Guidelines to determine flame arrestor type in inland waterway barges for shipment of certain substances and mixtures

A practical approach to deal with remark 44

Version : july 2019

Effective ADN 2019, remark 44 has been added to N.O.S. positions of (mention also the PSN) in Table C column 20:

- UN 1224 KETONES, LIQUID, N.O.S.
- UN 1267 PETROLEUM CRUDE OIL
- UN 1268 PETROLEUM DISTILLATES, N.O.S.
- UN 1863 FUEL, AVIATION, TURBINE ENGINE
- UN 1986 ALCOHOLS, FLAMMABLE, TOXIC, N.O.S.
- UN 1987, ALCOHOLS, N.O.S.
- UN 1989 ALDEHYDES, N.O.S.
- UN 1992 FLAMMABLE LIQUID, TOXIC, N.O.S.
- UN 1993 FLAMMABLE LIQUID, N.O.S.
- UN 2920 CORROSIVE LIQUID, FLAMMABLE, N.O.S. (2- PROPANOL AND DODECYLDIMETHYLAMMONIUM CHLORIDE, AQUEOUS SOLUTION)
- UN 2924 FLAMMABLE LIQUID, CORROSIVE, N.O.S.
- UN 2929 TOXIC LIQUID, FLAMMABLE, ORGANIC, N.O.S.
- UN 3271 ETHERS, N.O.S.
- UN 3272 ESTERS, N.O.S.
- UN 3286 FLAMMABLE LIQUID, TOXIC, CORROSIVE, N.O.S.
- UN 3295 HYDROCARBONS, LIQUID, N.O.S.
- UN 3494 PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC
- ID 9001 SUBSTANCES WITH A FLASHPOINT ABOVE 60 °C handed over for carriage or carried at a TEMPERATURE WITHIN A RANGE OF 15K BELOW THEIR FLASH-POINT OR SUBSTANCESWITH A FLASH-POINT > 60 °C, HEATED TO LESS THAN 15 K FROM THE FLASH-POINT
- ID 9002 SUBSTANCES HAVING A SELFIGNITION TEMPERATURE ≤ 200 °C, N.O.S.

Below an example from Table C and the remark.

1268	PETROLEUM DISTILLATES, N.O.S. or PETROLEUM PRODUCTS, N.O.S. WITH MORE THAN 10% BENZENE	3	F1	II	3+CMR+F+ (N1, N2, N3)	C	*	*	*	*	*		*	yes	T4 [3]	II B [4]	yes	*	1	27 *see 3.2.3.3
1268	PETROLEUM DISTILLATES, N.O.S. or PETROLEUM PRODUCTS, N.O.S. WITH MORE THAN 10% BENZENE	3	F1	II	3+CMR+F+ (N1, N2, N3)	C	*	*	*	*	*		*	yes	T4 [3]	II B [4] (II B3)	yes	*	1	27; 44 *see 3.2.3.3

44. A substance shall only be assigned to this entry where there is measurement data or verified information in accordance with IEC 60079-20-1 or equivalent that allows for an assignment to subgroup II B3 of explosion group II B.

What does this mean?

Remark 44 allows the use of a ship equipped with IIB3 flame arresters, provided that the substance to be carried can be assigned to explosion group IIB3, IIB2, IIB1 or IIA.

In the case that no measurement data or verified information in accordance with IEC 60079-20-1 is available, a ship equipped with IIB flame arresters would have to be used. These ships are hardly available. In fact, IIB flame arrestor are not common in the inland waterway tanker fleet.

Some background on Ex groups

ATEX (2014/34/EU of the European Parliament and of the council) distinguishes 3 explosion groups: IIA, IIB, and IIC. IIB is not further subdivided in IIB1, IIB2, IIB3 and IIB. Shore installations are laid out as one of these groups. A certain explosion group defines the type of (electrical/non-electrical) equipment.

Explosion groups on substances define the minimum ignition current or energy (MIC or MIE) needed to ignite an explosive mixture of gases or vapors. The explosion group assignment on ships is a reference to the type of equipment needed to prevent the propagation of a flame front. (see ADN 1.2.1 – Flame Arrester)

What is expected from the industry

For substances having remark 44 in column (20) of Table C, ADN, the industry is required to be able to prove that the substances loaded in IIB3 equipped ships are classified as IIB3 (or IIB2, IIB1 or IIA).

The issue

No explosion subgroups exist on shore, only explosion groups. Loading facilities/jetties are laid out as explosion group IIA, IIB or IIC, where IIC is the strictest and IIA the least strict.

On inland waterway tankers, the Ex classification of flame arrestors is determined based on their Maximum Experimental Safe Gap (MESG), according to ISO 16852:2016, see below table. Ex Group IIB has been divided in Explosion subgroups for flame arrestor. Note that IIB is also a subgroup of Ex Group IIB!

Ex Group IIB has a wide range of 0.5 – 0.9 mm MESG. Ex Subgroup IIB3 has a range of 0.65-0.75 mm MESG.

A ship equipped with IIB3 can load substances above 0.65mm MESG. (Ex Subgroups IIA, IIB1, IIB2, IIB3) but it cannot load substances with an MESG smaller than 0.65mm. It cannot load Ex Subgroup IIB (0.5-0.65mm MESG).

Ex Group	Ex Subgroup	Lower MESG (mm)	Upper MESG (mm)
IIC		0.0001	0.5
IIB		0.5001	0.9
	IIB	0.5001	0.65
	IIB3	0.6501	0.75
	IIB2	0.7501	0.85
	IIB1	0.8501	0.9
IIA		0.9001	1.2

IIB equipped jetties can safely handle products of IIA, IIB including the sub groups IIB, IIB1, IIB2 and IIB3, whereas IIB3 equipped ships (which form 97% of the inland waterway tankers fleet) can safely handle products as aforementioned, except for products of Ex Subgroup IIB.

Determination of Maximum Experimental Safe Gap (MESG): Different approaches

In line with IEC 60079-20-1, remark 44 allows different approaches:

> 44. A substance shall only be assigned to this entry where there is measurement data or verified information in accordance with IEC 60079-20-1 or equivalent that allows for an assignment to subgroup II B3 of explosion group II B.

1) Measurement data in accordance with IEC-60079-20-1

Depending on the individual situation, manufacturers can choose to determine the maximum experimental safe gap in accordance with IEC-60079-20 on individual substances. This option is for those manufacturers who produce a limited number of substances within strict production parameters.

Manufacturers who choose this option have a limited number of laboratories where they could test their substances to allow an assignment under a certain subgroup. In 2019 only PTB, Braunschweig, Germany, can perform this test.

2) Verified information in accordance with IEC-60079-20-1

For manufacturers who produce a wide range of substances, with a wide range of production parameters (mixtures), the calculation method by applying a form of Le Châtelier relationship in accordance with IEC 60079-20-1 is also possible:

$$MESG_{mix} = \frac{1}{\sum_i \left(\frac{X_i}{MESG_i} \right)}$$

Ch. 4.5 of IEC 60079-20-1: *When a gas or vapor is a member of a homologous series of compounds, the classification of the gas or vapor can provisionally be inferred from the data of the other members of the series with lower molecular weights*
Examples of homologous series of compounds are: Alkanes (including cycloalkanes), Alkenes (including dienes), Alkynes, Aromatics, Aldehydes, Oxiranes, Ketones, Alcohols, Ethers, Mercaptans, Amines, Amides, Halogenated hydrocarbons, H_2S, NH_3.

in general, within a homologous series of compounds, the lower MESG values belong to the compound with the lower molecular weight (methane being an exception within the alkane family)

A table of MESG values can be found in Attachment A. From this list it appears that most hydrocarbons can be classified as IIA, IIB1, IIB2 or IIB3, and only specific low molecular weight hydrocarbons or oxygen or fluor containing products are assigned to stricter gas groups.

The (non-exhaustive, based on IEC60079-20:2010 and Table C of ADN 2019) list of pure substances with a MESG ≤ 0.65mm is

Name	CAS #	MESG (mm)	Ex group	Ex sub group	Family
Ethene	74-85-1	0.65	IIB	IIB	Alkenes
Propyne	74-99-7	0.50	IIB	IIB	Alkynes
(Para)formaldehyde	30525-89-4	0.58	IIB	IIB	Aldehydes
Ethylene oxide	75-21-8	0.59	IIB	IIB	Oxiranes
Tetrafluoroethylene	116-14-3	0.6	IIB	IIB	Halogenated

Mixtures containing high percentages of these (low MESG) substances might have an MESG below 0.65mm, and therefore these cannot be loaded in a IIB3 equipped inland waterway tankers.

MESG calculations of hydrocarbons, alcohols, aldehydes, esters show that concentration of low MESG substances exceeding 10 percent[1] in those mixtures would still not lead to an assignment under Explosion Subgroup IIB (MESG between 0.5 and 0.65mm).

Substances and mixtures defined by the above-mentioned entries do not contain these low MESG compounds, according to the relevant SDSs: therefore, it can be concluded that these substances and mixtures can be conservatively allocated to a subgroup IIB3.

Conclusions

Substances or mixtures of hydrocarbons, alcohols, aldehydes, esters, having remark 44 in Column (20) of Table C ADN, and which do not contain significant concentration of products assigned to a IIB subgroup, can be assigned to explosion subgroup IIB3. Section 3 of the SDS can be used to verify the concentration of the low MESG component in those substances or mixtures.

APPENDIX A – Overview of MESG values for various products

(1) IEC 60079-20-1:2010 Material characteristics for gas and vapour classification - Test methods and data

(2) ADN 2019 table 3.2C

Alkanes	MESG (mm)	Ex group	Ex sub group	Source
Methane	1.12	IIA		(1)
Ethane	0.91	IIA		(1)
Propane	0.92	IIA		(1)
Butane	0.95	IIA		(1)
isobutane		IIA		(2)
isopentane	0.99	IIA		(1)

Alkenes	MESG (mm)	Ex group	Ex sub group	Source
Ethene	0.65	IIB	IIB	(1)
Propene	0.91	IIA		(1)
Isoprene			IIB2	(2)
Butene	0.94	IIA		(1)
1,3- Butadiene	0.79	IIB	IIB1	(1)
Methylcyclopentadiene-1,3	0.92	IIA		(1)
1,3-Cyclopentadiene	0.99	IIA		(1)
Dicyclopentadiene)	0.91			(1)
Furan	0.68	IIB	IIB3	(1)

Alkynes	MESG (mm)	Ex group	Ex sub group	Source
Ethyne	0.57	IIC		(1)

[1] This value is only theoretical: in practice high concentrations of light products will hardly be possible at real vapor-liquid equilibrium

Responsible Care

Propyne	0.50	IIB	IIB	(1)
Butyne	0.71	IIB	IIB3	(1)

Aromatics	MESG (mm)	Ex group	Ex sub group	Source
Benzene	0.99	IIA		(1)
Toluene	1.06	IIA		(1)
Ethylbenzene	0.90	IIB	IIB1	(1)
Xylene	1.09	IIA		(1)
Methylethylbenzene	0.90	IIB	IIB1	(1)
Napthalene	0.90	IIB	IIB1	(1)

Cycloalkanen	MESG (mm)	Ex group	Ex sub group	Source
Cyclopentane	1.01	IIA		(1)
Cyclohexane	0.94	IIA		(1)
Cyclohexene	0.94	IIA		(1)
Dicyclopentadiene	0.91	IIA		(1)
Penta-1,3-diene	0.97	IIA		(1)
Methylcyclopentadiene-1,3	0.92	IIA		(1)
1,3-Cyclopentadiene	0.99	IIA		(1)
Furan	0.68	IIB	IIB3	(1)

Aldehydes	MESG (mm)	Ex group	Ex sub group	Source
(para)formaldehyde	0.58	IIB	IIB	(1)
ethanal	0.98	IIA		(1)
proponal	0.72	IIB	IIB3	(1)
butanal	0.92	IIA		(1)

Alcohols	MESG (mm)	Ex group	Ex sub group	Source
Methanol	0.92	IIA		(1)
Ethanol	0.89	IIA		(1)
2-propanol	1.00	IIA		(1)
phenol		IIA		(2)

Ketones	MESG (mm)	Ex group	Ex sub group	Source
Acetone	1.01	IIA		(1)
Propione	0.90	IIA		(1)
Butanone	0.94	IIA		(1)
2-Hexanone	0.98	IIA		(1)

ethers	MESG (mm)	Ex group	Ex sub group	Source
Methyl ether	0.84	IIB	IIB2	(1)
ethyl ether	0.87	IIB	IIB1	(1)
diisopropyl ether	0.94	IIA		(1)

esters	MESG (mm)	Ex group	Ex sub group	Source

hydroxyacetic butylester	0.88	IIB	IIB1	(1)
hydroxyacetic pentylester	1.02	IIA		(1)

mercaptanes	MESG (mm)	Ex group	Ex sub group	Source
Ethyl Mercaptan	0.9	IIA		(1)
Methyl mercaptan)	1.15	IIA		(1)
Thiophene	0.91	IIA		

amines	MESG (mm)	Ex group	Ex sub group	Source
N,N,N',N'-Tetramethyl methanediamine	1.06	IIA		(1)
Methylamine	1.1	IIA		(1)
Ethylamine	1.2	IIA		(1)
2-Propaneamine	1.05	IIA		(1)
Trimethylamine	1.05	IIA		(1)
iso-Butylamine	1.15	IIA		(1)
1-Propaneamine	1.13	IIA		(1)
1,2-Ethanediamine	1.18	IIA		(1)
Diisopropylamine	1.02	IIA		(1)
3-Dimethylamino-propylamine	0.95	IIA		(1)
n-Butylamine	0.92	IIA		(1)
Diethylamine	1.15	IIA		(1)
Dipropylamine	0.95	IIA		(1)

Oxiranes	MESG (mm)	Ex group	Ex sub group	Source
Ethylene oxide	0.59	IIB	IIB	(1)
Propylene oxide	0.7	IIB	IIB3	(1)
Allyl 2,3- epoxypropylether)	0.7	IIB	IIB3	(1)
(Butoxymethyl)oxirane	0.78	IIB	IIB2	(1)
2-Méthyloxirane	0.7	IIB	IIB3	(1)

Halogenated	MESG (mm)	Ex group	Ex sub group	Source
Chloromethane	1.1	IIA		(1)
Chloroethene	0.99	IIA		(1)
2-Chloropropane	1.32	IIA		(1)
1,1-Dichloroethane	1.82	IIA		(1)
1,1-Difluoroethene	1.1	IIA		(1)
Chlorotrifluoroethene	1.5	IIA		(1)
Tetrafluoroethylene	0.6	IIB	IIB	(1)
1,1,2,2-Tetrafluoroethoxybenzene	1.22	IIA		(1)
Trifluoroethylene	1.4	IIA		(1)

Amides	MESG (mm)	Ex group	Ex sub group	Source
Dimethylformamide	1.08	IIA		(1)

Others	MESG (mm)	Ex group	Ex sub group	Source

Hydrogen sulphide	0.83	IIA	(1)
Ammonia	3.18	IIA	(1)
Acrylonitrile	0.87	IIA	(1)
Acetonitrile	1.5	IIA	(1)
Hydrogen cyanide	0.8	IIA	(1)

APPENDIX B - Description of calculations for “typical” worst case mixtures

Calculation of the Maximum Experimental Safe Gap (MESG) in accordance with IEC 60079-20-1 and determination of the Explosion (Sub) Group in accordance with ISO 16852

Example: Full Range Naphtha

Section 14 of the SDS:

UN 1268 PETROLEUM DISTILLATES, N.O.S. (Naphtha (Petroleum), light hydrocracked), 3, (N2, CMR, F), I, ENVIRONMENTALLY HAZARDOUS, NST/R 3212: Naphtha

This substance has 2 relevant entries in Table C:

1268	PETROLEUM DISTILLATES, N.O.S. or PETROLEUM PRODUCTS, N.O.S.	3	F1	I	3+(N1, N2, N3, CMR, F)	*	*	*	*	*	*		*	yes	T4[3)]	II B[4)]	yes	*	1	14; 27 *see 3.2.3.3
1268	PETROLEUM DISTILLATES, N.O.S. or PETROLEUM PRODUCTS, N.O.S.	3	F1	I	3+(N1, N2, N3, CMR, F)	*	*	*	*	*	*		*	yes	T4 [3)]	II B[4)] (II B3)	yes	*	1	14; 27; 44 *see 3.2.3.3

The objective:

To be able to make use of a IIB3 equipped barge, the substance Maximum Experimental Safe Gap (MESG) should fall within the bandwidth of one of the highlighted Explosion (sub) groups:

Ex Group	Ex Subgroup	Lower MESG	Upper MESG
IIC		0.0001	0.5
IIB		0.5001	0.9
	IIB	0.5001	0.65
	IIB3	0.6501	0.75
	IIB2	0.7501	0.85
	IIB1	0.8501	0.9
IIA		0.9001	1.2

Calculation of the Maximum Experimental Safe Gap in accordance with IEC 60079-20-1:

In alignment with remark 44, IEC 60079-20-1 provides the following equation:

$$MESG_{mix} = \frac{1}{\sum_i \left(\frac{X_i}{MESG_i} \right)}$$

Responsible Care

The values for the MESG of the constituents of a mixture can be derived from Annex I of IEC-60079-20-1, or these can be derived from ADN, table C column (16) by applying the most conservative value within the set bandwidth:

Example: if the mixture contains the below product, ADN Table C provides the following information:

1175	ETHYLBENZENE	3	F1	II	3+N3	N	2	2		10	97	0.87	3	yes	T2 [3]	IIA	yes	PP, EX, A	1	

In Table C, the substance is classified as Explosion group IIA. (MESG > 0.90).

For the calculation, we use the most conservative value of the explosion group (0.90).

Full Range Naphtha: Section 3.1 of the SDS:

Hazardous components

Chemical name	CAS-No. EC-No.	Concentration [%]
Naphtha (petroleum), light hydrocracked	64741-69-1 265-071-4	<= 100

Further information

Contains:

Chemical name	Identification number	Concentration [%]
Xylene, mixed isomers	1330-20-7, 215-535-7	>= 1 - <= 5
n-Hexane	110-54-3, 203-777-6	>= 5 - <= 20
cumene	98-82-8, 202-704-5	>= 0 - <= 1
toluene	108-88-3, 203-625-9	>= 1 - <= 5
cyclohexane	110-82-7, 203-806-2	>= 1 - <= 5
benzene	71-43-2, 200-753-7	>= 1 - <= 5
Ethylbenzene	100-41-4, 202-849-4	>= 1 - <= 2

The main constituent is Naphtha, which is IIA (MESG > 0.9 mm). To determine if the other constituents could drive the MESG to a level below 0.65mm (i.e. below IIB3) - and therefore unsuitable for a IIB3 barge -, the following calculation should be performed:

CAS	Name	EC Description (substances only)	%	MESG	Ex (sub) group
64741-69-1	Naphtha (petroleum), light hydrocracked	A complex combination of hydrocarbons from distillation of the products from a hydrocracking process. It consists predominantly of saturated hydrocarbons having carbon numbers predominantly in the range of C4 through C10, and	57%	0.9	IIA
1330-20-7	Xylene, mixed isomers		5%	1.09	IIA
110-54-3	n-Hexane		20%	0.88	IIB1
98-82-8	Cumene		1%	1.05	IIA
108-88-3	Toluene		5%	1.06	IIA
110-82-7	Cyclohexane		5%	0.94	IIA
71-43-2	Benzene		5%	0.99	IIA
100-41-4	Ethylbenzene		2%	0.9	IIA
Mixture	$\left(\frac{0.57}{0.9}+\frac{0.05}{1.09}+\frac{0.20}{0.88}+\frac{0.01}{1.05}+\frac{0.05}{1.06}+\frac{0.05}{0.94}+\frac{0.05}{0.99}+\frac{0.02}{0.9}\right)=\frac{1}{1.08909}=$			0.9182 mm	

Responsible Care

The MESG being 0.9182 mm means that the mixture can be conservatively classified as Explosion Group IIA and suitable for a IIB3 equipped barge.

In case 40% of naphtha is replaced (hypothetically!) by 40% propyne, the resulting MESG would be 069 mm, IIB3.

These Guidelines to determine flame arrestor type in inland waterway barges have been developed by the Royal VNCI in 2019.

Although these are established with utmost care, any errors or omissions cannot be guaranteed and therefor author(s), editor(s) and publisher do not accept any liability, nor for damages of any kind, which are the direct or indirect result of actions and / or decisions which were (partly) based on the information in this booklet. All rights reserved. They may not be used, stored or published for commercial purposes in any form or by any means, electronic, mechanical, by photocopying, recording or otherwise, without the prior written permission of the publisher: VNCI, PO Box 443, 2260 AK Leidschendam, The Netherlands.

Version : July 2019