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|  |  | **UN/SCETDG/59/INF.12** |

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| **Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classificationand Labelling of Chemicals 9 November 2021** |
| **Sub-Committee of Experts on the Transport of Dangerous Goods****Fifty-ninth session**Geneva, 29 November-8 December 2021Item 3 of the provisional agenda[**Listing, classification**](https://wiki.unece.org/display/tdg/6%2B%28c%29%3A%2BFibre-reinforced%2Bplastics%2B%28FRP%29%2Bportable%2Btanks) **and packaging** |

 Revision of classification of tetramethylammonium hydroxide (TMAH)

 Transmitted by the expert from the Netherlands

 Introduction

1. It has been brought to the attention of the expert from the Netherlands that TMAH, in addition to its corrosive properties, is also toxic and that several fatalities have occurred after spillage incidents involving TMAH solutions. The current classification of TMAH in the Dangerous Goods List does not reflect the acute toxic properties of the substance. The expert from the Netherlands believes it is important to revise the classification of TMAH in the Dangerous Goods List so that the hazard communication and transport conditions can be brought in line with the actual hazards of the substances.

2. Tetramethylammonium hydroxide (TMAH) is a quaternary ammonium compound used in the chemical industry in its solid form and as a solution. The solid form is assigned to UN 3423 TETRAMETHYLAMMONIUM HYDROXIDE, SOLID, Class 8, PG II, whereas TMAH solutions are assigned to UN 1835 TETRAMETHYLAMMONIUM HYDROXIDE SOLUTION Class 8, PG II or III. TMAH solutions are commonly transported at concentrations of 2.38 %, 20 %, and 25 %.

3. TMAH has alkaline corrosive properties that can cause chemical skin burns, as well as systemic neurotoxic (cholinergic agonistic) effects that can lead to respiratory failure and cardiac arrest. The corrosivity of TMAH solutions damages the skin allowing for increased dermal uptake of TMAH. Solid TMAH is hygroscopic and will take up water or dissolve into the surface moisture of the skin[[1]](#footnote-2). The current TMAH data sheets are shown in Annexes III (solid) and IV (solution) for information purposes.

4. The UN Model Regulations state in several places that assignment of packing groups shall take human experience into account:

* for toxic substances in section 2.6.2.2.2 *(“… account shall be taken of human experience in instances of accidental poisoning …”);*
* for corrosive substances in sections 2.8.3.1 and 2.8.3.2 *(“Existing human and animal data including information from single or repeated exposure shall be the first line of evaluation, as they give information directly relevant to effects on the skin” and ”In assigning the packing group in accordance with 2.8.2.3, account shall be taken of human experience in instances of accidental exposure...”), respectively.*

However, (quantitative) criteria for classification using evidence from human experience are not provided.

 Human data

5. Two literature studies report 14 incidents involving accidental human exposure, four of which have resulted in death (see Table 1 below). The first 13 cases are described in Lin CC et al., Tetramethylammonium hydroxide poisoning, *Clin Toxicol,* 2010,48:213‐217 (<https://www.ncbi.nlm.nih.gov/pubmed/20230335>), the last case is described in Park SH et al., Tetramethylammonium hydroxide poisoning during a pallet cleaning demonstration. *J Occup Health*., 2013, 55(2):120‐124 ([https://pubmed.ncbi.nlm.nih.gov/23327884/)](https://pubmed.ncbi.nlm.nih.gov/23327884/%29). The cases are listed per incident by the concentration of the solution that got spilled, the percentage of exposed body surface area, the time that elapsed from the spill and until the decontamination of the exposed person, the clinical and laboratory abnormalities, and the treatment/outcome. The original publications list additional information with regard to details of some of the cases and the clinical signs that were noted.

6. Corrosivity – three fatalities were exposed to 25 % TMAH solution and one fatality to 8.75 % TMAH solution. In six incidents, second to third degree chemical burns were observed after exposure to 25 % TMAH for less than a minute. This would correspond to a corrosivity hazard of PG I according to paragraph 2.8.3.3 of the Model Regulations. The available information on human incidents does not support more severe corrosive classification for TMAH solutions of lower concentrations or for solid TMAH.

7. Toxicity – in two of the lethal incidents, the persons were exposed to 25 % TMAH solution for less than one minute with a total exposure surface of 7 %. It is possible to provide an indication of human toxicity based on this information. It is assumed that the body surface[[2]](#footnote-3) of an average person is 17,000 cm2. The exposed surface would then be 7 % x 17,000 cm2 = 1,190 cm2. Due to the short exposure time and the low viscosity of water, most of the water will run down the skin. Assume that the thickness of the layer that contributes to the dermal toxicity is 0.01 cm. The exposure is then 1,190 cm2 x 0.01 cm = 11.9 cm3 of a 25 % (0.25 g/mL) solution. The total exposure to TMAH is 11.9 cm3 x 0.25 g/mL = 2.975 grams. If this is converted to kilograms bodyweight (average of 70 kg) this amounts to 2975 mg / 70 kg = 43 mg/kg bodyweight. This corresponds with classification criteria for PG I as stated in paragraph 2.6.2.2.4.1 of the Model Regulations. Although these criteria have been developed for animal models and not for humans, it does provide supportive evidence for the toxic properties of TMAH.

**Table 1: Incidents involving accidental human exposure to TMAH, dermal exposure**

| ***TMAH solution***  | ***Exposed body surface area)*** | ***Elapsed time to deconta-mination*** | ***Clinical abnormalities and laboratory abnormalities*** | ***Treatment/outcome*** |
| --- | --- | --- | --- | --- |
| 2.38 % | 28 % | 10 min | Second to third degree chemical burn, dyspnea, salivation, respiratory failure, weakness, hyperglycemia, leukocytosis | Intensive care/survived |
| 2.38 % | 5 % | <10 min | First to third degree chemical burn, dermal pain, skin rashes | Supportive/survived |
| 2.38 % | <1 % | <10 min | None | Supportive/survived |
| 2.38 % | <1 % | <10 min | None | Supportive/survived |
| 2.38 % | 18 % | unknown | First to second degree chemical burn | Supportive/survived |
| 2.38 % | 5 % (face) | <1 min | Limb weakness, skin rashes | Supportive/survived |
| 2.38 % | 1 % (finger) | 2 h  | Dermal pain and swelling, skin rashes | Supportive/survived |
| 2.38 % | Eye | <1 min | Conjunctivitis | Supportive/survived |
| 2.38 % | 2 % | <1 min | First to second degree chemical burn, dermal pain, skin rashes | Supportive/survived |
| 25 % | 3 % | <30 min | Second to third degree chemical burn, dermal pain, skin rashes | Supportive/survived |
| 25 % | 7 % | <1 min | Second to third degree chemical burn, coma, dyspnea, shock, ventricular tachycardia, hyperglycemia, leukocytosis, metabolic acidosis | Intensive care/died |
| 25 % | 7 % | <1 min | Second to third degree chemical burn, coma, dyspnea, shock, hyperglycemia, leukocytosis | Intensive care/died |
| 25 % | 29 % | >30 min | Bradycardia, second to third degree chemical burn, coma, miosis, shock, salivation, weakness, hyperglycemia, leukocytosis, metabolic acidosis | Intensive care/died |
| 8.75 % | 12 % | unknown | Chemical burns | Died |

 Animal data

8. There is also animal test data available on the hazardous properties of TMAH. However, not all of them meet the guidelines as set out in the Model Regulations. For example, some studies are carried out with different animal species than specified or the studies are not properly documented. Despite the drawbacks, all data do underline the toxic and corrosive properties of TMAH. An overview of the acute toxic and corrosive properties of TMAH, based on *in vivo* and *in vitro* studies, is shown in Annexes I and II.

9. A summary of acute toxicity studies in animals is shown in Table 2 below, for details see Annex I. Information is not available for inhalation toxicity. The results of the oral and dermal toxicity are extrapolated to pure TMAH by using the formula in paragraph 2.6.2.3.2. Solid TMAH is hygroscopic, and reacts with moisture on skin, increasing the dermal absorption of TMAH. The dermal studies have been performed on rats and not on rabbits as specified in paragraph 2.6.2.1.2 of the Model Regulations. Nevertheless, the results clearly indicate a toxic effect.

**Table 2. Summary of acute toxicity studies of TMAH.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Route of exposure | TMAH solution | Division | Packing Group | Comment |
| Oral toxicity | 25 % | 6.1 | III | None |
| Dermal toxicity | 25 % | 6.1 | I | Rat instead of rabbit |
| Oral toxicity | Solid | 6.1 | II | Extrapolation according to 2.6.2.3.2 |
| Dermal toxicity | Solid | 6.1 | I | Rat instead of rabbit and extrapolation according to 2.6.2.3.2 |

10. Corrosivity studies in experimental animals would support classification for PG III for 2.38 % TMAH solution and PG II for solid TMAH (Annex II Table 3). Not all studies are suitable for classification purposes. Nevertheless, the results do indicate dermal effects ranging from no effect to severe corrosive effects.

 Discussion

11. The available human and animal data thus indicate a corrosive and toxic hazard of TMAH. However, it is not clear how to assign the appropriate packing group. The data do show that a distinction in packing groups is necessary, due to the various outcomes of the incidents and test results.

12. The Netherlands therefore seeks the view of the Sub-Committee on how to take the existing human experience information on TMAH into account in the assignment of packing groups, in particular with regard to the following questions:

(a) Acute toxicity of TMAH solutions. Fatalities have occurred after accidental short-term human exposure to TMAH solutions at and above 8.75 %. Based on human experience, should TMAH solutions ≥ 8.75 % be assigned to Division 6.1 PG I?

(b) Corrosivity of TMAH solutions. Second and third degree chemical burns have been observed after accidental human exposure to 25 % TMAH solutions for less than a minute. Based on human experience, should TMAH solutions ≥ 25 % be assigned to Class 8 PG I?

(c) Specific concentration limits. Taking the above two questions into account, should specific concentration limits be introduced for UN 1835 TETRAMETHYLAMMONIUM HYDROXIDE, SOLUTION? This can provide better guidance on the assignment of packing groups, also with regard to precedence of hazards. If so, what limits would be appropriate?

(d) Acute toxicity of solid TMAH. Taking the information on animal data into account, should solid TMAH also be classified as Division 6.1 PG I based on extrapolation of animal test data?

13. A formal proposal for a change in classification will be prepared for a future session based on the feedback obtained from the Sub-Committee on the assignment of packing groups and concentration limits. This will also include any changes related to the transport conditions.

Annex I

 Experimental acute toxicity studies in animals

*1.1 Oral route*

Acute toxicity studies via the oral route are available for 2.5 % and 25 % concentrations of TMAH. All studies were performed in rats. The results are shown in table 1. Column 2 shows the LD50 value obtained with the test material with the corresponding packing group shown in parenthesis. Column 3 shows the LD50 values extrapolated to the pure form using the formula in section 2.6.2.3.2 of the Model Regulations, with the corresponding packing group shown in parenthesis.

**Table 1: Acute toxicity in rats, oral route**

|  |  |  |  |
| --- | --- | --- | --- |
| ***TMAH solution tested ( %)*** | ***LD50 in mg/kg using the test solution (PG)*** | ***LD50 in mg/kg if extrapolated pure TMAH (PG)*** | ***Reference*** |
| 2.5 % | 300-2000 mg/kg bw(NDG\*)  | 7.5-50 mg/kg bw (PG II) | <https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/2/?documentUUID=>622eb57f-8b8c-4545-ad14-c22f42c63d52 |
| 25 % | 50-500 mg/kg bw(PG III/NDG) | >12.5- <125 mg/kg bw (PG II/III) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/2/?documentUUID=39c2112b-b0a1-467b-833d-a4c7dfa9efbd |
| 25 % | 175 mg/kg bw(PG III) | 43.7 mg/kg bw (PG II) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/2/?documentUUID=e82b7080-68ff-4d37-941a-acaa1773e451 |
| 25 %  | 50-300 mg/kg bw(PG III) | 12.5-75 mg/kg bw (PG II) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/2/?documentUUID=c50d0add-7b8e-45f4-8ff9-2214e8b6a531 |

\*NDG = not dangerous goods

The above data on oral toxicity would lead to the classification of TMAH 25 % solution as Division 6.1 PG III and solid TMAH as Division 6.1 PG II.

*1.2 Dermal route*

Acute toxicity studies via the dermal route are available for 2.38 %, 2.5 % and 25 % concentrations of TMAH. All studies were performed in rats and the results are shown in table 2. Column 2 shows the LD50 value obtained with the test material with the corresponding packing group shown in parenthesis. Column 3 shows the LD50 values extrapolated to the pure form using the formula in section 2.6.2.3.2 of the Model Regulations, with the corresponding packing group shown in parenthesis.

**Table 2: Acute toxicity in rats, dermal route**

|  |  |  |  |
| --- | --- | --- | --- |
| ***TMAH solution tested ( %)*** | ***LD50 in mg/kg using the test solution (PG)*** | ***LD50 in mg/kg if extrapolated to pure TMAH (PG)*** | ***Reference*** |
| 2.38 % | 85.9 mg/kg (PG II) | 2.0 mg/kg (PG I) | <https://pubmed.ncbi.nlm.nih.gov/21310775/> |
| 2.5 % | 1000-2000 mg/kg bw (NDG) | 25-50 mg/kg bw (PG I) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=51d64548-5ca0-41d2-8c10-e89bbaa9f54a |
| 25 %  | >50-<200 mg/kg bw (PG II) | >12.5-<50 mg/kg bw (PG I) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=36b998e2-2d19-4ee1-ac93-eda93a611185 |
| 25 % | 499 mg/kg bw (PG III) | 112 mg/kg bw (PG II) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=d5b226a5-aa8f-4922-93dc-72947b04ba1b |
| 25 % | 200-1000 mg/kg bw (PG III) | 50-250 mg/kg bw (PG II) | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=420d8f38-3e2d-4314-9c2d-70d7c4247193 |
| 25 % | 28.7 mg/kg bw (PG I) | 7.2 mg/kg bw (PG I) | <https://pubmed.ncbi.nlm.nih.gov/21310775/> |

The data presented above shows different results for the same or comparable concentrations. The above data on dermal toxicity indicates a classification of TMAH 2.38 % solution as Division 6.1 PG II, TMAH 25 % solution as Division 6.1 PG I and solid TMAH as Division 6.1 PG I. However, the studies have been performed on rats instead of on rabbits as specified in paragraph 2.6.2.1.2 of the Model Regulations.

*1.3 Acute toxicity via the inhalation route*

No acute toxicity studies via the inhalation route have been identified for TMAH.

Annex II

 Experimental corrosivity studies in animals and in vitro

There are few experimental studies available on the corrosive properties of TMAH:

1. In an *in vivo* study, a 2.38 % solution was tested according to OECD Guideline 404 and the results correspond to packing group III (https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/4/2/?documentUUID=803ad984-f2c4-4804-b90e-4a4534a8806c).

2. In an in vitro study, TMAH pentahydrate (solid) is classified as packing group II for transport based on experimental results from Corrositex testing in compliance with OECD Guideline 435 (<https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/4/2/?documentUUID=60d2e288-0a41-4843-861e-8d72b1575014>).

3. Supporting but incomplete information on the corrosive effects of TMAH is available. Table 3 lists the information on corrosive effects that was included in the study summaries of the acute dermal toxicity studies in rats in the REACH dossier. Also included is a secondary reference on a guinea pig corrosivity study that was included in the OECD High Production Volume Chemical review on TMAH.

**Table 3: Corrosive effects of TMAH in dermal acute toxicity studies in rats (solution) and guinea pigs (solid)**

|  |  |  |
| --- | --- | --- |
| ***TMAH test material***  | ***Effects described in the study summary*** | ***Reference*** |
| 2.5 % solution | Scales, scabs and /or erythema maculate were noted in the treated skin area of several animals between days 3 and 10.  | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=51d64548-5ca0-41d2-8c10-e89bbaa9f54a |
| 25 % solution | Necropsy of the animals that died revealed abnormalities of the treated skin. At all dosages, dermal effects were seen ranging from well-defined to severe on day 1 and absent to severe on days 7 and 14. Surviving animals showed slight oedema and eschar formation. | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=36b998e2-2d19-4ee1-ac93-eda93a611185 |
| 25 % solution | No effects on the skin of exposed animals were observed. | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=d5b226a5-aa8f-4922-93dc-72947b04ba1b |
| 25 % solution | At treated skin site: erythema, scales and scabs during the study period. | https://echa.europa.eu/registration-dossier/-/registered-dossier/14295/7/3/4/?documentUUID=420d8f38-3e2d-4314-9c2d-70d7c4247193 |
| Solid | Solid tetramethylammonium hydroxide pentahydrate moistened with water was applied to the skin of guinea pigs by occlusive covering at doses of 25 to 1000 mg/kg bw. 24 hours: Slight edema. All of patch area was necrotic with band either severe erythema or hemorrhagic at periphery. 1 week: Depressed heavy eschar breaking away at edges. Some raw areas and secondary eschar forming. 2 weeks: Depressed eschars with raised edges. Scarring at periphery. Five animals died within 24 hours after application. Based on these observations, it was concluded that tetramethylammonium hydroxide pentahydrate is extremely severe corrosive irritant to skin. | <https://hpvchemicals.oecd.org/UI/SIDS_Details.aspx?key=b63d44db-8c7b-424a-9400-0e75b0cc6140&idx=0>; section 5.2.1 |

The results in the table are not sufficient to be used for classification purposes. Nevertheless, the results do indicate dermal effects ranging from no effect to severe corrosive effects.

Annex III

 Data sheet to be submitted to the United Nations for new or amended classification of substances

Submitted by SACHEM Date November 2, 2021

Supply all relevant information including sources of basic classification data. Data should relate to the product in the form to be transported. State test methods. Answer all questions ‑ if necessary state "not known" or "not applicable" ‑ If data is not available in the form requested, provide what is available with details. Delete inappropriate words.

**Section 1. SUBSTANCE IDENTITY**

* 1. Chemical name

**Tetramethylammonium hydroxide (pentahydrate)**

* 1. Chemical formula

**C4H12N.5H2O.HO**

* 1. Other names/synonyms

Methanaminium, N,N,N,N-tetramethyl-, hydroxide, hydrate (1:1:5)

Tetramethylammonium hydroxide pentahydrate

Tetramethylazanium hydroxide pentahydrate

1.4.1 UN number

 UN 3423

1.4.2 CAS number

 10424-65-4

1.5 Proposed classification for the Recommendations

1.5.1 Proper shipping name (3.1.2)

**Tetramethylammonium hydroxide, solid**

1.5.2 Class/division with subsidiary hazard(s) **8 packing group II**

1.5.3 Proposed special provisions, if any

1.5.4 Proposed packing instruction(s)

**Section 2. PHYSICAL PROPERTIES**

2.1 Melting point or range ………..63-70°C (solid)

2.2 Boiling point or range ………..Not available.

2.3 Relative density at:

2.3.1……**1.13 (20 °C)**

2.4 Vapour pressure at:

2.4.1……**0.154 mPa @ 25 °C**

2.5 Viscosity at 20 °C ……………….**No data available**

2.6 Solubility in water at 20 °C 100 g/100ml

2.7 Physical state at 20°C (2.2.1.1) **solid** **crystalline**

2.8 Appearance at normal transport temperatures, including colour and odour
Solid crystalline, white, light yellow. Slight amine odour.

2.9 Other relevant physical properties in water: pH>13

**Section 3. FLAMMABILITY – the product is not flammable**

3.1 Flammable vapour

3.1.1 Flash point (2.3.3) **No data available**

3.1.2 Is combustion sustained? (2.3.1.3)

3.2 Autoignition temperature No data available

3.3 Flammability range (LEL/UEL) Not applicable

3.4 Is the substance a flammable solid? (2.4.2[[3]](#footnote-4)1) **No**

3.4.1 If yes, give details

**Section 4. CHEMICAL PROPERTIES**

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity? **No**

If yes, state:

4.1.1 Inhibitor/stabilizer used

4.1.2 Alternative method

4.1.3 Time effective at 55 °C

4.1.4 Conditions rendering it ineffective

4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.1**1**) **No**

4.2.1 If yes, give details

4.3 Is the substance a desensitized explosive? (2.4.2.4**1**) **No**

4.3.1 If yes, give details

4.4 Is the substance a self-reactive substance? (2.4.1**1**) **No**

If yes, state:

4.4.1 Exit box of flow chart

What is the self-accelerating decomposition temperature (SADT) for a 50 kg package? ..................°C

Is the temperature control required? (2.4.2.3.4**1**) yes/no

4.4.2 Proposed control temperature for a 50 kg package °C

4.4.3 Proposed emergency temperature for a 50 kg package °C

4.5 Is the substance pyrophoric? (2.4.31) **No**

 4.5.1 If yes, give details

4.6 Is the substance liable to self-heating? (2.4.3[[4]](#footnote-5)1) **No**

 4.6.1 If yes, give details

4.7 Is the substance an organic peroxide (2.5.1) **No**

If yes state:

4.7.1 Exit box of flow chart

What is the self accelerating decomposition temperature (SADT) for a 50 kg package? ……………°C

Is temperature control required? (2.5.3.4.1**1**) yes/no

4.7.2 Proposed control temperature for a 50 kg package °C

4.7.3 Proposed emergency temperature for a 50 kg package °C

4.8 Does the substance in contact with water emit flammable gases? (2.4.4**1**) **No**

4.8.1 If yes, give details

4.9 Does the substance have oxidizing properties (2.5.1**1**) **No**

4.9.1 If yes, give details **.**

4.10 Corrosivity (2.8**1**) to: **No information available**

4.10.1 ……mild steel yes

4.10.2 ……aluminium yes mm/year at °C

4.10.3 ……other packaging materials (specify)

4.11 Other relevant chemical properties

**Section 5. HARMFUL BIOLOGICAL EFFECTS**

5.1 LD50, oral (2.6.2.1.1[[5]](#footnote-6)1) **oral LD50 of 7.5-50 mg/kg bw in rat**

5.2 LD50, dermal (2.6.2.1.21) **dermal LD50 of 2.0 mg/kg bw in rat**

5.3 LC50, inhalation (2.6.2.1.31) mg/l Exposure time hours **No information available**

or ml/m3 Animal species

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.31) **No information available**

5.5 Skin exposure (2.81) results

**Skin irritation/corrosion:**

An acute dermal irritation /corrosion test according to OECD 404 with 2.38% TMAH was performed under GLP circumstances. No dermal irritation was observed following application for 3 minutes. Application for one hour elicited well-defined dermal irritation. Application for 4 hours resulted in well-defined to severe dermal irritation in all animals, with necrosis in one animal. Due to the severity in this animal and the irreversibility of the effect, the 2.38% TMAH-solution was shown to be corrosive to the skin, category 1C (according to EC regulation No 1272/2008).

The pH of a 10% TMAH solution in water is 13.6.

According to the Corrositex database, TMAOH pentahydrate should be classified as packing group II for transport (ADR/DOT) based on experimental results from Corrositex testing. (Based on the fact that the criteria for packing group II are identical to the criteria for the classification as skin corrosive 1B from OECD guideline 435, TMAOH pentahydrate is classified as skin corrosive 1B.)

5.6 Other data.

5.7 Human experience

Several fatal incidents have occurred with TMAOH.

**Section 6. SUPPLEMENTARY INFORMATION**

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents)

**Suitable Extinguishing Media**

Use. Water spray. Carbon dioxide (CO2). Foam. Dry chemical.

**Specific hazards arising from the chemical**

Causes severe burns. Hazardous combustion products. Carbon monoxide. May burn violently. Decomposition may be

self-accelerating and produce large amounts of gases. May be fatal if inhaled, absorbed through skin, or swallowed.

**Protective equipment and precautions for firefighters**

In the event of fire and/or explosion do not breathe fumes. In case of fire: Wear self-contained breathing apparatus. Wear personal protective clothing. Avoid contact with eyes, skin and clothing.

6.1.2 Spillage
**Personal precautions, protective equipment and emergency procedures**

Avoid dust formation. Do not breathe dust/fume/gas/mist/vapors/spray. Do not ingest. Do not get in eyes, on skin, or on clothing. Wear personal protective clothing.

**Environmental precautions**

Prevent further leakage or spillage if safe to do so. Prevent product from entering drains. Local authorities should be advised if significant spillages cannot be contained. Do not flush into surface water or sanitary sewer system.

**Methods and materials for containment and cleaning up**

Contain and collect spillage with non-combustible absorbent material, (e.g. sand, earth, diatomaceus earth, vermiculite) and place in container for disposal according to local / national regulations (see section 13)

**Methods for cleaning up**

Pick up and transfer to properly labelled containers. Soak up with inert absorbent material. Clean contaminated surface thoroughly. Retain washings as contaminated waste.

6.2 Is it proposed to transport the substance in:

 6.2.1 Bulk Containers (6.8**1**)?

 6.2.2 Intermediate Bulk Containers (6.5**1**)?

 6.2.3 Portable tanks (6.71)?

 If yes, give details in Sections 7, 8 and/or 9.

**Section 7. BULK CONTAINERS (only complete if yes in 6.2.1)**

7.1 Proposed type(s)

**Section 8. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.2)**

8.1 Proposed type(s)

**Section 9. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.3)**

9.1 Description of proposed tank (including IMO tank type if known)

9.2 Minimum test pressure

9.3 Minimum shell thickness

9.4 Details of bottom openings, if any

9.5 Pressure relief arrangements

9.6 Degree of filling

* 1. Unsuitable construction materials ………………………………………………………………………………

Annex IV

 Data sheet to be submitted to the United Nations for new or amended classification of substances

Submitted by SACHEM Date November 2, 2021

Supply all relevant information including sources of basic classification data. Data should relate to the product in the form to be transported. State test methods. Answer all questions ‑ if necessary state "not known" or "not applicable" ‑ If data is not available in the form requested, provide what is available with details. Delete inappropriate words.

**Section 1. SUBSTANCE IDENTITY**

* 1. Chemical name

**Tetramethylammonium hydroxide solution**

* 1. Chemical formula

**C4H12N.HO**

* 1. Other names/synonyms

Tetramethylazanium hydroxide solution

1.4.1 UN number

 UN 1835

1.4.2 CAS number

 75-59-2

1.5 Proposed classification for the Recommendations

1.5.1 Proper shipping name (3.1.2)

**Tetramethylammonium hydroxide solution**

1.5.2 Class/division with subsidiary hazard(s)

**8 packing group II and III**

1.5.3 Proposed special provisions, if any

1.5.4 Proposed packing instruction(s)

**Section 2. PHYSICAL PROPERTIES**

2.1 Melting point or range ………..63-70°C (solid)

2.2 Boiling point or range ………...ca. 102°C

2.3 Relative density at: **No information available**

2.4 Vapour pressure at:

2.4.1……**16.0 mm Hg @ 25**°**C**

2.5 Viscosity at 20 °C ……………….**3.13 centipoise @ 19**°**C**

2.6 Solubility in water at 20 °C (solid: 100 g/100ml )

2.7 Physical state at 20°C (2.2.1.1)  **liquid**

2.8 Appearance at normal transport temperatures, including colour and odour
Liquid, colorles, light yellow. Slight amine odour.

2.9 Other relevant physical properties pH>13

**Section 3. FLAMMABILITY – not flammable**

3.1 Flammable vapour

3.1.1 Flash point (2.3.3) **>95°C**

3.1.2 Is combustion sustained? (2.3.1.3) **No information available**

3.2 Autoignition temperature No information available

3.3 Flammability range (LEL/UEL) No information available

3.4 Is the substance a flammable solid? (2.4.2[[6]](#footnote-7)1)

3.4.1 If yes, give details

**Section 4. CHEMICAL PROPERTIES**

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity? **No**

If yes, state:

4.1.1 Inhibitor/stabilizer used

4.1.2 Alternative method

4.1.3 Time effective at 55 °C

4.1.4 Conditions rendering it ineffective

4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.1**1**) **No**

4.2.1 If yes, give details

4.3 Is the substance a desensitized explosive? (2.4.2.4**1**) **No**

4.3.1 If yes, give details

4.4 Is the substance a self-reactive substance? (2.4.1**1**) **No**

If yes, state:

4.4.1 Exit box of flow chart

What is the self-accelerating decomposition temperature (SADT) for a 50 kg package? ..................°C

Is the temperature control required? (2.4.2.3.4**1**) yes/no

4.4.2 Proposed control temperature for a 50 kg package °C

4.4.3 Proposed emergency temperature for a 50 kg package °C

4.5 Is the substance pyrophoric? (2.4.31) **No**

 4.5.1 If yes, give details

4.6 Is the substance liable to self-heating? (2.4.3[[7]](#footnote-8)1) **No**

 4.6.1 If yes, give details

4.7 Is the substance an organic peroxide (2.5.1) **No**

If yes state:

4.7.1 Exit box of flow chart

What is the self accelerating decomposition temperature (SADT) for a 50 kg package? ……………°C

Is temperature control required? (2.5.3.4.1**1**) yes/no

4.7.2 Proposed control temperature for a 50 kg package °C

4.7.3 Proposed emergency temperature for a 50 kg package °C

4.8 Does the substance in contact with water emit flammable gases? (2.4.4**1**) **No**

4.8.1 If yes, give details

4.9 Does the substance have oxidizing properties (2.5.1**1**) **No**

4.9.1 If yes, give details **.**

4.10 Corrosivity (2.8**1**) to:

4.10.1 ……mild steel **yes**

4.10.2 ……aluminium **yes** mm/year at °C

4.10.3 ……other packaging materials (specify)

4.11 Other relevant chemical properties

**Section 5. HARMFUL BIOLOGICAL EFFECTS**

5.1 LD50, oral (2.6.2.1.1[[8]](#footnote-9)1) **oral LD50 of 50-300 mg/kg bw in rat**

5.2 LD50, dermal (2.6.2.1.21) **dermal LD50 of 28.7 mg/kg bw in rat**

5.3 LC50, inhalation (2.6.2.1.31) mg/l Exposure time hours **No information available**

or ml/m3 Animal species

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.31) **No information available**

5.5 Skin exposure (2.81) results

**Skin irritation/corrosion:**

An acute dermal irritation /corrosion test according to OECD 404 with 2.38% TMAH was performed under GLP circumstances. No dermal irritation was observed following application for 3 minutes. Application for one hour elicited well-defined dermal irritation. Application for 4 hours resulted in well-defined to severe dermal irritation in all animals, with necrosis in one animal. Due to the severity in this animal and the irreversibility of the effect, the 2.38% TMAH-solution was shown to be corrosive to the skin, category 1C (according to EC regulation No 1272/2008).

The pH of a 10% TMAH solution in water is 13.6.

According to the Corrositex database, TMAOH pentahydrate should be classified as packing group II for transport (ADR/DOT) based on experimental results from Corrositex testing. (Based on the fact that the criteria for packing group II are identical to the criteria for the classification as skin corrosive 1B from OECD guideline 435, TMAOH pentahydrate is classified as skin corrosive 1B.)

5.6 Other data.

5.7 Human experience

Several fatal incidents have occurred with TMAOH.

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents)

**Suitable Extinguishing Media**

Use. Water spray. Carbon dioxide (CO2). Foam. Dry chemical.

**Specific hazards arising from the chemical**

Causes severe burns. Hazardous combustion products. Carbon monoxide. May burn violently. Decomposition may be

self-accelerating and produce large amounts of gases. May be fatal if inhaled, absorbed through skin, or swallowed. Product may decompose into trimethylamine, which is a flammable gas and methanol, which can produce flammable vapors.

**Protective equipment and precautions for firefighters**

In the event of fire and/or explosion do not breathe fumes. In case of fire: Wear self-contained breathing apparatus. Wear personal protective clothing. Avoid contact with eyes, skin and clothing.

6.1.2 Spillage
**Personal precautions, protective equipment and emergency procedures**

Do not breathe vapor or mist. Do not ingest. Do not get in eyes, on skin, or on clothing. Wear personal protective clothing (see section 8).

**Environmental precautions**

Prevent further leakage or spillage if safe to do so. Prevent product from entering drains. Local authorities should be advised if significant spillages cannot be contained. Do not flush into surface water or sanitary sewer system. Do not release into waterways or aquatic systems.

**Methods and materials for containment and cleaning up**

Contain and collect spillage with non-combustible absorbent material, (e.g. sand, earth, diatomaceus earth, vermiculite) and place in container for disposal according to local / national regulations (see section 13)

**Methods for cleaning up**

Soak up with inert absorbent material. Clean contaminated surface thoroughly. Retain washings as contaminated waste. Product may decompose into trimethylamine, which is a flammable gas and methanol, which can produce flammable vapors. Empty containers may contain one or both flammable gases and should be handled appropriately. All equipment used in cleaning containers should be grounded and bonded, including the container, to prevent build-up and discharge of static electricity which may cause fire or explosion.

6.2 Is it proposed to transport the substance in:

 6.2.1 Bulk Containers (6.8**1**)?

 6.2.2 Intermediate Bulk Containers (6.5**1**)?

 6.2.3 Portable tanks (6.71)?

 If yes, give details in Sections 7, 8 and/or 9.

**Section 7. BULK CONTAINERS (only complete if yes in 6.2.1)**

7.1 Proposed type(s)

**Section 8. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.2)**

8.1 Proposed type(s)

**Section 9. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.3)**

9.1 Description of proposed tank (including IMO tank type if known)

9.2 Minimum test pressure

9.3 Minimum shell thickness

9.4 Details of bottom openings, if any

9.5 Pressure relief arrangements

9.6 Degree of filling

* 1. Unsuitable construction materials ………………………………………………………………………………

1. <https://pubchem.ncbi.nlm.nih.gov/compound/>Tetramethyl ammonium-hydroxide [↑](#footnote-ref-2)
2. HEEG OPINION Biocidal products: model for dipping of hands/forearms in a diluted solution (https://echa.europa.eu/documents/10162/19680902/heeg\_opinion\_16\_dipping\_of\_hands\_forearms\_en.pdf/471333fe-84d3-4601-b7cf-89881c5a2cff [↑](#footnote-ref-3)
3. 2 See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods. [↑](#footnote-ref-4)
4. 1 This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods. [↑](#footnote-ref-5)
5. [↑](#footnote-ref-6)
6. 2 See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods. [↑](#footnote-ref-7)
7. 1 This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods. [↑](#footnote-ref-8)
8. [↑](#footnote-ref-9)