Committee for Risk Assessment

RAC

Opinion

proposing harmonised classification and labelling
at EU level of

trichlorosilane

EC Number: 233-042-5
CAS Number: 10025-78-2

CLH-O-0000006809-60-01/F

Adopted

11 June 2020

11 June 2020

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OPINION OF THE COMMITTEE FOR RISK ASSESSMENT ON A DOSSIER PROPOSING HARMONISED CLASSIFICATION AND LABELLING AT EU LEVEL

In accordance with Article 37 (4) of Regulation (EC) No 1272/2008, the Classification, Labelling and Packaging (CLP) Regulation, the Committee for Risk Assessment (RAC) has adopted an opinion on the proposal for harmonised classification and labelling (CLH) of:

Chemical name: **trichlorosilane**

EC Number: **233-042-5**

CAS Number: **10025-78-2**

The proposal was submitted by **Germany** and received by RAC on **29 April 2019.**

In this opinion, all classification and labelling elements are given in accordance with the CLP Regulation.

PROCESS FOR ADOPTION OF THE OPINION

Germany has submitted a CLH dossier containing a proposal together with the justification and background information documented in a CLH report. The CLH report was made publicly available in accordance with the requirements of the CLP Regulation at ***http://echa.europa.eu/harmonised-classification-and-labelling-consultation/*** on **1 July 2019**. Concerned parties and Member State Competent Authorities (MSCA) were invited to submit comments and contributions by **30 August 2019**.

ADOPTION OF THE OPINION OF RAC

Rapporteur, appointed by RAC: **Beata Pęczkowska**

The opinion takes into account the comments provided by MSCAs and concerned parties in accordance with Article 37(4) of the CLP Regulation and the comments received are compiled in Annex 2.

The RAC opinion on the proposed harmonised classification and labelling was adopted on **11 June 2020** by **consensus**.

Classification and labelling in accordance with the CLP Regulation (Regulation (EC) 1272/2008)

	Index No	Chemical name	EC No	CAS No	Classification		Labelling			Specific Conc. Limits, M-factors and ATE	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	014-001-00-9	trichlorosilane	233-042-5	10025-78-2	Flam. Liq. 1 Pyr. Liq. 1 Acute Tox. 4* Acute Tox. 4* Skin Corr. 1A	H224 H250 H332 H302 H314	Dgr GHS02 GHS05 GHS07	H224 H250 H332 H302 H314	EUH014 EUH029	STOT SE 3; H335: C ≥ 1 %	Note T
Dossier submitters proposal	014-001-00-9	trichlorosilane	233-042-5	10025-78-2	Flam. Liq. 1 Water-react 1 Acute Tox. 3 Acute Tox. 4 Skin Corr. 1B Eye Dam. 1	H224 H260 H331 H302 H314 H318	Dgr GHS02 GHS05 GHS06	H224 H260 H331 H302 H314	EUH014 EUH029 EUH071	inhalation: ATE =7.65 mg/L (vapour) oral: ATE = 1030 mg/kg bw	
RAC opinion	014-001-00-9	trichlorosilane	233-042-5	10025-78-2	Flam. Liq. 1 Water-react. 1 Acute Tox. 3 Acute Tox. 4 Skin Corr. 1A Eye Dam. 1	H224 H260 H331 H302 H314 H318	Dgr GHS02 GHS05 GHS06	H224 H260 H331 H302 H314	EUH014 EUH029 EUH071	inhalation: ATE = 7.6 mg/L (vapour) oral: ATE= 1000 mg/kg bw	
Resulting Annex VI entry if agreed by COM	014-001-00-9	trichlorosilane	233-042-5	10025-78-2	Flam. Liq. 1 Water-react. 1 Acute Tox. 3 Acute Tox. 4 Skin Corr. 1A Eye Dam. 1	H224 H260 H331 H302 H314 H318	Dgr GHS02 GHS05 GHS06	H224 H260 H331 H302 H314	EUH014 EUH029 EUH071	inhalation: ATE = 7.6 mg/L (vapour) oral: ATE= 1000 mg/kg bw	

GROUNDS FOR ADOPTION OF THE OPINION

RAC evaluation of physical hazards

Summary of the Dossier Submitter's proposal

Trichlorosilane is liquid at 20 °C and 101.3 kPa.

Summary for relevant physico-chemical studies submitted by Dossier submitter (DS):

Method	Results	Remarks	Reference
Pyrophoric liquids UN Test Method N.3	not pyrophoric	In a study performed in accordance with UN Test Method N.3, trichlorosilane was demonstrated to be not pyrophoric because it could not be ignited in the first part of the test and did not ignite or char the filter paper in the second part of the test (BAM (2014b)).	Pyrophoricity 4.13.391 BAM 2014 Report on testing of the substance "trichlorosilane" and Expert's Opinion on Transport and GHS
Substances which in contact with water emit flammable gases UN Test Method N.5	in contact with water liberates highly flammable gases	Trichlorosilane produces a flammable gas in contact with water at a maximum rate of gas of more than 10 L/(kg min), determined by UN Test Method N.5 (BAM (2014a)). It was not possible to determine the relative amounts of hydrogen and hydrogen chloride gas produced. This represents a worst-case scenario for classification independent on the chemical identity of the gas evolved.	Flammability in contact with water 4.13.392-394 BAM 2014 Report on testing of the substance "trichlorosilane" and Expert's Opinion on transport and GHS classification

The result of the new experimental guideline study shows that trichlorosilane is not a phyrophoric liquid, but rather water reactive. Therefore, removal of the current harmonised classification Pyr. Liq. 1; H250 and adding of Water-react. 1; H260 according to regulation (EC) 1272/2008 (CLP regulation) was proposed by the DS. As consequence of the re-assessment of the physical hazard, note T is no longer appropriate.

Comments received during public consultation

One company/manufacturer supported the proposal by the DS to remove the classification as Pyrophoric Liquid Cat. 1 and add Water-react. 1.

Assessment and comparison with the classification criteria

Pyrophoric liquids

According to section 2.9. of Annex I to CLP Regulation, a pyrophoric liquid shall be classified in a single category for this class using test N.3 in Part III, sub-section 33.3.1.5 of the UN RTDG, Manual of Tests and Criteria according to the following criterion: The liquid ignites within 5 min. when added to an inert carrier and exposed to air, or it ignites or chars a filter paper on contact with air within 5 min.

Trichlorosilane tested with UN Test Method N.3 does not ignite within 5 minutes when added to an inert carrier and exposed to air, nor does it ignite or char a filter paper on contact with air within 5 min.

Therefore, it does not meet the criterion for classification as pyrophoric liquid, and thus, **removal of the current harmonised classification as Pyr. Liq. 1; H250 is justified according to the CLP Regulation, as well as the removal of Note T.**

Substances which in contact with water emit flammable gases

According to section 2.12. of Annex I to CLP Regulation, a substance or mixture which, in contact with water, emits flammable gases shall be classified as 'substances or mixtures which in contact with water emit flammable gases' category 1, using test N.5 in Part III, sub-section 33.4.1.4 of the UN RTDG, Manual of Tests and Criteria, in accordance with the following criterion. Any substance or mixture which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures, such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.

Trichlorosilane tested with UN Test Method N.5 (BAM, 2014a) produces a flammable gas in contact with water at a maximum rate of gas of 68.0 L/(kg min). The composition of the evolved gas in the UN Test N.5 was not analysed at BAM. According to procedure of UN Test Method N.5, if the chemical identity of the gas is unknown, the gas should be tested for flammability. Therefore, in the additional autoclave experiment it was shown that the gas which was evolved during the reaction of trichlorosilane with water is flammable. This represents a worst-case scenario for classification independent on the chemical identity of the gas evolved.

Thus, trichlorosilane fulfils the criterion for Category 1 of 'substances or mixtures which in contact with water emit flammable gases' and addition of classification as Water-react. 1 and hazard statement H260 (In contact with water releases flammable gases, which may ignite spontaneously) is warranted according to the CLP Regulation.

In conclusion, **RAC supports the DS's proposal classify Trichlorosilane as Water-react. 1; H260**.

HUMAN HEALTH HAZARD EVALUATION

RAC evaluation of acute toxicity

Summary of the Dossier Submitter's proposal

Oral route

For the oral LD_{50}, only one study was available and reported for trichlorosilane (Mellon Institute, 1948). The study is comparable to the meanwhile deleted OECD TG 401 and pre-dating GLP requirements. Ten male rats (no information on strain) per dose were administered oral doses of 795, 1000, 1260 and 1580 mg/kg of trichlorosilane diluted in corn oil (10%). There was a 14-day post observation period.

The death rate per dose was 2/10 (795 mg/kg bw), 5/10 (1000 mg/kg bw), 7/10 (1260 mg/kg bw), and 9/10 (1580 mg/kg bw). An LD_{50} of 1030 mg/kg bw was calculated according to the method of Thompson. No clinical signs were reported. Observations from necropsy indicated that direct injury to the gastrointestinal tract was the cause of death. The stomach and intestines haemorrhaged and where the stomach contacted the liver and kidney, the latter organs had a cooked appearance.

Classification of trichlorosilane for acute oral toxicity as Acute Tox. 4; H302 (Harmful if swallowed), oral: ATE = 1030 mg/kg bw was proposed by the DS.

Inhalation route

Six inhalation acute toxicity studies were considered by the DS.

The DS considers the study from (Dow Corning, 1987) as having high reliability and the exposure via nose-only as adequate. This was also chosen as the key study.

The study was performed according to OECD TG 403 in compliance with GLP; however, the exposure period was modified from four hours to one hour. Sprague-Dawley rats (5/sex/dose) were exposed to trichlorosilane via nose-only administration. The following concentrations were tested: 1687, 2287, 2683 and 3770 ppm (as measured by IR spectroscopy).

In males, 1/5 (1687 ppm), 2/5 (2287 ppm), 1/5 (2683 ppm), and 5/5 (3770 ppm) animals died. In females, 1/5 (1687 ppm), 0/5 (2287 ppm), 4/5 (2683 ppm), and 4/5 (3770 ppm) animals died. An LC_{50} of 2767 ppm was calculated; however, no details on the procedure were given.

When this value is adjusted for the exposure of one hour according to CLP, section 3.1.2.1 and notes to table 3.1.1, item c) by dividing by a factor of 2 for gases and vapours, the LC_{50} becomes approximately 7.65 mg/L.

Clinical signs seen in all groups included nasal crust, rough coat, sores on the face and corneal opacity. Mouth breathing was seen in all groups except in the 3770 ppm dose group. Other less frequently observed signs included rales, ocular discharge and an absent nasal septum for one male rat of the 3770 ppm group.

Necropsy findings noted in all groups were changes in the external nares (N = 15), corneal opacity (N = 11) and dark areas on the lungs (N = 5, not seen on the 2287 ppm group). Exudate on the nasal turbinates (N = 5) and gas in the stomach (N = 11) were seen in a number of animals but not in all dose groups. There were no other necropsy findings. The clinical signs and the necropsy findings in the mentioned acute inhalation study are consistent with local corrosive effects that are covered by classification for acute inhalation toxicity and by applying EUH071.

Another study on acute toxicity after inhalation was performed (Nachreiner and Dodd, 1986), also following OECD guideline (non-GLP). Male and female Sprague-Dawley rats (5/sex/dose) were exposed for one hour in a whole body chamber. Three different chamber concentrations were used with different amounts of relative humidity (RH): 703 ppm (29% RH), 962 ppm (78% RH) and 995 ppm (29% RH). The trichlorosilane concentrations were verified by gas chromatographic analysis.

No rats died during the exposure or during the 14-day post exposure period.

Clinical signs were observed in all exposure groups. These included lacrimation, periocular, perioral and perinasal wetness (and/or audible respiration) and eye opacity. Clinical signs were partially attributed to hydrogen chloride since trichlorosilane per se was not detected during animal exposures.

No test material was detected in the exposure chambers, presumably due to decomposition in the presence of water vapour. The results of analysis for hydrogen chloride gas, a product of the hydrolysis of trichlorosilane, were highly variable and ranged from < 250 ppm (the minimum limit of detection by gas chromatography) to 1850 ppm for the three exposure groups.

Another study (Mellon Institute, 1948) did not meet current guideline requirements due to lack of detail on exposure, test animals, test substance and test conditions. In this study, three groups of six rats/group were exposed to substantially saturated vapour produced at room temperature (concentration not determined), 1000, or 500 ppm.

The inhalation of substantially saturated vapour produced at room temperature was lethal to 6 rats within an exposure of five minutes. A concentration of 1000 ppm killed 3 out of 6 rats in 4 hours, while 500 ppm killed 1 out of 6 rats.

For all other studies considered by the DS, no information is available about the experimental details.

The classification of trichlorosilane for acute inhalation toxicity as Acute Tox. 3; H331 (Toxic if inhaled), inhalation: ATE = 7.65 mg/L (vapour) was proposed by the DS.

To avoid double classification, in line with CLP guidance 3.1.6.1.7, the DS proposed to remove the classification as STOT SE 3 when the concentration is ≥ 1%.

Comments received during public consultation

Two Member State Competent Authorities (MSCA) agreed with the classification proposed by the DS for oral and inhalation acute toxicity. The first MSCA was of the opinion that, considering the weakness of the data available for the endpoint, a generic ATE would be more appropriate. The second MSCA agreed with the supplemental labelling with phrase EUH071.

One Company-Manufacturer was of the opinion that the mortalities observed in the acute studies were linked to the local corrosive effects and are covered by the classification for skin corrosion and by applying EUH071, and therefore classification for acute oral and inhalation toxicity is not required.

Assessment and comparison with the classification criteria

The results of one available acute oral toxicity study for trichlorosilane in rats indicate an LD_{50} of 1030 mg/kg bw. Therefore, trichlorosilane meets the criteria of the CLP regulation for classification in acute oral toxicity Category 4 ($300 < ATE \leq 2000$), with an oral ATE of 1000 mg/kg bw (rounded value to 2 significant figures) instead of the ATE value of 1030 mg/kg bw proposed by DS.

Only the Dow Corning (1987) acute inhalation toxicity study (with exposure via nose-only), conducted in rats in accordance with OECD TG 403 and GLP, can be considered for classification purposes.

The concentrations in inhalation acute toxicity studies considered by the DS are expressed as gases (in ppm); however, if the substance is a liquid at room temperature the inhalation exposure is likely to be to vapours.

The LC_{50} value of 7.65 mg/L (vapour) was derived after correction for the reduced exposure time (one hour only) by dividing by a factor of 2 (for gases and vapours). Comparing the results of this acute inhalation toxicity study (Dow Corning, 1987) with the CLP criteria ($2.0 < LC_{50} \leq 10.0$ mg/l for vapours) trichlorosilane meets the classification criteria for category 3 of acute inhalation toxicity, with an ATE of 7.6 mg/L (rounded value to 2 significant figures) instead of the ATE value of 7.65 mg/L proposed by DS.

In the second study performed (Nachreiner and Dodd, 1986) following OECD guidelines (non-GLP), male and female Sprague-Dawley rats (5/sex/dose) were exposed for one hour in a whole body chamber. No rats died during the exposure to three dose levels: 703 (3.90), 962 (5.33), 995 (5.51) ppm (mg/L); or during the 14-day post exposure period. The results of this study are not conclusive due to too low doses tested (between 3.90-5.51 mg/L).

Other studies (Mellon Institute, 1948; Carpenter et al., 1949; Izmerov, 1982; Mellon Institute, 1951) submitted by the DS were of low reliability (no guidelines followed, no data on dose levels, no information on the experimental details). Hence, these studies could not be used for classification purposes.

The clinical signs and the necropsy findings (audible respiration, absent nasal septum, dark areas on the lungs, exudate on the nasal turbinates) in acute inhalation studies (Dow Corning, 1987; Nachreiner and Dodd, 1986) indicate that the mechanism of toxicity is corrosivity. Thus, trichlorosilane should also be labelled as EUH071: 'corrosive to the respiratory tract' in addition to classification for acute inhalation toxicity (according to Note 1 in section 3.1.4.1. of Annex I to CLP Regulation).

In conclusion, RAC supports the DS proposal for revising the classification of trichlorosilane after rounding to 2 significant figures the ATE values. Overall, RAC considers the following classification is warranted for trichlorosilane:

- **Acute Tox. 4; H302 (Harmful if swallowed) with an ATE of 1000 mg/kg bw** and;
- **Acute Tox. 3; H331 (Toxic if inhaled) with an ATE of 7.6 mg/L** and labelling with;
- **EUH071 (Corrosive to the respiratory tract).**

RAC evaluation of skin corrosion/irritation

Summary of the Dossier Submitter's proposal

In two non-guideline studies (Mellon Institute, 1951, 1948), trichlorosilane was investigated for 24-hour exposure in the rabbit belly vesicant test. In both studies, no information was given on the strain, sex, number of animals or on the test system. An erythema/oedema score of 2/5 was reported in the first test, and an activity grade of 2 in the second test.

No other data from guideline-conform *in vitro* or *in vivo* studies on skin irritation/corrosion are available.

However, a concern can be identified based on the fact that this substance is a chlorosilane that generates hydrogen chloride in the presence of moisture. Trichlorosilane hydrolyses in contact with water, releasing 3 moles of hydrogen chloride (HCl) for each mole of parent material ($SiHCl_3$ + 3 H_2O → $HSi(OH)_3$ + 3 HCl). Based on the hydrolysis to hydrogen chloride under humid conditions (such as after contact with sweating skin) the same classification as for hydrogen chloride as Skin Corr. 1B was proposed by the DS.

Comments received during public consultation

Two MSCAs supported the proposed classification as Skin Corr. 1B; H314 for trichlorosilane.

One company-manufacturer did not agree with classification as Skin Corr. 1B proposed by the DS and considered that the classification Skin Corr. 1A should be retained. Based on the hydrolysis under humid conditions, trichlorosilane produces hydrogen chloride, which is classified as Skin Corr. 1A in Annex VI of the CLP Regulation2, and not hydrochloric acid, which is classified as Skin Corr. 1B. In support of this interpretation, the company-manufacturer also referred to three studies (two of them according to OECD TG 404) for three different chlorosilanes, which support Category 1A rather than 1B.

Assessment and comparison with the classification criteria

The available studies (Mellon Institute) were performed in 1948 and 1951 and indicate mild skin reaction and formation of erythema/oedema but they do not allow to decide on the need for classification as neither the number of affected/tested animals, nor the mean scores for 24 h, 48 h and 72 h and recovery were documented.

Trichlorosilane currently has a harmonised classification in Annex VI of the CLP Regulation as Skin Corr. 1A. The justification and underlying data for Category 1A is not known. Trichlorosilane is known to vigorously hydrolyse in contact with water, humidity and the potentially in protic solvents (e.g. ethanol) with the release of hydrogen chloride (index no. 017-002-00-2) classified as Skin Corr. 1A in Annex VI of the CLP Regulation. In the presence of moisture (as in contact with sweating skin), hydrogen chloride dissolves in water and forms hydrochloric acid (index no. 017-002-01-X, hydrochloric acid …%), which is classified as Skin Corr. 1B under the CLP Regulation.

Taking into account results from OECD TG 404 studies with structurally related chlorosilanes (study summaries can be found in Supplemental information, below) and harmonised classification of gaseous HCl as Skin Corr. 1A, RAC supports the read across from other chlorosilanes and gaseous HCl instead of the read across from the hydrolysis product - aqueous HCl, proposed by the DS.

In conclusion, **RAC agreed to retain the classification of trichlorosilane as Skin Corr. 1A; H314 (Causes severe skin burns and eye damage)**.

RAC evaluation of serious eye damage/irritation

Summary of the Dossier Submitter's proposal

In a non-guideline study (Union Carbide, 1947), 7 animals were exposed to 250, 500 and 1000 ppm trichlorosilane for 3 minutes. The effects on the eye were evaluated at different time points after exposure for symptoms such as opacity, dullness of the cornea or internal congestion. Immediate and evident eye injury was seen in rabbits following 3-minute exposure to vapours of trichlorosilane at a nominal concentration of 500 ppm. Delayed eye damage was observed following exposure to 250 ppm.

No guideline-conform *in vivo* studies on eye irritation have been performed. However, the available studies by Mellon Institute published in 1948 using 5 % dilution in 'deobase' (a solvent based on refined petroleum) indicated severe eye damage ('ruined eyes'). The wording "ruined eyes" correspond to category 1 "effects on the cornea, iris or conjunctiva that are not expected to reverse …". This severe eye damage was noted in at least one animal (without data on the total number of affected animals).

Classification of trichlorosilane as Eye Dam. 1; H318 (Causes serious eye damage) was proposed by DS.

Comments received during public consultation

Two MSCAs supported the proposed classification Eye Dam. 1; H318 for trichlorosilane.

Assessment and comparison with the classification criteria

In the presence of moisture (as on the ocular surface), trichlorosilane generates hydrogen chloride, which is a known corrosive agent and classified as Skin Corr. 1A under the CLP Regulation. The eye effects observed in two non-guideline rabbit studies (Union Carbide, 1947, Mellon Institute, 1948) with trichlorosilane are consistent with corrosive/damaging effects.

Trichlorosilane currently has a harmonised classification as Skin Corr. 1A; H314 (Causes severe skin burns and eye damage) in Annex VI of the CLP Regulation. Taking into account section 3.3 of the Guidance on the Application of the CLP Criteria (Version 5.0 – July 2017) – '*if a substance or mixture is classified as Skin corrosion Category 1 then serious damage to eyes is implicit as reflected in the hazard statement for skin corrosion (H314: Causes severe skin burns and eye damage). Thus, the corrosive substance or mixture is also classified, but the corresponding hazard statement (H318: Causes serious eye damage) is not indicated on the label to avoid redundancy*'.

RAC supports the DS's proposal for **classification of trichlorosilane as Eye Dam. 1; H318 (Causes serious eye damage)**; however, to avoid redundancy, only the hazard statement H314 (Causes severe skin burns and eye damage) should be indicated on the label.

Additional references

Holleman-Wiberg, Lehrbuch der anorganischen Chemie", 101st edition, 1995, p. 897

ANNEXES:

Annex 1 The Background Document (BD) gives the detailed scientific grounds for the opinion. The BD is based on the CLH report prepared by the Dossier Submitter; the evaluation performed by RAC is contained in 'RAC boxes'.

Annex 2 Comments received on the CLH report, response to comments provided by the Dossier Submitter and RAC (excluding confidential information).