

**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

Forty-seventh session

Geneva, 22 – 26 June 2015

Item 3 of the provisional agenda

Listing, classification and packing

**Introduction of a new entry for Phosphorothioic acid, O-
[(cyanophenylmethylene)azanyl]O,O-diethyl ester
("Phoxim") in n-Butanol**

Transmitted by the European Chemical Industry Council (CEFIC)

Introduction

1. The title compound is the active ingredient of a formulation used in veterinary medicine as an insecticide and acaricide for the treatment of farm animals. The mixture consists of the (E) and (Z) isomers with an assay of 82-91 % Z isomer in n-butanol.

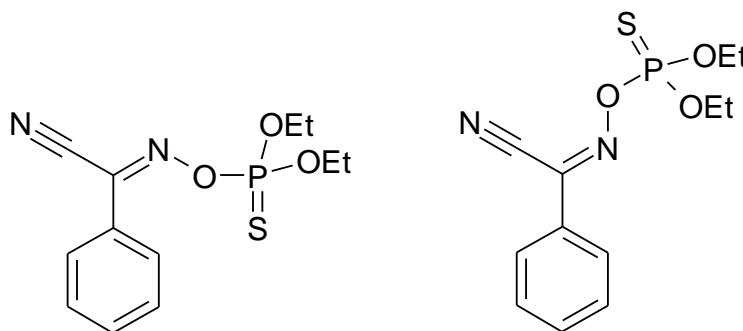


Figure 1: Chemical structure of Phosphorothioic acid, O-[(cyanophenyl methylene)azanyl] O,O-diethyl ester ("Phoxim"), (E) and (Z) isomers

2. By request from industry, the German Competent Authorities had issued a temporary approval for the transport of the mixture classified as UN 3227 SELF-REACTIVE LIQUID, TYPE E. This paper is meant to inform the Subcommittee about industry's intention to submit a formal proposal for the December session with the request for the creation of a corresponding new entry in the list of self-reactive substances of chapter 2.4.2.3.2.3.

3. Members of the Subcommittee are requested to review the data submitted in this paper and to forward any comments to the CEFIC delegation.

Test data

4. All tests were performed according to the methods specified in the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, fifth revised edition, with amendments 1 and 2.

5. The classification procedure led to the final result (Figure 20.1 of the UN Test Manual)

Exit E, accepted for transport in packages of not more than 400 kg/ 450 litres.

Details are specified in the test report in Annex I.

Proposal

6. In chapter 2.4.2.3.2.3, create an entry in the list of self-reactive substances as follows

SELF-REACTIVE SUBSTANCE	Concentration (%)	Packing method	Control temperature (°C)	Emergency temperature (°C)	UN generic entry	Remarks
Phosphorothioic acid, O-[(cyanophenyl methylene) azanyl] O,O-diethyl ester	82-91 (Z isomer)	OP 8			3227	(10)

7. Add a new remark (10) at the end of the same chapter as follows:

(10) This entry applies to the technical mixture in n-Butanol with the concentration limits of the (Z) isomer.

Justification

8. The fact that the product is carried in large quantities and is used worldwide justifies a new entry in the list of self-reactive substances. The test results are clear, and a formal temporary approval has been issued for all modes by the German authorities. The concentration limits apply to the product as registered for veterinary purposes.

Annex I

Test report

1.	Name of substance	Phosphorothioic acid, O-[(cyanophenyl methylene) azanyl] O,O-diethyl ester
2.	General data	
2.1	Composition	88.1 % active ingredient 2.1 % sum of impurities Solution in n-Butanol
2.2	Molecular formula:	C ₁₂ H ₁₅ N ₂ O ₄ PS
2.3	Available oxygen content	Not applicable
2.4	Activator content	Not applicable
2.5	Physical form	Liquid
2.6	Colour	Dark yellow
2.7	Apparent density	1130 kg/m ³
2.8	Particle size	Not applicable
3.	Detonation (test series A)	
	Box 1 of the flow chart	Does the substance propagate a detonation?
3.1	Method	BAM 50/60 steel tube test (test A.1), test in cavitated state (German method)
3.2	Sample conditions	Ambient temperature
3.3	Observations	190 mm of tube fragmented, unreacted substance remained in the tube



3.4	Result	No
3.5	Exit	1.3
4.	Deflagration (test series C)	
	Box 5 of the flow chart	Does the substance propagate a deflagration?
4.1	Method 1	Time/pressure test (test C.1)
4.2	Sample conditions	Ambient temperature
4.3	Observations	Time 310-330 ms
4.4	Result	Yes, slowly
4.5	Method 2	Deflagration test (test C.2)
4.6	Sample conditions	Temperature 40 °C
4.7	Observations	Deflagration rate 0.30 mm/s
4.8	Result	No
4.9	Overall result	No
4.10	Exit	5.3
5.	Heating under confinement (test series E)	
	Box 9 of the flow chart	What is the effect of heating it under defined confinement?
5.1	Method 1	Koenen test (test E.1)
5.2	Sample conditions	Mass 32.1 g
5.3	Observations	Limiting diameter 1.0 mm (time to reaction 28 s, duration of reaction 14 s)
5.4	Result	Low
5.5	Method 2	Dutch pressure vessel test (test E.2)
5.6	Sample conditions	10.0 g
5.7	Observations	Limiting diameter 2.0 mm (time to reaction 51 s) No rupture of the disc with an orifice of 3.5 mm but rupture of the disc with an orifice of 2.0 mm
5.8	Result	Low
5.9	Overall result	Low
5.10	Exit	9.3
6.	Box 11 of the flow chart	Is the self-reactive substance to be considered for transport in IBCs or tanks, or for exemption?
6.1	Result	No

6.2	Exit	11.2	Accepted for transport in packages of not more than 400kg/450 litres
7.			Thermal stability (test series H)
7.1	Method		Heat accumulation storage test (H.4)
7.2			Sample conditions 400 ml substances in Dewar vessel, heat loss 35-42 mW/kgK
7.3	Observations		Auto-accelerating decomposition at 75 °C, No reaction at 50°C and 60 °C
7.4	Result		No temperature control required
8.	Additional data (see 20.5.3)		
8.1	Method		BAM fallhammer test (test 3 (a) (ii))
8.2	Sample conditions		Ambient temperature
8.3	Observations		No explosion up to an impact energy of 40 J
8.4	Result		Not sensitive to impact
8.5	Method		BAM friction apparatus (test 3 (b) (i))
8.6	Sample conditions		Ambient temperature
8.7	Observations		No explosion up to a friction load of 360 N
8.8	Result		Not sensitive to friction
8.9	Method		DSC
8.10	Sample conditions		Closed glass crucible, heating rate 3 K/min)
8.11	Observations		Exothermic decomposition of about 1100 kJ/kg, onset of 90 °C.
9.	Proposed assignment		
9.1	Proper shipping name		SELF-REACTIVE LIQUID, TYPE E
9.2	UN number		3227
9.3	Division		4.1
9.4	Technical name		Phosphorothioic acid, O-[(cyanophenyl methylene) azanyl] O,O-diethyl ester
9.5	Concentration		82-91 % (Z isomer)
9.6	Diluent		n-Butanol
9.7	Subsidiary risks		None
9.8	Packing group		
9.9	Packing method		OP8
9.10	Control temperature		Not required
9.11	Emergency temperature		Not required

Annex II

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

Submitted by Bayer HealthCare AG, 51368 Leverkusen, Germany Date:
May 12th, 2015

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 Chemical name Phosphorothioic acid, O-[(cyanophenyl methylene) azanyl] O,O-diethyl ester, mixture of (E) and (Z) isomers dissolved in n-Butanol (concentration of Z isomer 82-91 %)
- 1.2 Chemical formula $(C_6H_5)-C(CN)=N-O-PS(OEt)_2$
- 1.3 Other names/synonyms Phoxim VL, Phoxim VL 80, Sebacil VL 80, Volaton;
- 1.4.1 UN number: 3227
- 1.4.2 CAS number 14816-18-3 (Phoxim), CAS 71-36-3 (butanol)
- 1.5 Proposed classification for the Recommendations
- 1.5.1 Proper shipping name (3.1.2¹) SELF-REACTIVE LIQUID, TYPE E
- 1.5.2 class/division 4.1 subsidiary risk(s)
packing group
- 1.5.3 proposed special provisions, if any 274
- 1.5.4 proposed packing instruction(s) P520, OP8

Section 2: Physical properties

- 2.1 Melting point or range -90 °C (n-butanol)
- 2.2 Boiling point or range 116 °C – 118 °C (n-butanol)
- 2.3 Relative density at:
- 2.3.1 15 °C not known
- 2.3.2 20 °C 1.13 g/cm³
- 2.3.3 50 °C not known
- 2.4 Vapour pressure at:
- 2.4.1 20 °C 0.35 kPa
- 2.4.2 50 °C not known
- 2.4.3 65 °C not known

¹ This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

- 2.5 Viscosity at 20 °C² not known
- 2.6 Solubility in water at 20 °C.....: not miscible
- 2.7 Physical state at 20°C (2.2.1.1¹) liquid²
- 2.8 Appearance at normal transport temperatures, including colour and odour:
yellow-brownish liquid, aromatic odour
.....
- 2.9 Other relevant physical properties: pH 3.9 at 10 g/l
.....
.....

Section 3: Flammability

- 3.1 Flammable vapour
- 3.1.1 Flash point (2.3.3¹) 38 °C (closed cup)
- 3.1.2 Is combustion sustained? (2.3.1.3¹) yes
- 3.2 Autoignition temperature not known
- 3.3 Flammability range (LEL/UEL) 1.4 / 11.3 % (n-butanol)
- 3.4 Is the substance a flammable solid? (2.4.2¹) no
- 3.4.1 If yes, give details not applicable
-
-
-

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 not applicable
- 4.1.2 Alternative method not applicable
- 4.1.3 Time effective at 55 °C not applicable
- 4.1.4 Conditions rendering it ineffective not applicable
- 4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.1¹) no
- 4.2.1 If yes, give details not applicable
-
-
-

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

¹ This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

- 4.3 Is the substance a desensitized explosive? (2.4.2.4¹) no
 4.3.1 If yes, give details not applicable
- 4.4 Is the substance a self-reactive substance? (2.4.1¹) yes
 If yes, state:
 4.4.1 exit box of flow chart: E
 What is the self-accelerating decomposition temperature (SADT) for a 50 kg package?
 60 °C < SADT < 75 °C
 Is the temperature control required? (2.4.2.3.4¹) no
 4.4.2 proposed control temperature for a 50 kg package not applicable
 4.4.3 proposed emergency temperature for a 50 kg package not applicable
- 4.5 Is the substance pyrophoric? (2.4.3¹) no
 4.5.1 If yes, give details not applicable
- 4.6 Is the substance liable to self-heating? (2.4.3¹) no
 4.6.1 If yes, give details not applicable
- 4.7 Is the substance an organic peroxide (2.5.1¹) no
 If yes state:
 4.7.1 exit box of flow chart not applicable
 What is the self accelerating decomposition temperature (SADT) for a 50 kg package? °C
 Is temperature control required? (2.5.3.4.1¹) no
 4.7.2 proposed control temperature for a 50 kg package not applicable
 4.7.3 proposed emergency temperature for a 50 kg package not applicable
- 4.8 Does the substance in contact with water emit flammable gases? (2.4.4¹) no
 4.8.1 If yes, give details not applicable
- 4.9 Does the substance have oxidizing properties (2.5.1¹) no
 4.9.1 If yes, give details not applicable

¹ This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

- 4.10 Corrosivity (2.8¹) to:
- 4.10.1 mild steel not known atC
- 4.10.2 aluminium not known at.....C
- 4.10.3 other packaging materials (specify)
not known..... atC
- 4.11 Other relevant chemical properties: see test report in Annex I

Section 5. Harmful biological effects

- 5.1 LD₅₀, oral (2.6.2.1.1¹) 300 – 2000 mg/kg Animal species..... rat (Phoxim (ISO))
- 5.2 LD₅₀, dermal (2.6.2.1.2¹) > 2000 mg/kg Animal species..... rat (Phoxim (ISO))
- 5.3 LC₅₀, inhalation (2.6.2.1.3¹)....> 4 mg/litre Exposure time 4 hours
..... Animal species..... rat (Phoxim (ISO))
- 5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3¹) not known
- 5.5 Skin exposure (2.8¹) results Exposure time hours/minutes
Animal species.....
- 5.6 Other data: Causes skin irritation (GHS H315)
.....
.....
- 5.7 Human experience not known
.....
.....

Section 6. Supplement information

- 6.1 Recommended emergency action
- 6.1.1 Fire (include suitable and unsuitable extinguishing agents)
Suitable: alcohol-resistant foam, dry chemical or carbon dioxide; unsuitable: water
- 6.1.2 Spillage. Keep away from sources of ignition. Cover spilled product with liquid-binding material (sand, silica gel, acid binder, universal binder, hybilat).
Take up mechanically and fill into labelled, closable containers.
- 6.2 Is it proposed to transport the substance in:
- 6.2.1 Bulk Containers (6.8¹) no
- 6.2.2 Intermediate Bulk Containers (6.5¹) no
- 6.2.3 Portable tanks (6.7¹)? no
- If yes, give details in Sections 7, 8 and/or 9.

¹ This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

¹ This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

Section 7: Bulk containers (only complete if yes in 6.2.1)

7.1 Proposed type(s) not applicable

Section 8: Intermediate bulk containers (IBCs) (only complete if yes in 6.2.2)

8.1 Proposed type(s) not applicable

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) not applicable.....

9.2 Minimum test pressure not applicable

9.3 Minimum shell thickness not applicable.....

9.4 Details of bottom openings, if any not applicable.....

9.5 Pressure relief arrangements not applicable.....

9.6 Degree of filling not applicable

9.7 Unsuitable construction materials not applicable.....
