

SUB-COMMITTEE ON BULK LIQUIDS AND GASES 16th session Agenda item 3 BLG 16/3/7 25 November 2011 Original: ENGLISH

EVALUATION OF SAFETY AND POLLUTION HAZARDS OF CHEMICALS AND PREPARATION OF CONSEQUENTIAL AMENDMENTS

Review of the requirements for fire-fighting media to be used when transporting Hexamethylenediamine (molten)

Submitted by INTERTANKO

SUMMARY						
Executive summary:	This document comments on the report of the Working Group on the Evaluation of Safety and Pollution Hazards of Chemicals (ESPH) and proposes a review of the requirements for the carriage of fire-fighting equipment as stated in chapter 17 of the IBC Code when transporting Hexamethylenediamine (molten)					
Strategic direction:	5.2					
High-level action:	5.2.3					
Planned output:	5.2.3.10					
Action to be taken:	Paragraph 14					
Related documents:	ESPH 1/5/1; BLG 16/3; IBC Code and MEPC.1/Circ.512					

Background

1 This document is submitted in accordance with the Guidelines on the organization and method of work contained in MSC-MEPC.1/Circ.4.

2 The Working Group on the Evaluation of Safety and Pollution Hazards of Chemicals (ESPH), at its last session, was advised of the requirements for Hexamethylenediamine (molten) for fire protection equipment (column "I"), and noted that currently, the only fire-fighting media specified is "C" (Water Spray).

3 The working group, noting that the manufacturer has indicated that other fire-fighting media are also suitable, also noted that Hexamethylenediamine solution specifies fire-fighting media "A" (Alcohol-resistant foam).

4 Following discussion, the working group proposed that a submission should be made to BLG 16 with a completed BLG Data Reporting form in order to re-evaluate this product.



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Discussion

5 The IBC Code contains only two cargoes which under the carriage requirement for column "I" require the exclusive use of water-spray as the fire-fighting agent. These are Carbon Disulphide and Hexamethylenediamine (molten).

6 Carbon Disulphide has the use of water-spray also stated as a requirement in column o where the requirements of paragraph 15.3.21 are imposed. In comparison, it must be noted that for Hexamethylenediamine (molten), the requirement for exclusive use of a water spray is not reaffirmed anywhere else within the Code (other than in chapter 17 – column "I").

7 As a further point, it should be also noted that Propylene Oxide has a water spray requirement as per 15.8.29 in column "o", yet in chapter 17 column "I" it has both A & C (alcohol resistant foam and water spray), specified as the requirements for fire-fighting media.

A manufacturer of Hexamethylenediamine (HMD) has been asked to comment on both Solubility (as per IBC Code, paragraph 21.4.12.1) and the Water Reactivity Index (WRI) (as per MEPC.1/Circ.512, annex, page 27) for HMD grades of 90%, 98% and 100%. From feedback received from this manufacturer, for all three concentrations the Solubility can be considered to be > 10% (>100 000 mg/l) and the WRI=0.

9 It should be noted that information submitted in the original BLG data reporting form (MEPC/Circ.265) also states that dry chemical powder, foam and carbon dioxide are considered as suitable fire-fighting media and furthermore, the fire-fighting requirements specified for Hexamethylenediamine solution are both A & C (alcohol resistant foam and water spray).

10 It is recommended that, as per IBC Code, paragraph 21.4.12, the chapter 17 fire-fighting requirement for Hexamethylenediamine (molten) should be "A, C" or "A", instead of "C" as it is now. A BLG Data reporting form based on the original information submitted for this product is attached in the annex to this document.

11 This change would be consistent with the position reflected in the industry Material Safety Data Sheets (MSDS) on HMD 85%-100% which state that suitable extinguishing media under Fire Fighting Measures to be used are dry chemical, carbon-dioxide, water spray or alcohol resistant foam.

Proposal

12 It is proposed that in light of the ongoing review of the IBC Code and in order to achieve consistency with current industry practice, the requirements for fire-fighting media to be used for Hexamethylenediamine (molten) should be reviewed.

13 In reviewing these requirements, the information provided above should be considered and the requirements for Hexamethylenediamine (molten) in column "I" of chapter 17 should be changed to "A, C", instead of "C" as it is now.

Action requested of the Sub-Committee

14 The Sub-Committee is invited to consider the above proposal and take action as appropriate.

ANNEX

BLG Product Data Reporting Form

(Characteristics of Products proposed for Bulk Marine Transport)

1 <u>Product Identity</u>

Product Name:

The product name shall be used in the shipping document for any cargo offered for bulk shipments. Any additional name may be included in brackets after the product name.

1.1 Other Names and Identification Numbers

Main Trade Name: 1,6 – Hexanediamine; 1,6 – Diaminohexane

Main Chemical Name: Hexamethylenediamine (molten)

Chemical Formula: H₂N(CH₂)₆NH₂

C.A.S. Number:	Structure
EHS Number:	
BMR Number	
RTECS Number:	

1.2 Associated Synonyms

Synonym Name	Туре

1.3 <u>Composition</u>

Component Name	%	Туре

2 <u>Physical Properties</u>

Property	Units	Qual.	Lower Value	Upper Value	References/ Comments
Molecular weight					
Density @ 20°C	(kg/m ³)				RD 0.8358 at 55 °C
Flashpoint (cc)	(°C)		85		
Boiling Point	(°C)		202		
Melting Point/Pour Point	(°C)		41		
Water solubility @ 20°C	(mg/l)				Completely miscible
Viscosity @ 20°C	(mPa.s)		N/A		0.018pa/s at 55 °C
Vap. Press. @ 20ºC	(Pa)		N/A		0.16 at 45 °C; 0.28 at 55°C
Autoignition Temp.	(°C)		390	420	
Explosion Limits	(% v/v)		0.7	6.3	
Carriage Temperature	(°C)		55		
Unloading Temperature	(°C)				
MESG	(mm)				

3 <u>Relevant Chemical Properties</u>

Water Reactivity Index	(0-2)0
0 = No Reactivity	Details
1 = Reactive	
2 = Highly Reactive	

Does the product react with air to cause a potentially hazardous situation? (Y/N) N If so, provide details: ...Slowly neutralized by carbon dioxide..... Reference

Is an Inhibitor or Stabilizer needed to prevent a hazardous reaction? (Y/N)

If so, provide details Reference

Ν

Is refrigeration needed to prevent a hazardous reaction? (Y/N)

If so, provide details Reference

Ν

4 <u>Mammalian Toxicity</u>

4.1 <u>Acute Toxicity</u>

	Qual	Lower Value	Upper Value	Species	Reference/ Comments
Oral LD ₅₀ (mg/kg)		750 mg/kg		Rat	
Dermal LD ₅₀ (mg/kg)		1110 mg/Kg		Rabbit	
Inhalation LD ₅₀ (mg/l/4 h)		> 200 ppm		Rat	4hrs

4.2 Corrosivity and Irritation

	Qual.	Lower Value	Upper Value
Skin Corrosion time (hours)			

	Resultant Observation	Species	Reference/ Comments
Skin Irritation (4 h exposure)	Necrosis in Less than 3 min.	Rabbit	Less than 3 min.
Eye Irritation			

Not irritating, Slightly irritating, Mildly irritating, Moderately irritating, Severely irritating or Corrosive

4.3 <u>Sensitization</u>

Respiratory Sensitizer (in humans)	(Y/N)	Υ	
Skin Sensitization	(Y/N)	Υ	

4.4 Other Specific Long-Term Effects

Carcinogen	(Y/N)		
Mutagen	(Y/N)		
Toxic to Reproduction	(Y/N)	Υ	
Other Long-term	(Y/N)	Υ	

4.5 <u>Other Relevant Mammalian Toxicity</u>

TO HUMANS

ACUTE EFFECTS

Inhalation – can cause pulmonary irritation after inhalation of excessive amounts. 'The irritation caused by this compound to the nose and throat should act as a warning about excessive exposure. Massive exposure to HMO vapours would cause immediate pain in the nose, throat and lungs followed by mental confusion and, if not immediately removed from exposure, convulsions and death.

Ingestion – HMD is corrosive; ingestion will cause immediate damage to the tissues of the alimentary canal.

Skin – HMD contact can lead to burns similar to third degree thermal burns with complete destruction of the skin in the area of contact.

Eye – HMD is a serious eye irritant and can cause permanent sight impairment. The action of HMD in this case is not that of caustic corrosion alone but is probably associated with rapid extraction from the eye tissue.

IRRITATION AND SENSITIZATION

Sub-acute exposure of the skin to HMD can cause dermatitis. Upon re-exposure sensitivity may develop. There is very little data on the ability of HMD to cause sensitization of the lungs; however, it has been implicated in studies carried out by Engibaryan and Frangulyan.

REPEATED EXPOSURE EFFECTS

There is no data on chronic exposures in humans. However, considering the acute toxicity it is probable that repeated exposure to sub-acute levels could cause chronic symptoms. These symptoms would probably be associated with irritation of the eyes and upper respiratory tract, pulmonary distress, possible blood changes and liver and kidney damage.

HARMFUL BIOLOGICAL EFFECTS TO OTHER MAMMALS

In a sub-acute aerosol inhalation study rats were exposed to 12.8, 51. 0 and 215 mg/m³ for six hours/day, five days/week for seven weeks. The study was terminated at the seventh week due to a high mortality rate at 215 mg/m³.

Respiratory irritation was observed in both the high and mid dose groups. Microscopic changes in the lung were observed in the high exposure group only. The no effect level was 12.8 mg/m³.

Inhalation of an aerosol of up to 262 mg/day for six hours/day and five days/week for four weeks produced no adverse effects other than those resulting from the irritant action of this compound.

5 GESAMP Hazard Profile and Carriage Requirements

5.1 GESAMP Hazard Profile

Column	Property	Value
A1	Bioaccumulation	0
A2	Biodegradation	R
B1	Acute Aquatic Toxicity	2
B2	Chronic Aquatic Toxicity	NI
C1	Acute Oral Toxicity	1
C2	Acute Dermal Toxicity	1
C3	Acute Inhalation Toxicity	(3)
D1	Skin Irritation/Corrosivity	3A
D2	Eye Irritation/Corrosivity	3
D3	Specific Health Concerns	SR
E1	Tainting and Odour	
E2	Wildlife and Seabeds	D
E3	Beaches and Amenities	3

5.2 Proposed Carriage Requirements

Column in the IBC Code	Property	Value
с	Pollution Category	Υ
d	Safety/Pollution Properties	S/P
е	Ship Type	2
f	Tank Type	2G
g	Tank Vents	Cont
h	Tank Environmental Control	No
i'	Electrical Equipment – Class	
i''	Electrical Equipment – Group	
i'''	Electrical Equipment – Flashpoint>60°C	Yes
j	Gauging	С
k	Vapour Detection	Т
1	Fire Protection	A, C
n	Emergency Equipment	Yes
0	Special Requirements	15.12; 15.17; 15.18; 15.19.6; 16.2.9