Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

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Sub-Committee of Experts on the Transport of Dangerous Goods

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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 skin¹. 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.

¹ https://pubchem.ncbi.nlm.nih.gov/compound/Tetramethyl ammonium-hydroxide

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/). 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 of an average person is $17,000 \, \mathrm{cm^2}$. The exposed surface would then be $7 \, \% \, x \, 17,000 \, \mathrm{cm^2} = 1,190 \, \mathrm{cm^2}$. 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 $1,190 \, \mathrm{cm^2} \, x \, 0.01 \, \mathrm{cm} = 11.9 \, \mathrm{cm^3} \, \text{of a 25 } \% \, (0.25 \, \text{g/mL})$ solution. The total exposure to TMAH is $11.9 \, \mathrm{cm^3} \, x \, 0.25 \, \mathrm{g/mL} = 2.975 \, \mathrm{grams}$. If this is converted to kilograms bodyweight (average of $70 \, \mathrm{kg}$) this amounts to $2975 \, \mathrm{mg} \, / \, 70 \, \mathrm{kg} = 43 \, \mathrm{mg/kg}$ 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	Exposed body	Elapsed time	Clinical abnormalities and laboratory	Treatment/outcome
solution	surface area)	to deconta-	abnormalities	
		mination		
2.38 %	28 %	10 min	Second to third degree chemical burn,	Intensive
			dyspnea, salivation, respiratory failure,	care/survived
			weakness, hyperglycemia, leukocytosis	
2.38 %	5 %	<10 min	First to third degree chemical burn, dermal	Supportive/survived
			pain, skin rashes	
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,	Supportive/survived
			dermal pain, skin rashes	
25 %	3 %	<30 min	Second to third degree chemical burn,	Supportive/survived
			dermal pain, skin rashes	

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_e n.pdf/471333fe-84d3-4601-b7cf-89881c5a2cff

25 %	7 %	<1 min	Second to third degree chemical burn,	Intensive care/died
			coma, dyspnea, shock, ventricular	
			tachycardia, hyperglycemia, leukocytosis,	
			metabolic acidosis	
25 %	7 %	<1 min	Second to third degree chemical burn,	Intensive care/died
			coma, dyspnea, shock, hyperglycemia,	
			leukocytosis	
25 %	29 %	>30 min	Bradycardia, second to third degree	Intensive care/died
			chemical burn, coma, miosis, shock,	
			salivation, weakness, hyperglycemia,	
			leukocytosis, metabolic acidosis	
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	TMAH solution	Division	Packing Group	Comment
exposure				
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 $\geq 8.75 \%$ 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 \geq 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	LD50 in mg/kg using	LD50 in mg/kg if extrapolated	Reference
tested (%)	the test solution (PG)	pure TMAH (PG)	
2.5 %	300-2000 mg/kg bw	7.5-50 mg/kg bw (PG II)	https://echa.europa.eu/registration-dossier/-
	(NDG*)		/registered-
			dossier/14295/7/3/2/?documentUUID=622eb
			57f-8b8c-4545-ad14-c22f42c63d52
25 %	50-500 mg/kg bw	>12.5- <125 mg/kg bw (PG	https://echa.europa.eu/registration-dossier/-
	(PG III/NDG)	II/III)	/registered-
			dossier/14295/7/3/2/?documentUUID=39c21
			12b-b0a1-467b-833d-a4c7dfa9efbd
25 %	175 mg/kg bw	43.7 mg/kg bw (PG II)	https://echa.europa.eu/registration-dossier/-
	(PG III)		/registered-
			dossier/14295/7/3/2/?documentUUID=e82b7
			080-68ff-4d37-941a-acaa1773e451
25 %	50-300 mg/kg bw	12.5-75 mg/kg bw (PG II)	https://echa.europa.eu/registration-dossier/-
	(PG III)		/registered-
			dossier/14295/7/3/2/?documentUUID=c50d0
			add-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

		LD50 in mg/kg if extrapolated to pure TMAH (PG)	Reference
	` /	1	
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	25-50 mg/kg bw (PG I)	https://echa.europa.eu/registration-dossier/-
	(NDG)		/registered-
			dossier/14295/7/3/4/?documentUUID=51d64
			548-5ca0-41d2-8c10-e89bbaa9f54a
25 %	>50-<200 mg/kg bw (PG	>12.5-<50 mg/kg bw (PG I)	https://echa.europa.eu/registration-dossier/-
	II)		/registered-
			dossier/14295/7/3/4/?documentUUID=36b99
			8e2-2d19-4ee1-ac93-eda93a611185

UN/SCETDG/59/INF.12

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=d5b22
			6a5-aa8f-4922-93dc-72947b04ba1b
25 %	200-1000 mg/kg bw (PG	50-250 mg/kg bw (PG II)	https://echa.europa.eu/registration-dossier/-
	III)		/registered-
			dossier/14295/7/3/4/?documentUUID=420d8
			f38-3e2d-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=51d 64548-5ca0-41d2-8c10-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=36b 998e2-2d19-4ee1-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=d5b 226a5-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=420 d8f38-3e2d-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-

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

1.1	Chemic	cal name				
	Tetran	nethylammonium hydroxide (pentahydrate)				
1.2	Chemic	cal formula				
	C4H12	N.5H2O.HO				
1.3	Other r	names/synonyms				
	Metha	naminium, N,N,N,N-tetramethyl-, hydroxide, hydrate (1:1:5)				
	Tetran	nethylammonium hydroxide pentahydrate				
	Tetran	nethylazanium hydroxide pentahydrate				
1.4.1	UN nu	mber				
	UN 342	23				
1.4.2	CAS n	umber				
	10424-6	55-4				
1.5	Propos	Proposed classification for the Recommendations				
	1.5.1	Proper shipping name (3.1.2)				
	Tetran	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. PHYS	ICAL PROPERTIES				
2.1	Melting	g point or range63-70°C (solid)				
2.2	Boiling	point or rangeNot available.				
2.3	Relativ	Relative density at:				
	2.3.1	1.13 (20 °C)				
2.4	Vapou	r pressure at:				
	2.4.1	0.154 mPa @ 25 °C				
2.5	Viscos	Viscosity at 20 °C No data available				
2.6	Solubil	ity in water at 20 °C 100 g/100ml				
2.7	Physica	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 Section 3	Other relevant physical properties in water: pH>13 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	Autoign	ition temperatureNo data available		
3.3	Flamma	bility range (LEL/UEL) Not applicable		
3.4	Is the su	abstance a flammable solid? (2.4.2¹) No		
	3.4.1 If	yes, give details		
Section 4	4. CHEM	ICAL PROPERTIES		
4.1		e substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent us reactivity? No		
	If yes, s	tate:		
	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	T. 41	L. (2.11.19.(2.11.N)		
4.2		abstance an explosive according to paragraph 2.1.1.1? (2.1¹) No		
	4.2.1	If yes, give details		
4.3		ostance a desensitized explosive? (2.4.2.4¹) No		
4.4	4.3.1	If yes, give details		
4.4		ostance a self-reactive substance? (2.4.1¹) No		
	If yes, sta 4.4.1	Exit box of flow chart		
	4.4.1	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 su	abstance pyrophoric? (2.4.3 ¹) No		
4.6	4.5.1 Is the su	If yes, give details		
4.7	4.6.1 Is the su	If yes, give details abstance an organic peroxide (2.5.1) No		
	If yes st	ate:		

² See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods.

This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

	4.7.1 Exit box of flow chart			
		What is the self accelerating decomposition	n 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 p	ackage°C	1
	4.7.3	Proposed emergency temperature for a 50 l	kg package°C	•
4.8	Does th	e substance in contact with water emit flamma	able gases? (2.4.4 ¹) No	
	4.8.1	If yes, give details		
4.9	Does th	e substance have oxidizing properties (2.5.11)	No	
	4.9.1	If yes, give details		
4.10	Corrosi	vity (2.8 ¹) to: No information available mild steel yes		
		•	/year at	°C
		aluminium yes mmother packaging materials (specify)	year at	C
4.11				
4.11	Other re	elevant chemical properties		
Section	5. HARM	IFUL BIOLOGICAL EFFECTS		
5.1	LD ₅₀ , or	ral (2.6.2.1.1 ¹) oral LD50 of 7.5-50 mg/kg l	ow in rat	
5.2	LD_{50} , dermal (2.6.2.1.2 ¹) dermal LD50 of 2.0 mg/kg bw in rat			
5.3 LC ₅₀ , inhalation (2.6.2.1.3 ¹)mg/1Exposure time hours No information available			able	
	or	ml/m ³ Animal species	s	
5.4	Saturate	Saturated vapour concentration at 20 °C (2.6.2.2.4.3¹) No information available		
5.5	Skin exposure (2.8 ¹) 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)

10

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 (6.8¹)?
 - 6.2.2 Intermediate Bulk Containers (6.5¹)?
 - 6.2.3 Portable tanks (6.7^1) ?

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
- 9.7 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

1.4	Chemic	cal name
	Tetran	nethylammonium hydroxide solution
1.5	Chemic	cal formula
	C4H12	N.HO
1.6	Other n	names/synonyms
	Tetran	nethylazanium hydroxide solution
1.4.1	UN nui	mber
	UN 183	35
1.4.2	CAS nu	umber
	75-59-2	
1.5	Propos	ed classification for the Recommendations
	1.5.1	Proper shipping name (3.1.2)
	Tetran	nethylammonium hydroxide solution
	1.5.2 8 pack	Class/division with subsidiary hazard(s) ing group II and III
	1.5.3	Proposed special provisions, if any
	1.5.4	Proposed packing instruction(s)
Section 2	. PHYS	ICAL PROPERTIES
2.1	Melting	g point or range63-70°C (solid)
2.2	Boiling point or rangeca. 102°C	

2.2	Boiling point or rangeca. 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
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? (2.4.21) 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? If yes, state: 4.1.1 Inhibitor/stabilizer used 4.1.2 Alternative method Time effective at 55 °C 4.1.3 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? (2.4.2.4¹) **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? (2.4.2.3.41) 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? $(2.4.3^1)$ **No** 4.5.1 If yes, give details 4.6 Is the substance liable to self-heating? (2.4.31) No 461 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

² See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods.

This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

		Is temperature control required? (2.5.3.4.1¹)		yes/no
	4.7.2	Proposed control temperature for	°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? (2.4.41) No			
	4.8.1	If yes, give details		
4.9	Does the substance have oxidizing properties (2.5.11) 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
	4.10.3other packaging materials (specify)			
4.11	Other relevant chemical properties			
Section 5. HARMFUL BIOLOGICAL EFFECTS				
5.1	LD ₅₀ , oral (2.6.2.1.1 ¹) oral LD50 of 50-300 mg/kg bw in rat			
5.2	LD_{50} , dermal (2.6.2.1.2 ¹) dermal LD50 of 28.7 mg/kg bw in rat			
5.3	LC ₅₀ , inhalation (2.6.2.1.3 ¹)mg/lExposure time hours No information available			
J.3	or			
5.4	Saturated vapour concentration at 20 °C (2.6.2.2.4.3¹) No information available			
5.5	Skin exposure (2.8 ¹) 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 (6.8¹)?
 - 6.2.2 Intermediate Bulk Containers (6.5¹)?
 - 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)

9.1

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

9.2 Minimum test pressure
9.3 Minimum shell thickness
9.4 Details of bottom openings, if any

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

- 9.5 Pressure relief arrangements
- 9.6 Degree of filling
- 9.8 Unsuitable construction materials