Biocidal Products Committee (BPC)

Opinion on the application for approval of the active substance:

Methylene dithiocyanate

Product type: 12

ECHA/BPC/322/2022

Adopted

08 March 2022

Opinion of the Biocidal Products Committee

on the application for approval of the active substance Methylene dithiocyanate for product type 12

In accordance with Article 89(1) of Regulation (EU) No 528/2012 of the European Parliament and of the Council 22 May 2012 concerning the making available on the market and use of biocidal products (BPR), the Biocidal Products Committee (BPC) has adopted this opinion on the non-approval in product type 12 of the following active substance:

Common name:	Methylene dithiocyanate (MBT)
Chemical name:	Thiocyanic acid, methylene ester
EC No.:	228-652-3
CAS No.:	6317-18-6

Existing active substance

This document presents the opinion adopted by the BPC, having regard to the conclusions of the evaluating Competent Authority. The assessment report, as a supporting document to the opinion, contains the detailed grounds for the opinion.

Process for the adoption of the BPC opinion

Following the submission of an application by EUMTC Task Force/ SOLVAY SOLUTIONS UK LIMITED and AQUAPHARM CHEMICALS PVT. LIMITED on 3 November 2008, the evaluating Competent Authority France submitted an assessment report and the conclusions of its evaluation to the Commission on 7 August 2013. In order to review the assessment report and the conclusions of the evaluating Competent Authority, the Agency organised consultations via BPC (BPC-42) and its Working Groups (WG-IV-2021). Revisions agreed upon were presented and the assessment report and the conclusions were amended accordingly.

Adoption of the BPC opinion

Rapporteur: France

The BPC opinion on the application for approval of the active substance Methylene dithiocyanate in product type 12 was adopted on 8 March 2022.

The BPC opinion was adopted by consensus.

The opinion is published on the ECHA webpage at: http://echa.europa.eu/regulations/biocidal-products-regulation/approval-of-active-substances/bpc-opinions-on-active-substance-approval.

Detailed BPC opinion and background

1. Overall conclusion

The overall conclusion of the BPC is that the Methylene dithiocyanate in product type 12 may not be approved. The detailed grounds for the overall conclusion are described in the assessment report.

2. BPC Opinion

2.1. BPC Conclusions of the evaluation

a) Presentation of the active substance including the classification and labelling of the active substance

This evaluation covers the use of Methylene dithiocyanate in product type 12.

The active substance, Methylene dithiocyanate (CAS nº. 6317-18-6) as manufactured has a minimum purity of 94 % w/w.

The evaluation of the data submitted by the applicant for the five batch analysis reveals the following issues or data gaps according to the requirements of Annex II of the BPR:

- the mass balances of several batches are lower than 98% which is not in accordance with the requirements of the relevant guidance under the BPR[1];
- the specifications of several impurities cannot be set as there is a difference of content between the 5-batch analysis provided in 2016 and the additional data submitted by the applicant in 2019 (data gap relating to point 2.11 of the Annex II of the BPR);
- no validation data was provided for the determination of analytical methods for several impurities (data gap relating to point 5.1 of the Annex II of the BPR);
- the identity of one impurity cannot be determined due to a lack of data (data gap relating to point 2.10 of the Annex II of the BPR).

As the 5-batch analysis is not acceptable, it was not possible to confirm that the (eco)toxicological studies cover the specifications. Moreover, the assessment of the relevance of impurities was performed, but considering the lack of (eco)toxicological data for some of the impurities, it was not possible to conclude on the relevance. Therefore, based on the available data, it is not possible to confirm the minimum purity of the active substance (data gap relating to point 2.9 of the Annex II of the BPR) and to set a reference specification for Methylene dithiocyanate.

The physico-chemical properties of Methylene dithiocyanate and the reference biocidal product have been evaluated and are deemed acceptable for the appropriate use, storage and transportation of the active substance and biocidal product.

Analytical methods for analysis of Methylene dithiocyanate and impurities in the active substance as manufactured, have been provided but are not fully validated for some impurities. Analytical methods for the analysis of residues of Methylene dithiocyanate in soil, air, drinking and fresh water have been provided but are not fully validated. However, as air compartment is not relevant for environmental and toxicological risk assessment, no further data is required. Moreover, validated analytical methods for the determination of hydrolysis

[1] Guidance on the Biocidal Products Regulation Volume I: Identity of the active substance/physico-chemical properties/analytical methodology – Information requirements, Evaluation and Assessment. Parts A+B+C Version 2.0 May 2018.

residues of Methylene dithiocyanante (thiocyanate and formic acid) in water and validated analytical methods for the determination of thiocyanate and cyanide in animal and human body fluids and tissues are missing.

The current classification of Methylene dithiocyanate (ATP 25, Directive 98/98/EC) according to Regulation (EC) No 1272/2008 (CLP) is:

Current Classification according to the CLP Regulation	
Hazard Class and Category Codes	Acute Tox. 2 (inhalation)* Acute Tox. 3 (oral)* Skin Corr. 1B Skin Sens. 1 Aquatic Acute 1
Labelling	
Pictogram codes	Dgr GHS05 GHS06 GHS09
Signal Word	Danger
Hazard Statement Codes	H330 Fatal if inhaled H301 Toxic if swallowed H314 Causes severe skin burns and eye damage H317 May cause an allergic skin reaction H400 Very toxic to aquatic life
Specific Concentration limits, M-Factors	-

In light of the available studies, it is proposed to revise the classification of Methylene dithiocyanate as follows:

Proposed Classification according to the CLP Regulation	
Hazard Class and Category Codes	Acute Tox. 1 (inhalation) Acute Tox. 2 (oral) Skin Corr. 1B Eye Dam. 1 Skin Sens. 1A STOT RE 1 Aquatic acute 1 Aquatic chronic 1
Labelling	
Pictogram codes	Dgr GHS05 GHS06 GHS08 GHS09
Signal Word	Danger
Hazard Statement Codes	H330 Fatal if inhaled H300 Fatal if swallowed H314 Causes severe skin burns and eye damage H317 May cause an allergic skin reaction. H372 Causes damage of organs through prolonged or repeated exposure H400 Very toxic to aquatic organisms (M-factor = 100) H410 Very toxic to aquatic life with long lasting effects (M-factor = 10)
Specific Concentration limits, M-Factors	M = 100 (acute) M = 10 (chronic)

b) Intended use, target species and effectiveness

The Methylene dithiocyanate based products are intended to be used by professionals via intermittent or shock dosing in papermaking processes (PT 12) to control microbial proliferation of fungi including yeast, bacteria and algae.

Methylene dithiocyanate is a toxicant for microbial cells. In normal respiration, trivalent iron accepts electrons from primary cytochrome dehydrogenase but in the presence of Methylene dithiocyanate, the thiocyanate part of the molecule blocks the transfer of electrons by reacting with ferric iron to form the weak salt $Fe(CNS)_3$, or in excess, the red complex $Fe(CNS)_6$. Ferric iron is thus deactivated causing the immediate death of the cell.

The data on Methylene dithiocyanate demonstrated basic innate efficacy against bacteria and fungi including yeasts.

The occurrence of resistance is unlikely because of its mode of action which involves cell death by inactivation of ferric ion cytochromes micro-organisms and no resistance literature data has been reported.

c) Overall conclusion of the evaluation including need for risk management measures

Human health

The active substance Methylene dithiocyanate is fatal by inhalation (H330) and fatal if swallowed (H300). Methylene dithiocyanate is corrosive to skin (H314), damaging to the eye (H318), and a skin sensitizer (H317). In addition, hazard of serious damage to health (mortality) by prolonged exposure (H372) is expected if Methylene dithiocyanate is swallowed.

The table below summarises the exposure scenarios assessed.

Summary table: human health scenarios			
Scenario	Primary or secondary exposure[2] and description of scenario	Exposed group	Conclusion
Mixing and Loading	Primary exposure during the loading of the product in process water systems PPE: protective coverall, protective gloves and face mask	Professional (water treatment service worker)	Acceptable with PPE and RMM
Post-application	Primary exposure to the product during the cleaning of the dispensing pumps PPE: protective coverall, protective gloves and face mask	Professional (water treatment service worker)	Acceptable with PPE and RMM (rinsing step)
Post-application	Primary exposure to the product during the maintenance of the equipment	Professional (papermill worker)	Acceptable without PPE

[2] See document: Terminology primary and secondary exposure (available from https://webgate.ec.europa.eu/s-circabc/d/a/workspace/SpacesStore/80f71044-fce2-43b3-a73c-e156effc9fcb/Terminology%20primary%20and%20secondary%20exposure.pdf).

Summary table: human health scenarios			
Post-application	Primary exposure to the product during the process water sampling	Professional (water treatment service worker)	Acceptable without PPE
Post-application	Primary exposure to the product during waste disposal	Professional (water treatment service worker)	Acceptable without PPE
Post-application	Secondary exposure to the humidified air containing the biocidal product and when paper is manipulated	Professional (papermill worker)	Acceptable without PPE
Indirect exposure via food – food and feed packaging	Secondary exposure to residues in food - Migration into foodstuffs/feedstuffs from paper packaging	General public	Acceptable
Indirect/ secondary exposure - ingestion of treated paper	Secondary exposure through ingestion of paper	General public	Acceptable

Acceptable risks were identified for professionals of the paper industry (primary exposure) and for secondary exposure of professionals and the general public.

The following provisions should be taken into consideration to limit the risk for human health:

- the loading of the product should be automated, otherwise performed with adequate personal protective equipment;
- the dispensing pumps should be rinsed with water before cleaning;
- the containers of the products should be designed to prevent spillages during pouring;
- protective coveralls, gloves and face-mask should be worn during the mixing, loading and cleaning phase.

Migration into foodstuffs from paper packaging that may contain Methylene dithiocyanate residues has been considered. No unacceptable risk is associated with indirect exposure to Methylene dithiocyanate *via* food from food and feed paper packaging.

Environment

Methylene dithiocyanate has been shown to be not readily and not inherently biodegradable and is stable to hydrolysis in the acidic pH-range. At pH 7, Methylene dithiocyanate showed hydrolytic degradation with a half-life of 21.2 days. Methylene dithiocyanate is not a persistent substance based on the results of degradation studies in water/sediment systems (DT_{50} = 2.1 days in the whole system at 12°C). Several major metabolites were formed in the environmental compartments. According to the BPR Vol IV Part B+C Guidance, a risk assessment for the relevant metabolites is required. However, as the risks for the parent substance Methylene dithiocyanate were found unacceptable for the environmental compartments without taking into account these metabolites and the final conclusion will not change (if these metabolites are assessed), for this specific case no assessment of the relevant metabolites is needed.

The active substance does not indicate a potential for bioaccumulation in the aquatic compartment and the B criterion is not fulfilled. Based on aquatic studies with fish, daphnia and algae (short-term and one long-term) it can be concluded that the substance is classified as very toxic to aquatic life and can cause long lasting effects.

The tables below summarise the exposure scenarios assessed. Please note that the exposure assessment was done only for the active substance and not for the relevant metabolites as a non-approval is proposed based on the risk assessment of the parent substance.

As indicated by the Emission Scenario Document (ESD 2003 for PT 12, slimicides), in most European countries different types of wastewater treatment are applied prior to discharge, either on-site or at a sewage treatment plant (STP). To take into account the variety of situations, the ESD distinguishes two scenarios for PT12 products:

- a realistic worst case where:
    - the papermill is not connected to a pulp mill;
    - water from the papermill is subjected to settling and mechanical/chemical treatment before being discharged directly to surface or marine waters (without treatment by an STP) where the predicted environmental concentration of the active substance in surface water is estimated assuming dilutions factors of 10, 200 and 1000 in the receiving aquatic compartment;
- a typical case where:
    - the papermill is connected to a pulp mill which induces an additional dilution factor of 0.5 to be introduced into the model due to the effluent water from the pulp mill;
    - the wastewater from the papermill after settling is discharged to an industrial STP and afterwards into surface or marine waters. The emission to an STP is estimated taking into account the effluent discharge rate of a paper mill (5000 $m^3.d^{-1}$) and a dilution factor of 10 in the receiving aquatic compartment. (according to ENV TAB (Technical Agreements on Biocides - Environment) entry, dilution factors of 200 and 1000 were applied in addition in the exposure assessment).

The typical case scenario represents a best case in comparison to the realistic worst-case scenario due to the connection to a pulp mill and treatment of the wastewater at an STP.

Summary table: environment scenarios (standard ESD approach)		
Scenario	Description of scenario including environmental compartments	Conclusion
PT12: Paper mill Slimicide – Realistic worst-case	Paper mill with no connection to the pulp mill. Wastewater is discharged to the aquatic compartment without treatment in an STP.	Not acceptable for all exposed compartments
PT12: Paper mill Slimicide – Typical case	Paper mill with connection to untreated pulp mill; Wastewater is discharged to STP and afterwards into aquatic compartment and sludge applied to terrestrial compartment.	Not acceptable for all exposed compartments

Refinements of the above standard PT12 ESD approaches have been discussed and agreed at ENV WG-III-2020 (Working Group – Environment) leading to a “new approach” including

more realistic parameters such as application of an industrial treatment plant for both the realistic worst case and the typical case scenario and applying dilution factors of 10, 200 and 1000 to the receiving aquatic compartment. In the new approach, the calculation equations are adapted to comply with the Best Available Techniques for STP (IPPC Directive). Currently, however, there is no formal agreement by the ENV WG and AHEE (Ad hoc Working Group – Environmental Exposure) on these revised PT 12 scenarios. Therefore, the new exposure approach is provided for information only to demonstrate that a safe use was not possible to identify even with this more realistic approach.

Summary table: environment scenarios (new approach discussed at ENV WG-III-2020)		
Scenario	Description of scenario including environmental compartments	Conclusion
PT12: Paper mill Slimicide – Realistic worst-case	Paper mill with no connection to the pulp mill. Wastewater is discharged to an on-site industrial STP and afterwards into the aquatic compartment and sludge applied to terrestrial compartment.	Not acceptable for all exposed compartments
PT12: Paper mill Slimicide – Typical case	Paper mill with connection to untreated pulp mill. Wastewater is discharged to an on-site industrial STP and afterwards into the aquatic compartment and sludge applied to terrestrial compartment.	Not acceptable for all exposed compartments

No safe use can be identified for the sewage treatment plant (STP), groundwater and the aquatic and terrestrial compartments for the slimicide application of Methylene dithiocyanate in both scenarios (realistic worst case and typical case) and with both the standard ESD approach and the new approach (previously discussed in ENV WG III 2020 and accepted for Methylene dithiocyanate in ENV WG IV 2021), even with a refined exposure assessment at the minimal effective dose (2 g/m^3). No risk mitigation measure is considered feasible to reduce the unacceptable risks for the use of Methylene dithiocyanate in papermills, even for a ‘best-case approach’ assuming a dilution through the untreated pulp mill (typical case scenario).

Overall conclusion

With respect to human health acceptable risks are identified for professionals of the paper industry (primary exposure) and for secondary exposure of professionals and the general public. For professionals PPE and RMMs are required for some scenarios. No unacceptable risks are identified for indirect exposure. However, for the environment unacceptable risks are identified for all the environmental compartments. These risks cannot be mitigated by introducing risk mitigation measures.

2.2. Exclusion, substitution and POP criteria

2.2.1. Exclusion and substitution criteria

The table below summarises the relevant information with respect to the assessment of exclusion and substitution criteria:

Property		Conclusions	
CMR properties	Carcinogenicity (C)	No classification required	Methylene dithiocyanate does not fulfil criterion (a), (b) and (c) of Article 5(1)
	Mutagenicity (M)	No classification required	
	Toxic for reproduction (R)	No classification required	
PBT and vPvB properties	Persistent (P) or very Persistent (vP)	Not P or vP Metabolites not P or vP	Methylene dithiocyanate does not fulfil criterion (e) of Article 5(1) and does not fulfil criterion (d) of Article 10(1)
	Bioaccumulative (B) or very Bioaccumulative (vB)	Not B or vB	
	Toxic (T)	T	
Endocrine disrupting properties	Section A of Regulation (EU) 2017/2100: ED properties with respect to humans	Based on the available data, no conclusion could be drawn on endocrine disrupting properties of Methylene dithiocyanate. However, for reports submitted before 1 September 2013 (which is the case for MBT), it is mentioned in the note CA-March18-Doc.7.3a-final[5] that the evaluating Competent Authority has to conclude based on the already available data and/or the data provided by the applicant and, in case the data is insufficient to reach a conclusion, the BPC may conclude in its opinion that no conclusion could be drawn.	
	Section B of Regulation (EU) 2017/2100: ED properties with respect to non-target organisms		
	Article 57(f) and 59(1) of REACH		
	Intended mode of action that consists of controlling target organisms via their endocrine system(s)		
Respiratory sensitisation properties	No classification required		
Concerns linked to critical effects other than those related to endocrine disrupting properties	Methylene dithiocyanate does not fulfil criterion (e) of Article 10(1)		
Proportion of non-active isomers or impurities	Methylene dithiocyanate does not fulfil criterion (f) of Article 10(1)		

Consequently, the following is concluded:

Methylene dithiocyanate does not meet the exclusion criteria laid down in Article 5 of Regulation (EU) No 528/2012.

Methylene dithiocyanate does not meet the conditions laid down in Article 10 of Regulation (EU) No 528/2012 and is therefore not considered as a candidate for substitution.

The exclusion and substitution criteria were assessed in line with the "Note on the principles for taking decisions on the approval of active substances under the BPR"[3], "Further guidance on the application of the substitution criteria set out under article 10(1) of the BPR"[4] and "Implementation of scientific criteria to determine the endocrine –disrupting properties of active substances currently under assessment[5]" agreed at the 54th, 58th and 77th meeting respectively, of the representatives of Member States Competent Authorities for the implementation of Regulation 528/2012 concerning the making available on the market and use of biocidal products. This implies that the assessment of the exclusion criteria is based on Article 5(1) and the assessment of substitution criteria is based on Article 10(1)(a, b, d, e and f).

For the endocrine-disrupting properties as defined in Regulation (EU) No 2017/2100, no conclusion can be drawn on the available data. For reports submitted before 1 September 2013, it is mentioned in the CA meeting note mentioned above that the evaluating Competent Authority has to conclude based on the already available data and/or the data provided by the applicant and, in case the data is insufficient to reach a conclusion, the BPC may conclude in its opinion that no conclusion could be drawn. It is noted that the evaluation of Methylene dithiocyanate for PT 12 was submitted before 1 September 2013. Furthermore, since a non-approval is proposed, no ED conclusion is required.

2.2.2. POP criteria

Methylene dithiocyanate does not fulfil criteria for being a persistant organic pollutant (POP). Indeed, P and B criteria are not met. Moreover, the half-life in air is <2 days, which supports that Methylene dithiocyanate has no potential for long-range transboundary atmospheric transport.

2.3. BPC opinion on the application for approval of the active substance Methylene dithiocyanate in product type 12

In view of the evaluation, it is concluded that biocidal products containing Methylene dithiocyanate used as a preservative in paper processing may not be expected to meet the criteria laid down in point (b)(iii) of Article 19(1) of Regulation (EU) 528/2012. Consequently, it is proposed that Methylene dithiocyanate shall not be approved and included in the Union list of approved active substances.

The evaluation of the data submitted for the 5-batch analysis reveals a number of issues and data gaps (points 2.9, 2.10, 2.11 and 5.1 of the Annex II of the BPR) which leads to the impossibility to confirm the minimum purity of the active substance and to set a reference specification for Methylene dithiocianate. Moreover, it was not possible to

[3] See document: Note on the principles for taking decisions on the approval of active substances under the BPR (available from https://circabc.europa.eu/d/a/workspace/SpacesStore/c41b4ad4-356c-4852-9512-62e72cc919df/CA-March14-Doc.4.1%20-%20Final%20-%20Principles%20for%20substance%20approval.doc).

[4] See document: Further guidance on the application of the substitution criteria set out under article 10(1) of the BPR (available from https://circabc.europa.eu/d/a/workspace/SpacesStore/dbac71e3-cd70-4ed7-bd40-fc1cb92cfe1c/CA-Nov14-Doc.4.4%20-%20Final%20-%20Further%20guidance%20on%20Art10(1).doc).

[5] See document: Implementation of scientific criteria to determine the endocrine –disrupting properties of active substances currently under assessment (available from https://circabc.europa.eu/sd/a/48320db7-fc33-4a91-beec-3d93044190cc/CA-March18-Doc.7.3a-final-%20EDs-%20active%20substances%20under%20assessment.docx).

confirm that the (eco)toxicological studies cover the specifications and to conclude on the relevance of the impurities due to the lack of (eco)toxicological data.

Additionally, no safe use can be identified for all the environmental compartments for the slimicide application of Methylene dithiocyanate, even with a refined exposure assessment at the minimal effective dose (2 g/m^3). No risk mitigation measure is considered feasible to reduce the unacceptable risks for the use of Methylene dithiocyanate in papermills, even for a ‘best-case approach’ assuming a dilution through the untreated pulp mill (typical case scenario).

Consequently, it is proposed that Methylene dithriocyanate shall not be approved under Regulation (EU) 528/2012 as an active substance in paper processing (PT 12).

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