Molybdenum Consortium

An initiative of the International Molybdenum Association

EBRC

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Assessment of 'Consumer Exposure' under REACH for MoCon Substances

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1 Background

As part of the REACH registration for substance produced or imported in quantities > 10 tpy, the Chemical Safety Report (CSR) needs to be generated, which documents the results of the hazard assessment. If as a result of the hazard assessment, a substance needs to be considered a hazardous substance (in accordance with directive 67/548/EEC or the replacing regulation 1272/2008/EC), the CSR also needs to include the documentation of the exposure assessment. Ultimately, safe production and use of hazardous chemicals needs to be documented in the form of exposure scenarios.

An estimation of exposure levels shall be performed for all human populations (workers, consumers and humans liable to exposure indirectly via the environment) and environmental spheres for which exposure to the substance is known or reasonably foreseeable.

2 Aim

The aim of this document is to assess whether exposure of consumers to the hazardous substances in the portfolio of the Molybdenum Consortium (MoCon) is known or reasonably foreseeable. Where exposure of consumers is known or reasonably foreseeable, an attempt will be made to quantify these exposures.

3 Which substances within the portfolio of MoCon need to be considered?

The Molybdenum consortium's portfolio contains the following 11 substances for registration under REACH:

EC Substance Name	Synonyms	Formula	EC	CAS
Molybdenum Sulfide (MoS2), roasted	**Roasted Molybdenite Concentrate, tech oxide, moly oxide technical grade, molybdic oxide**	**MoO_3 is the formula of the main component. Complex compound sintered. Composition is 80-90% ($MoO_3/Mo_4O_{11}/MoO_2$)**	**289-178-0**	**86089-09-0**
Molybdenum Trioxide	**Molybdenum Trioxide (pure)**	**MoO_3**	**215-204-7**	**1313-27-5**
Molybdenum	Molybdenum Metal	Mo	231-107-2	7439-98-7
Disodium Molybdate	Sodium Molybdate, SoMo	Na_2MoO_4 $Na_2MoO_4 \cdot 2H_2O$	231-551-7 & 231-551-7	7631-95-0 & 10102-40-6
Diammonium Dimolybdate	Ammonium Dimolybdate, ADM	$(NH_4)_2Mo_2O_7$	248-517-2	27546-07-2
Hexaammonium Heptamolybdate	Ammonium Heptamolybdate	$(NH_4)_6Mo_7O_{24} \cdot X\ H_2O$ $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$	234-722-4 & 234-320-9	12027-67-7 & 12054-85-2
Tetraammonium Hexamolybdate	Ammonium Octamolybdate	$(NH_4)_4Mo_8O_{26} \cdot 5\ H_2O$	235-650-6	12411-64-2
Slags, Ferromolybdenum	Ferromolybdenum Slags, FeMo Slags		282-217-2	84144-95-6
Molybdenum Dioxide	Mo Dioxide	MoO_2	242-637-9	18868-43-4
Calcium Molybdate	CaMo	$CaMoO_4$	232-192-9	7789-82-4
Diiron Trimolybdenum Dodecaoxide	Iron Molybdate	$Fe_2Mo_3O_{12}$	237-389-3	13769-81-8

Of these 11 substances, only molybdenum trioxide (MoO_3) and roasted molybdenite concentrate ("RMC") are each considered a hazardous substance. There is an existing, EU harmonised classification for MoO_3. This classification includes the classification (acc. to EU CLP regulation) of MoO_3 as a "Carcinogen Category 2 - Suspected of causing cancer **via inhalation**". After extensive assessment and consideration of the differences and similarities between MoO_3 and RMC, the Molybdenum Consortium has concluded it is appropriate to read-across this classification from MoO_3 to RMC, i.e. applying this classification also to RMC, which is a technical form of mixed molybdenum oxides.

For all other compounds in the portfolio, the hazard assessment has concluded, that these do not require classification as hazardous substances.

4 Is consumer exposure to MoO_3 or RMC known or reasonably foreseeable?

4.1 Roasted Molybdenite Concentrate (RMC)

4.1.1 What is RMC and how is it produced?

RMC (EC No. 289-178-0, CAS No. 86089-09-0, CAS Name: “Molybdenum sulfide (MoS_2), roasted”). RMC is produced as follows: The chemical form of molybdenum in these ores is molybdenum disulfide (MoS_2, also designated “molybdenite”). After mining the ores are purified by technical means (e.g. flotation), where a chemical reaction of the Mo component is not involved. The resulting product is the enriched ore, namely “molybdenite concentrate” (chemically: MoS_2). The “molybdenite concentrate” is then roasted at temperatures > 400°C, typically in multiple hearth furnaces. During this process, the majority of molybdenum is oxidised from MoS_2 to Mo oxides and sulphur is turned into sulphur dioxide. Due to the nature of the process and material, the reaction to MoO_3 is not complete. The resulting product, now called roasted molybdenite concentrate (RMC), is composed primarily of a mixture of molybdenum oxides.

4.1.2 How is RMC used?

According to information from the International Molybdenum Association (IMOA), roasted molybdenite concentrate is solely used in industrial processes, in which it is converted into other chemicals/products.

The four major use sectors for RMC are:

- Production of iron and steel
- Production of Ferromolybdenum (an alloy consisting of iron and molybdenum, which is further used in the industrial production of steels and alloys)
- Production of other molybdenum containing alloys
- Production of molybdenum chemicals, such as the pure oxide, or sodium- and ammonium molybdates

During all these (purely) industrial uses, RMC in chemically converted into other substances, which are then further processed.

4.1.3 Are consumers (people of the general public) exposed to RMC?

In all uses identified for RMC, this substance is only used in industrial processes. In the steel- and alloy industries, RMC is used as a source for elemental molybdenum, which is then included in the steel/alloy matrix. During the production of molybdenum chemicals, RMC is chemically converted to another substance. **In consequence, there is no known or foreseeable exposure of consumers to RMC.**

4.2 Molybdenum trioxide (MoO_3)

4.2.1 What is MoO_3 and how is it produced?

Molybdenum trioxide (MoO_3, EC No. 215-204-7, CAS No. 1313-27-5), is a pure chemical substance. The typical production process uses ammonium dimolybdate ($(NH_4)_2Mo_2O_7$) as the educt. Ammonium molybdate is calcined at approx. 500°C. During this process, ammonia is liberated and pure molybdenum trioxide is obtained.

4.2.2 How is MoO_3 used?

As no list of identified consumer products for MoO_3 is available, for the time being the list of EU uses for molybdenum compounds including MoO_3, published on the molybdenum consortium website (http://www.molybdenumconsortium.org/assets/files/Mo_Uses_for_MoCon_website_public_page(1).pdf, latest update 05-Jan-2010) was used as a starting point for the consumer exposure assessment.

Besides a number of purely industrial uses, in which MoO_3 is chemically transformed, the following uses of molybdenum trioxide as/in/for the production of... were initially identified as possibly being associated with exposure of consumers:

water treatment chemicals; ceramic additives/enamel frits; flame retardants/smoke suppressants; pigments; metal surface treatment; sintered metal additives;

These uses and the potential for consumer exposure are discussed individually below.

4.2.3 Are consumers (people of the general public) exposed to MoO_3?

4.2.3.1 Water treatment chemicals

During a questionnaire survey conducted by MoCon amongst producers and downstream users of molybdenum chemicals, one relevant response on this issue has been received from a downstream user.

“*We use molybdenum trioxide in water treatment chemicals for domestic central heating protectors. The substance is added to water based products and dissolved using simple stirring. The finished products being filled into small containers (0.5-4Ltrs) and sold through distribution warehouses to the general public for use in their heating systems. Concentration: 0.02 – 0.6% molybdenum trioxide in product.”*

Based on this information, the potential exposure of consumers to MoO_3 via this type of product was assessed further:

1) According to REACH Article 14 (2), a further assessment of this use is formally not required, since the concentration of MoO_3 in this formulation is below the specific concentration limit of 1%.
2) In the use in water treatment chemicals, molybdenum trioxide is dissolved in water (the water solubility of MoO_3 is 1 g/L [1]). When molybdenum trioxide is dissolved in water, a chemical reaction takes place, yielding molybdate ions (MoO_4^{2-}) in the aqueous solution. MoO_3 is turned into a non-hazardous species in solution, therefore consumer exposure to MoO_3 using the water treatment products is not possible.

<u>In consequence, exposure of consumers to MoO_3 via this application (“water treatment chemicals”) does not need to be assessed.</u>

[1] unpublished study report for the International Molybdenum Association (IMOA): “Water Solubility of Molybdenum Trioxide, Eurofins-GAB, Niefern-Öschelbronn, Germany, Study No. 20071505/01-PCSB, August 2008

4.2.3.2 Ceramic additives / enamel frits / glazes

During a questionnaire survey conducted by MoCon amongst producers and downstream users of molybdenum chemicals, no response on this issue was received, but this reported use has been communicated to MoCon in December 2009 by an Only Representative. An internet search gave some indication that MoO_3 can be used in ceramics glazes or enamel. There are some chemical vendors/distributors who promote MoO_3 for such uses. Also, some patents and some published literature could be found in which MoO_3 is use in/for/on ceramics. It is cited as a wetting agent or surface tension reducer in borate/silicate fluxes. Further, various metal salts can be incorporated into ceramics and enamel to affect properties such as colour and opacity. Below we address all these types of products under the broader term “ceramics”.

Further information for example on quantities of MoO_3 used in ceramics and details on production processes involving MoO_3 could not be obtained. Based on the little available data it is assumed that only small quantities are used.

Regarding consumer exposure, ceramics are used in a wide range of applications, most predominantly for tableware (plates and cups), decorative objects (e.g. vases), floor or wall tiles, toilets and washing basis. All products are specifically designed for stability, hardness and wear resistances.

During the production process any additives (eventually including MoO_3) are included into a solid, compact matrix.

During normal use of ceramics any release of inhalable particles / dust is not foreseeable. Oral exposure to the ceramic ware is only relevant for food contact material like cups which are exempted from human health risk assessment acc. article 14, 5a. For other ceramic products is the oral exposure not an intended product use. The only foreseeable route of exposure due to the intended product use would be the dermal exposure. However, dermal exposure does not need to be considered, due to the absence of dermal toxicity and the low percutaneous transfer rate (please refer to EBRC Report “Hazard assessment and derivation of DNELs for molybdenum compounds”).

Furthermore, the production of ceramics typically involves high temperature processes like sintering and baking, during which a ceramic microstructure is built. It can safely be assumed that any added MoO_3 is no longer present in the finished ceramic product in the form of molecular MoO_3.

In consequence, exposure of consumers to MoO_3 via this application does not need to be assessed further.

4.2.3.3 Flame retardants / smoke suppressants

During a questionnaire survey conducted by MoCon amongst producers and downstream users of molybdenum chemicals, no-one selected this as a use. It was however communicated as an identified use to MoCon in December 2009 by an Only Representative (OR), representing a non-EU manufacturer. The OR subsequently followed up (April 2010) with a confirmation that its principal in fact does <u>not</u> place MoO_3 on the European market (countries within the scope of REACH) for this use and withdrew its earlier request to have it included as an identified use.

<u>Therefore, this use will not be considered further in the registration dossier prepared by MoCon.</u>

The following initial information, which has already been gathered on this use, is kept in this report for information purposes only.

> The following initial information was obtained from the IMOA website:
> (http://www.imoa.info/moly_uses/moly_compounds/smoke_suppressants.html , accessed 2010-01-28)
>
> *“In electronic technology, wire and cable insulation represents a potential fire and smoke hazard to fire fighters and others in confined spaces of aircraft and hospitals. Ammonium octamolybdate is used with PVC to suppress the formation of smoke. These uses and other developments will increase as video, telephone and computing networks increase.*
>
> *Ammonium octamolybdate and <u>molybdenum trioxide</u> are used as smoke suppressants in, for example, PVC cabling. They are thought to act by undergoing reduction to lower valent molybdenum, e.g. molybdenum dioxide, which then cross links the plastic to form a char. Molybdenum stabilises the char so preventing the formation of smoke particles.”*
>
> In addition, there are some chemical vendors/distributors who promote MoO_3 for such uses. The following additional information was also found elsewhere on the internet: “*Molybdenum Trioxide is used as Halogen synergist fire retardants and smoke suppressants for wide range polymers applications (plastics, rubbers, paper and textiles)*.”
>
> In addition to the above, a series of articles by Moore and Tsigdinos (1977/78)[2] explicitly discusses the role of molybdenum compounds in flame retardancy and smoke retardation in plastics. Besides showing the effectiveness of molybdenum compounds, studies of burning polyvinyl chloride samples treated with molybdenum have shown that all the molybdenum remains in the char.

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[2] Moore, FW and Tsigdinos, GA: The role of molybdenum in flame retardancy and smoke retardation. Journal of the Less Common Metals. Volume 54, Issue 1, July 1977, Pages 297-309.
Moore, FW and Tsigdinos, GA: Advances in the use of molybdenum additives as smoke suppressants and flame retardants for polyvinyl chloride. Research Laboratory Climax Molybdenum Company of Michigan. Proceedings of the 1978 International symposium on flammability and fire retardants.

4.2.3.4 Pigments and paints (anticorrosion)

During a questionnaire survey conducted by MoCon amongst producers and downstream users of molybdenum chemicals, no response on this issue was received, but this reported use has subsequently been communicated to MoCon in December 2009. It was not initially clear, whether MoO_3 would be contained in pigments itself or whether it is used in the production process and converted to another chemical.

Information on the use of molybdenum compounds in/as pigments can be found on the website of the International Molybdenum Association (accessed 2010-01-28):
(http://www.imoa.info/moly_uses/moly_compounds/pigments_corrosion_inhibitors.html

According to this information *“Molybdate-based pigments are used for two properties: stable colour formation and corrosion inhibition. Molybdenum oranges are prepared by co-precipitating lead chromate, lead molybdate and lead sulfate. They are light- and heat-stable pigments with colours from bright red-orange to red-yellow and are used in paints and inks, plastic and rubber products, and ceramics….”*

The webpage continues to list some examples, according to which only soluble and insoluble molybdate salts (such as sodium molybdate, zinc molybdate) are used in pigments and as corrosion inhibitors.

“Corrosion inhibiting pigments, primarily zinc molybdate, but also molybdates of calcium and strontium are used commercially in paints. These pigments are white and can be used as a primer or as a tint with any other colour.”

Based on this information, molybdenum oxide (MoO_3) is not itself contained in a pigment or corrosion inhibitor. MoO_3 is used as a feedstock for the preparation of the molybdate solution that is used for pigment production. During this synthesis, MoO_3 is chemically transformed into other substances, which are outside the scope of MoCon.

<u>In consequence, there is no (consumer) use of MoO_3 in pigments.</u>

4.2.3.5 Metal surface treatment

During a questionnaire survey conducted by MoCon amongst producers and downstream users of molybdenum chemicals, no response on this issue was received, but this reported use has been communicated to MoCon in December 2009 by an Only Representative.

Further information was provided from the Climax Molybdenum company. It was explained that MoO_3 can be used for metal surface treatment as follows: Molybdate is used in surface treatment as a protector/passivator for steel during storage. Sometimes steel is stored in plants/stockyards, before moving it to the next stage of the process. To stop it going rusty whilst in storage a solution of MoO_3 dissolved in either potassium hydroxide or lithium hydroxide is applied to the surface of the steel to encourage passivation.

The application developed when chromates were originally eliminated for environmental reasons. The passivation film is a mixture of chemicals and depends on the metal being protected. Typically, the solution for the passivation film would be made with the soluble sodium molybdate. If for any reason sodium would not be wanted in the solution, it can be made in situ from pure oxide plus caustic KOH or LiOH. Once dissolved and in place the corrosion inhibiting mechanism is based on the ionic molybdate and solid, molecular MoO_3 is no longer present. Further this is merely an industrial application with no foreseeable consumer exposure.

<u>In consequence, exposure of consumers to MoO_3 via this application (“metal surface treatment”) is not known or foreseeable, and a further assessment is not required.</u>

4.2.3.6 Sintered metal additives

During a questionnaire survey conducted by MoCon amongst producers and downstream users of molybdenum chemicals, no response on this issue was received, but this reported use has been communicated to MoCon in December 2009 by an Only Representative (OR). The OR subsequently provided some additional information obtained from downstream users.

Molybdenum trioxide is added to alloys produced via sintering in a similar fashion as elemental molybdenum or molybdenum dioxide. When MoO_3 or MoO_2 are used the production of the alloy typically involves a reducing hydrogen atmosphere in which the sintering takes place. Finally, elemental molybdenum in a metallic matrix is obtained.

Any consumer contact with such alloys is not known but may hypothetically be possible. Even in this unlikely case, any exposure would most likely via the dermal route and not to the hazardous molybdenum trioxide, since it has been converted to elemental molybdenum metal.

In consequence, exposure of consumers to MoO_3 via this application (“sintered metal additive”) is not known or foreseeable, and a further assessment is not required.

5 Summary and conclusion

Within the portfolio of molybdenum substance addressed by the molybdenum consortium, only pure molybdenum trioxide (MoO_3) and roasted molybdenite concentrate (RMC) are considered to be of toxicological concern. Due to toxicological considerations only the oral and inhalation route need to be considered for exposure.

Known and identified uses of both substances have been assessed with regards to potential consumer exposure with these substances.

In conclusion, exposure of consumers to either roasted molybdenite concentrate (RMC) or pure molybdenum trioxide (MoO_3) is not known or foreseeable.