/5 in males and 1, 2, 5, 4/5 in females at 501, 631, 794, 1000 mg/kg bw, respectively),seen within one to two days, and decrease in body-weight gain of survivors (56.1, 45.9 28.3 and -3.4 g at 501, 631, 794 and 1000 mg/kg bw, respectively) showed a clear dose-response relationship.

The clinical symptoms and pathological organ lesions (hyperemia of the stomach and intestines, congestion in spleens, mottled livers and kidneys, discoloration of kidneys and pancreas) are largely nonspecific and can be explained primarily by the local corrosive character of formic acid, and by associated secondary systemic effects. There may have been a trend of a higher sensitivity of female animals, but no significant difference between male and female animals was indicated in the report.

The combined oral LD50 value was 730 mg/kg bw (618 (in female) – 863 (in male) mg/kg bw) in this study.

An additional study (registration dossier (study report, Anonymous 2, 1969)), which not followed guideline or not GLP, mentioned a LD50 of 1100 mg/kg bw. This study is poorly reported and the results cannot be verified.

Several case reports report on fatal suicidal ingestion of formic acid (Westphal et al., 2001; Verstraete *et al.*, 1989; Rajan *et al.*, 1985; Naik *et al.*, 1980; Jefferys and Wiseman, 1980; von Muehledahl *et al.*, 1978; Dalus *et al.*, 2013). Due to the corrosivity of formic acid, local effects occur at all dose levels. The amount ingested and the concentration determine the grade and the location of the effects. Therefore, the observations range from moderate burns around the mouth to severe corrosion of the gastro-intestinal tract with destruction of the esophagus, perforation of the stomach, and corrosion of the small intestine together with massive bleeding and systemic toxicity. Systemic toxicity was seen after ingestion of 30 g formic acid or more. Prognosis is poor after massive oral ingestion (>45 to 200 g formic acid); prognosis is moderate after moderate oral ingestion (approx. 30 to 45 g); lesions, but low mortality, are expected in most cases with low amounts ingested (<30g); persistent lesions due to tissue corrosion must be expected in cases with >10 g formic acid ingested. Tissue destruction of the gastrointestinal tract may result in fatal bleeding, septic shock, or stricture which may require surgical treatment. Reversibility of effects was often seen in cases with low amounts ingested (<10 g formic acid).

10.1.2 Comparison with the CLP criteria

According to the criteria of the CLP Regulation, substances should be classified as acute tox. 4, H302 when the oral LD_{50} is between 300 and 2000 mg/kg bw. Formic acid is of moderate toxicity via the oral route when tested in the rat. Oral LD_{50} = 730 mg/kg bw.

10.1.3 Conclusion on classification and labelling for acute oral toxicity

Proposed classification and labelling for formic acid: acute oral Tox. Cat. 4; H302

10.2 Acute toxicity - dermal route

Hazard class not assessed in this dossier.

10.3 Acute toxicity - inhalation route

Also see § 3.3 of the Confidential Annex I to this CLH report.

Table 12. Summary table of animal studies on acute inhalation toxicity

Method, guideline, deviations if any	Species, strain, sex, no/group	Test substance, , form and particle size (MMAD)	Dose levels, duration of exposure	Value LC_{50}	Reference
Comparable to OECD TG 403 GLP: no (not compulsory at the time the study was conducted) Key study Reliability 1	Rat Sprague-Dawley m+f 10/sex/group	Formic acid purity 98% vapour	2.82, 6.60, 8.08, 10.6, 14.7 mg/l (analytical); 4 hours whole body	7.4 mg/l (m+f) Males: 7.3 mg/l Females : 7.5 mg/l Clinical signs (in all treated groups): Closed lids, snout swiping, discharge from the nose and eye, corrosion of nose and eyes, salivation, corneal opacity, loss of pain reflex, dyspnea, respiration sounds, flatulence, apathy, hunched posture, unsteady gait Symptoms persisted until d14 after treatment (except for the 2.82 mg/l group: symptom free at d11) Mortality: within 7 days post exposure (inflated lungs, dilated hearts). BW at d7: dose-dependent decrease	REACH registration dossier, Anonymous 3, 1980
OECD TG 403 Not GLP	Rat / Wistar / both sexes 6 animals	Formic acid (purity unknown)	Saturated atmosphere (nominal saturated concentration : 44168ppm) Duration of exposure : 10min	All animals died Clinical signs : ocular nasal irritation, gasping, increased salivation Pupils of eyes opaque after 3-4min	REACH Registration dossier (Anonymous 4, 1982)
OECD TG 403 Not GLP	Rat / Wistar Both sexes	Formic acid Purity : > 99%	Saturated atmosphere Duration of	Mortality was of 75% after 3min of exposure	REACH Registration dossier

Method, guideline, deviations if any	Species, strain, sex, no/group	Test substance, , form and particle size (MMAD)	Dose levels, duration of exposure	Value LC_{50}	Reference
	18 animals	Inhalation (nose only) Vehicle : air	exposure : 3, 10 and 116min	100% after 10min of exposure Most death occurred within 24h after treatment	(Anonymous 5, 1981)

Table 13. Summary table of human data on acute inhalation toxicity

Human case reports on accidental and suicidal inhalation exposure to formic acid are available.

Species Sex, No/group	Route of exposure	Test substance	Observations	Result	Reference
1 male, 39-year-old Case report	Inhalation	Formic acid 98%	Accidental spray (aerosol) into the face with concomitant inhalation (occupational) Clinical signs: facial burns (3% of total body surface), dyspnea Nasopharyngoscopy: mild supraglottic erythema, normal vocal cords Skin: second-degree burns Pulmonary function tests: Vital capacity reduced on d1, recovered largely within 14 days. Complains of dyspnea till d15 <u>Day 1</u> FVC (L): 3.74 (79% predicted) FEV_1 (L): 2.86 (73% predicted) FEV_1/FVC: 76.38 (92% predicted) $FEF_{25\%-75\%}$ (l/sec): 2.32 (56% predicted) <u>Day 15</u> FVC (L): 4.35 (92% predicted) FEV_1 (L): 3.62 (92% predicted) FEV_1/FVC: 83.09 (101% predicted) $FEF_{25\%-75\%}$ (l/sec): 3.82 (92% predicted)	Reversible Pulmonary dysfunction: Reactive Airway Dysfunction Syndrome	Yelon *et al.*, (1996). Formic acid inhalation injury: a case report. J. Burn Care Rehab. 17, 241-242. BPD ID A6.12.2_10 Summary : BPR: Ann II 8.12.2.10
(1) 1 male, 22-year-	inhalation	Fumes from formic acid	Suicide by mixing formic acid with concentrated sulphuric	External chemical	Bakovic M, *et al.* (2015) Suicidal chemistry: combined

old Case report		(85%) and carbon monoxide (concentration not known)	acid in a confined space Death due to CO intoxication; corrosion/irritation of skin, trachea, lungs, stomach due to formic acid fumes.	burns Internal injuries mainly to the respiratory tract. Injury to the oropharyngeal area and trachea, pulmonary edema, and subpleural petechiae Complete lack of the respiratory epithelium of the trachea, edema of mucosa, and submucosa of the trachea, thrombi, and hemolysis inside the small vessels of the trachea, pulmonary edema, hemolysis, and thrombosis in the lung vessels	intoxication with carbon monoxide and formic acid. Int. J Legal Med FA_BPR_Ann_II_8_12_2_11
(2)1 male, 26-year-old Case report	inhalation	Fumes from formic acid (concentration not reported, amount 950 ml) and carbon monoxide (concentration not known)	Suicide by mixing formic acid with concentrated sulphuric acid in a confined space. Death. The body showed pronounce bright pink-red lividity. The autopsy was otherwise unremarkable.	See observations, no further info on formic acid effects	Lin PT and Dunn (2014) Suicidal Carbon Monoxide Poisoning by Combining Formic Acid and Sulfuric Acid Within a Confined Space. J. Forensic Science, January 201, Vol 59, No. 1 FA_BPR_Ann_II_8_12_2_12
(3)1 male, 26-year-old; 1male, 53-year-old, 1 female, 53-year-old Case report	inhalation	Fumes from formic acid (98-100%) and carbon monoxide (concentration not known)	Suicide by mixing formic acid with concentrated sulphuric acid in a confined space 26-year-old: death. No autopsy 53-year-old father: coma, hypoxemia, metabolic acidosis, and a carboxyhemoglobin level of 45.8%. Developed acute respiratory distress syndrome. Transient ulceration of vocal cords. 53-year-old mother: dizziness, headache, carboxyhemoglobin level of 23.0%	See observations. In addition to the toxicities of carbon monoxide, concomitant inhalation of formic acid fumes can cause severe lung injury, which may complicate the management	Yang CC et *al.* (2008) Formic acid: A rare but deadly source of carbon monoxide poisoning. Clinical Toxicology, 46:4, 287-289 FA_BPR_Ann_II_8_12_2_13

				of carbon monoxide poisoning.	

Table 14. Summary table of other studies relevant for acute inhalation toxicity

Species Sex, No/group	Method	Test substance	Route dose levels duration of exposure	Result	Reversi-bility	Reference
Rat, Fischer 344/N, m + f 10/sex Supportive data Rel 1	In accordance with OECD TG 413 (Subchronic inhalation toxicity : 90-day study)	Formic acid purity 95%	0, 15, 30, 61, 122, 244 mg/m^3 6h/d, 5d/wk, 13 weeks Vapour, whole body	No clinical signs Local effects: nasal irritation, squamous metaplasia of the respiratory epithelium, olfactory degeneration, severity minimal to mild. Respiratory epithelium squamous metaplasia: mg/m³ 0 15 30 61 122 244 male 0 0 0 0 0 9 female 0 0 0 0 0 6 Olfactory epithelium degeneration: minimal to mild mg/m³ 0 15 30 61 122 244 male 0 0 0 0 0 9 female 0 0 0 1 1 5	NOAEL$_{local}$: 30 mg/m^3 LOAEL$_{local}$: 61 mg/m^3	Thompson M (1992) NTP Technical Report on Toxicity Studies of Formic Acid. Administered by inhalation to F344/N rats and B6C3F$_1$ mice. US Department of Health and Human Services, Public Health Service, National Institutes of Health NIH, Toxicity Report Series No: 19, NIH Publication No: 92-3342, July 1992 (published). BPD ID A6.4.3_01 Summary: BPR: Ann II 8.9.2.03
Mice B6C3F$_1$ m + f 10/sex Supportive data Rel 1	In accordance with OECD TG 413 (Subchronic inhalation toxicity : 90-day study)	Formic acid purity 95%	0, 15, 30, 61, 122, 244 mg/m^3 6h/d, 5d/wk, 13 weeks Vapour, whole body	No clinical signs Local effects: nasal irritation, olfactory degeneration, severity minimal but dose-related. Olfactory epithelium degeneration: minimal mg/m³ 0 15 30 61 122 244 male 0 0 0 0 0	NOAEL$_{local}$: 61 mg/m^3 LOAEL$_{local}$: 122 mg/m^3	BPD ID A6.4.3_02 Thompson, 1992 (see above)

				2 TG female 0 0 0 0 2 5		

10.3.1 Short summary and overall relevance of the provided information on acute inhalation toxicity

In a rat inhalation study, male and female Wistar rats (10 per sex and dose level) were exposed in a whole body exposure chamber in groups of 5 to formic acid vapours at concentrations of 2820, 6600, 8080, 10600, 14700 mg/m³ (analytical) (Zeller & Klimisch, 1980). The exposure period was 4 hours. The concentration levels were measured using IR photometry. The observation period was 14 days.

Clinical signs (Closed lids, snout swiping, discharge from nose and eye, corrosion of nose and eyes, salivation, corneal opacity, loss of pain reflex, dyspnea, respiration sounds, flatulence, apathy, hunched posture, unsteady gait) were noted in al treated groups and persisted until termination except the animals at 2.82 mg/L which were free of symptoms on day 11. Deaths occured within 7 days post treatment. Pathology revealed heart dilatation, hyperemia, and inflated lungs. Further, corneal opacity and corrosion of the dorsal nose was seen in some cases. Body weights were dose-dependently depressed in all survivors on day 7. Body weight gain was noted in the second week after treatment. Animals of the groups at 8.08 mg/l did not reach the initial weight.

Clinical signs indicated corrosive properties of the test substance, evidenced by the occurrence of corneal opacity and corrosion of the dorsal nose in some cases. Inflated lungs and dilated hearts were seen in animals that died; gross pathology revealed no changes in animals sacrificed at termination. The LC50 was 7.4 mg/L (m+f) in this study (males: 7.3 mg/L; females 7.5 mg/L).

Evidence of respiratory tract irritation is found in the histopathological data of the nasal cavity of the repeated dose inhalation toxicity studies performed with formic acid vapours (13-week inhalation, rat, mouse). Testing was conducted at concentrations of 0, 15, 30, 61, 122, 244 mg/m³ in rats and mice (Thompson, 1992). Both in the rat and the mouse, the inhalation of formic acid did not result in clinical effects. In the rat, microscopic changes occurred in the respiratory and olfactory epithelium of the nose. In the mouse, microscopic changes were limited to the degeneration of the olfactory epithelium of the nose. Both in the rat and the mouse the upper respiratory tract was the major target for toxicity.

Human case reports on acute accidental or suicidal inhalation exposure are rather rare. Besides local effects and respiratory tract irritation, patients suffered and recovered rapidly from metabolic acidosis following accidental inhalation (Yelon *et al.*, 1996). Inhalation of fumes created by mixing formic acid with concentrated sulphuric acid leads to injuries to the respiratory tract from formic acid, and deadly carbon monoxide intoxication (Bakovic *et al.*, 1996; Lin & Dunn, 2014; Yang *et al.*, 2008).

10.3.2 Comparison with the CLP criteria

According to the criteria of the CLP Regulation, substances should be classified as acute tox. Cat. 3, H331 when the inhalation (vapour) LC_{50} is between 2,0 and 10,0 mg/l. In the Zeller H and Klimisch H-J (1980) study, the LC is of 7.4 mg/l and thus fulfilled the criteria of the category 3. Additionally, the EUH071 phrase is proposed, as the corrosive properties determine the toxicity of formic acid (CLP Regulation Annex II, point 1.2.6).

10.3.3 Conclusion on classification and labelling for acute inhalation toxicity

Proposed classification and labelling for formic acid: acute inhalation Tox. Cat. 3 (vapour); H331.

Since data are available that indicate that the mechanism of toxicity is corrosivity, formic acid shall also be labelled as EUH071: ‘corrosive to the respiratory tract’.

10.4 Skin corrosion/irritation

Existing harmonised classification; hazard class not assessed in this dossier.

10.5 Serious eye damage/eye irritation

10.5.1 Short summary and overall relevance of the provided information on serious eye damage/eye irritation

No eye irritation study reports are available on formic acid itself. Due to the inherent properties of formic acid (strong acid), the substance has been classified as corrosive (C, R 35) in the EU (12th ATP to Directive 67/548/EEC). The European Union concludes that a similar effect (corrosivity) is expected for the eyes, and that no further testing is required. Corrosivity to the eyes may thus be assumed from the low pH-value of formic acid. Specific concentration limits for preparations have been set by the European Union. No caustic effect is assumed by concentrations below 10% (R36, irritant to the eye).

10.5.2 Comparison with the CLP criteria

N.A.

10.5.3 Conclusion on classification and labelling for serious eye damage/eye irritation

The current GHS classification is Skin corrosive cat. 1A, H314 at C≥90%, and 1B, H314 at 10% ≤C<90%.

According to the CLP regulation Annex I point 3.3.2.3, skin corrosive substances shall be considered as leading to serious damage to the eyes as well (Category 1).

In accordance with the footnote to Table 3.3.5 of the CLP regulation, formic acid at concentrations requiring classification as skin corrosion 1A or 1B (C≥10%) need not be labelled with H318.

10.6 Respiratory sensitisation

Hazard class not assessed in this dossier.

10.7 Skin sensitisation

Hazard class not assessed in this dossier.

10.8 Germ cell mutagenicity

Hazard class not assessed in this dossier

10.9 Carcinogenicity

Hazard class not assessed in this dossier

10.10 Reproductive toxicity

Hazard class not assessed in this dossier

10.11 Specific target organ toxicity-single exposure

Hazard class not assessed in this dossier

10.12 Specific target organ toxicity-repeated exposure

Hazard class not assessed in this dossier

10.13 Aspiration hazard

Hazard class not assessed in this dossier

11 EVALUATION OF ENVIRONMENTAL HAZARDS

11.1 Rapid degradability of organic substances

Parameter not assessed in this dossier.

11.2 Environmental fate and other relevant information

Parameter not assessed in this dossier.

11.3 Bioaccumulation

Parameter not assessed in this dossier.

11.4 Acute aquatic hazard

Hazard class not assessed in this dossier.

11.5 Long-term aquatic hazard

Hazard class not assessed in this dossier.

12 EVALUATION OF ADDITIONAL HAZARDS

12.1 Hazardous to the ozone layer

Hazard class not assessed in this dossier

13 ADDITIONAL LABELLING

Not assessed in this dossier

14 REFERENCES

Anonymous 1, 1985: see Confidential Annex I to CLH report

Anonymous 2, 1969: see Confidential Annex I to CLH report

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15 ANNEXES

Confidential ANNEX I to CLH report