BASF comments to the

Draft background document for N,N-dimethylformamide (DMF)

Submitted by ECHA on 24 June 2013

BASF provided already detailed comments during the public consultation of the proposal for identification of DMF as a SVHC. According to ECHA´s response in the RCOM (2012), comments on use, exposure, alternatives and risks may be considered at later stages of the risk management process. Therefore we include our former comments in this actual comment once again (see separate attachment).

General comments to the draft background document

2.2. Imports, exports, manufacture and uses

Use as solvent in industrial settings

The draft background document states that ~85% of the consumed DMF is used as process solvent in industrial settings for several purposes (synthesis of chemicals, production of artificial leather, production of synthetic fibres). In all these applications, DMF is removed very effectively from the final product or article. Almost no residual amount is left. In many cases, DMF is recycled several times. Finally all of the DMF consumed ends up in waste streams. Chemical waste from industrial sites is incinerated or efficiently biodegraded in a sewage treatment plant.

Industrial settings have to be constructed to fulfill legal requirements on minimizing emissions[1]. Technical equipment is selected accordingly (e.g. minimal leakage rates of machines). Measurement and control technology systems monitor the proper operation of the plants and prevent uncontrolled releases of substances. In industrial settings only well-trained personnel is handling the substance. Regular training of the workers addresses the control of the technical equipment as well as the correct use of personal protective equipment. Operating instructions covering all aspects (including cleaning and maintenance works) are available and continuously updated. Management measures are in place to control workplace exposure which is ensured by existing occupational community legislation[2] [3]

For DMF, an Indicative Occupational Exposure Limit (IOEL: 8h-TWA 15 mg/m³; 15 min STEL 30 mg/m³) value has been established in the EU, which is scientifically based on the available data[4].

[1] Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control, codified and replaced by Directive 2008/1/EC, which in turn is to be repealed by Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) as of 07/01/2014.

[2] Council Directive 92/85/EEC of 19 October 1992 on the introduction of measures to encourage improvements in the safety and health at work of pregnant workers and workers who have recently given birth or are breastfeeding.

[3] Council Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work.

[4] Commission Directive 2009/161/EU of 17 December 2009 establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC. (see Annex)

It shows clearly that any exposure below this threshold value causes no risk to human health. In industrial settings, especially compliance with the existing OEL is controlled by measurements and documented regularly.

By all these measures, exposure to DMF at industrial workplaces is minimized and any risk from using DMF at the industrial workplace can be excluded. Even uses as described by PROCs 4, 5 and 8a, which are addressed as bearing a potential risk in the draft background document, are performed without any risk to the health of the workers. This was the result of modeling as required for the registration and included in the Chemical Safety Report. Data from workplace measurements collected in the years 1998 - 2011 (see Table 1) prove that the current IOEL was never exceeded. The measured values are regularly far below the limit values, and in many cases no DMF is detectable at all.

Use in other applications

According to the draft background document, ~15% of the total volume of DMF is used in other applications. Since the registration dossiers only support industrial uses (except for the laboratory use), the above mentioned criteria for industrial settings are also applicable for these uses.

Example: use as cleaning solvent

BASF uses DMF in some cases as a cleaning agent for technical equipment (reactors, pipelines etc.). Use is industrial large scale solvent use to clean closed production lines from residual chemicals by flushing at a plant shut down before starting new synthesis. DMF is subsequently incinerated as it contains chemical waste. This is a non-standard use but large amounts are used at one cleaning procedure. The systems are closed (essentially the same as used in the production of substances), all transfers of material are performed according to the same standards as described above for chemical synthesis. (Details and amounts used see confidential comments).

Example: use as gas stabilizer in acetylene cylinders

This is no use as such, since at the welder´s site, only closed containers are handled. Any DMF that might evaoparte during welding is completely burnt. The production of the cylinders themselves is once again an industrial use, including dedicated facilities with a high technical standard including closed systems and local ventilation), due to the flammable properties of acetylene and the need to operate under high pressure.

Example: use in mixtures

In the draft background document, referring to the Annex XV report (2012) and the RCOM (2012) mixtures used as paints, coatings, adhesives, mastics, sealants, binding agents, finishes and compounds are mentioned. These uses are expected to be typically performed by professionals. On top, it is speculated that some use as stripper and in epoxy inks, as being reported from US-aerospace-company, might also be present in the EU, but this speculation was not substantiated (in chapter 2.3. ECHA states, that for the use of DMF in sealants for the aerospace industry an alternative seems to be available, so this use is no longer relevant). BASF is not aware of any of the cited uses. In our registration dossier, only industrial uses are included. We received no requests to include typical process categories for the use of such mixtures, as described by PROC 10 (roller application or brushing), PROC 11 (non- industrial spraying) or PROC 13 (treatment of articles by dipping and pouring). Therefore, we believe that such uses are at least no longer relevant.

2.3. Availability of information on alternatives

The safe use of reprotoxic solvents like DMF in industrial settings implies great efforts in equipment, organization and personnel of the companies. Therefore, it is of course desirable to use less hazardous solvents, and for many years industry has invested in research to find an appropriate substitute. For certain chemical reactions, the use of a aprotic dipolar solvent is indispensable. Therefore, solvents like N,N-dimethylacetamide (DMAC), N-methylpyrrolidone (NMP) and N-ethylpyrrolidone (NEP) have been investigated and proved suitable in relation to their technical performance in many cases. But unfortunately, their hazardous profile is similar to DMF regarding reproductive toxicity. So in many cases a substitution by any of them makes no sense with respect to risk reduction.

Furthermore, in some applications as a solvent in organic synthesis of active pharmaceutical ingredients or crop protection ingredients, it is not even possible to change the solvent without endangering the whole approval for the final product. Marketing authorizations granted by the European Medicines Agency (EMA) will have to be amended, causing high costs and requiring additional animal and human testing.

In cases where DMF is used as a cleaning solvent, the reason is it´s high solvating power especially for high-molecular weight substances. Such compounds are often left as residues in many synthesis reactions. Alternatives would include the same reprotoxic substances listed above. The use of water or steam for cleaning purposes is not appropriate, since a large amount of contaminated waste water would be created, that could not be easily incinerated. Further details on BASF´s use as cleaning solvent are provided in the confidential part of our comments.

We want to emphasize, that not only the solvating power of a solvent has to be considered when looking for alternatives, but also environmental and technical aspects have to be checked. In the draft background document, DMSO is discussed to be a “safer” alternative. But safety seems only to be related to the toxic profile, not including the following properties:

- DMSO is an aprotic solvent of high polarity (not medium, as required).
- DMSO decomposes auto-catalytically at the temperature of industrial processes (150-250°C). In a recent publication[5] it was recommended to substitute DMSO by NMP in the synthesis of pharmaceutical active ingredients due to safety concerns on decomposition products.
- Some decomposition products of DMSO are toxicologically relevant (e.g. formaldehyde).
- Decomposition of DMSO is limiting recycling and thus increases the waste burden for the environment.
- Corrosivity of DMSO was already mentioned in the draft recommendation document, however, we want to emphasise that this has consequences for process safety. Plant design has to consider corrosion of reactors, pipes etc.
- A clear environmental limitation of DMSO is it´s low biodegradability. This limitation becomes even more important as a mixture of DMSO and naphtha solvent (heavy aromatics) is sometimes discussed to replace aprotic solvents of medium polarity.
- DMSO decomposition products sticking to the manufactured product are of extremely pungent smell (deodorant substance or oxidative treatment required).

[5] Z. Whang et.al, *Org. Process Res. Dev.*, **2012**, (16), 1994.

Some other readily available solvents listed in the draft background document are highly flammable, which would, compared to DMF, pose definitely a much higher risk regarding plant safety.

2.4. Existing specific Community legislation relevant for possible exemption

In chapter “conclusion” (page 4) the draft background document states: “evidence is lacking that such risk management measures are applied across all uses”.

We consider the conclusion given in this chapter of the draft background document as wrong, because specific community legislation which is relevant for a possible exemption does indeed already exist.

The complete life cycle of DMF is covered by specific community legislation: manufacture, (industrial) use and waste are already regulated. Manufacture and waste are not subject to authorization. Potential occupational health risks are properly controlled by the application of Directive 2009/161/EU (establishing a third list of IOELs), Directive 98/24/EC (“Chemical Agents Directive”), Directive 92/85/EEC (concerning pregnant workers) and Directive 2010/75/EU (on industrial emissions). By these Directives, minimum requirements are imposed which have to be implemented by the Member States (see table 2). Furthermore there is a granted permit for any industrial installation. In short, we want to state the following key issues:

- Article 58.2 REACh should be interpreted and applied so that its full effectiveness is ensured.
- The exemption conditions are clearly laid out in Annex 58.2, and they should be applied so that exemptions are effectively and efficiently granted.
- The conditions for the exemption are met in the case of DMF, for the requested industrial uses, namely because of the adoption of the IOEL for DMF and the adoption of emission limits under the IED for DMF as part of a category of solvents.
- At a minimum, the use of DMF as an industrial solvent in industrial installations should be exempt from authorization in so far as the IOEL limit is respected.

Referring to EU legislation, it is rather a case of enforcement by national authorities to ensure that appropriate measures are indeed implemented at user´s site. For the question whether there are minimum requirements it is irrelevant whether all member states are compliant with the EU legislation introducing these minimum requirement. Compliance is an issue of enforcement and it is the duty of the EU Commission to check and take appropriate action for enforcement of the IOEL (see Directive 98/24/EC article 3).

Details are described in a Memorandum by Steptoe & Johnson LLP, prepared for the CEFIC Alkylamines Sector Group (13.9.2013) (see separate attachment).

3.1. Prioritisation

A Volume (v) score of 9 was given by ECHA based on DMF production and use of > 10,000 t/y. However, there are many substances on the European market used in amounts of even > 100,000 t/y. Consequently, to differentiate appropriately, a score of 7-9 is proposed.

For wide dispersive use (WDU) a score of 9 was used by ECHA. It seems that it has simply been assumed a high tonnage to be equivalent to a high number of sites combined with high release. This is neither true nor appropriate. Sites of use are very different:

- Most of the sites are rather laboratories using DMF in their Research analytics. As research use is exempted from authorization the number of laboratories should be excluded from the prioritization scoring.
- Most of the DMF tonnage is used at a small number of sites (e.g. chemical synthesis). Consequently, to classify the number of site as medium is more appropriate.
- Only industrial uses have been registered apart from Laboratory use (an example for professional use is research in universities).This implies clearly a non-wide dispersive use. This is also reflected in the ERCs.
- As only industrial uses are registered, it has to be assumed that emission control is in place as this is mandatory according to EU legislation already. Consequently, DMF release has to be classified as insignificant[6] or non-diffuse/controlled[7].

Result:

IP (inherent properties)	= 0
V (volume)	= 7-9
Sites	= 2-3
Release	= 0-1

Consequently overall score is: IP + V + Site*Release = 0 + (7 to 9) + (2 to 3) * (0 to 1) = **7-12.**

[6]ECHA Guidance document: *Insignificant* = negligible (i.e. very low) **releases** in relation to the likelihood that these releases could cause environmental or health effects.

[7] ECHA Guidance document: *Controlled* = releases at the workplace may occur but that risk management measures are in place to control workplace exposure. It is however not clear whether the RMMs in place render workplace releases negligible (if this is clear workplace exposure is considered *'insignificant'*).)

Conclusion

We consider the inclusion of DMF in Annex XIV as disproportionate for the following reasons:

- There is no additional risk-mitigation benefit to be expected. Risks are already adequately controlled as has been proven by measurements (see table page 2).
- EU manufacturers using DMF will suffer from a permanent competitive disadvantage towards non-EU manufacturers, since the imported products or articles do not contain DMF anymore and consequently are not subject to authorization.
- The manufacture of intermediates in the EU, which is exempt from authorization, would indirectly be included in the authorization process for the solvent used for manufacture. This was obviously not intended by excluding intermediates from authorization-requirements.
- The demand to substitute the substance is already included in existing regulations. As long as a suitable alternative is not available, the inclusion of DMF in Annex XIV will cause no benefit for human health.
- European producers will suffer from high costs to prepare and submit the application for authorization, accompanied by a substantial lack of planning reliability and asset protection. The result will be a loss of competitiveness, which is contrary to the aim and scope of REACh as outlined in Art. 1.

We request the performance of an analysis of the risk minimization options as outlined in the Roadmap on Substances of very High Concern. Including DMF in Annex XIV without exempting use of DMF as an industrial process solvent in industrial installations (e.g. in chemical synthesis and in the industrial manufacture of fibres and membranes) being already regulated causes high costs without providing any benefit and is thus disproportionate. The complete life cycle of DMF in the use as process solvent in industrial installations is regulated by EU legislation already. As laid out in this document, the conditions for the exemption are met in the case of DMF, for the requested industrial uses, namely because of the adoption of the IOEL for DMF and the adoption of emission limits under the IED for DMF as part of a category of solvents. Furthermore existing legislation (IED) already implemented a mechanism for substitution of CMR substances.

Table1: **BASF SE Workplace measurements**

Manufacturing process step	**Workplace concentration (e.g. mg/m3)**	**Basis for estimate (how measured or estimated)**
Production - PROC 1, 2: Use in closed process, no likelihood of exposure	<0.09 – <0.12 mg/m³ Personnel shift mean value	Routine OEL Measurement of BASF (not detectable in 6 measurement between 2005 and 2010)
Production - PROC 1,2 : Use in closed process, no likelihood of exposure (Distillation)	<0.034 – <0.16 mg/m³ Personnel shift mean value	Routine OEL Measurement of BASF (not detectable in 12 measurement between 2005 and 2010)
Filling - PROC 8b: Transfer of substance or preparation (charging/ discharging) from/to vessels/large Containers at dedicated facilities	<0.28 – <0.64 mg/m³ Personnel shift mean value	Routine OEL Measurement of BASF (not detectable in 9 measurement between 2005 and 2010)
Filling - PROC 8b: Transfer of substance or preparation (charging/ discharging) from/to vessels/large	0,189 mg/m³ Shift mean value Personnel Peak value	Routine OEL Measurement of BASF. (1 single value with detectable DMF – usually DMF is not detectable)
Use as solvent in product synthesis at BASF. Includes PROC 1, 2, 3, 4, 8a, 8b	<0.034 - < 0.59 mg/m³ Personnel shift mean value	Routine OEL Measurement of BASF (not detectable in 10 measurement between 2005 and 2010)
Use for industrial cleaning (Ludwigshafen) Includes PROC 1, 2, 3, 4, 8a, 8b	< 0.11 - < 0.12 mg/m³	Routine OEL Measurement of BASF (not detectable in 3 measurement between 2005 and 2010)
Use for industrial cleaning (Ludwigshafen) Includes PROC 1, 2, 3, 4, 8a, 8b	4.2 -6.9 mg/m³ Personnel shift mean value	Routine OEL Measurement of BASF (detectable in 2 measurement between 2005 and 2010)
Use for industrial cleaning (Antwerp) Includes PROC 1, 2, 3, 4, 8a, 8b	2.7-3.0 mg/m³ Stationary	Routine OEL Measurement of BASF (detectable in 10 measurement between 1998 and 2001)
Use for industrial cleaning (Antwerp) Includes PROC 1, 2, 3, 4, 8a, 8b	< 0.2 mg/m³ Stationary	Routine OEL Measurement of BASF (not detectable in 3 measurement after introduction of new technical measurement in 2001-2011)
Use for industrial cleaning (Antwerp) Includes PROC 1, 2, 3, 4, 8a, 8b	<0.2 mg/m³ Personnel shift mean value	Routine OEL Measurement of BASF (not detectable in 19 measurement between 2001 and 2011)

Table 2**: EU OEL and member state OEL**

Country	Year		TWA [mg/m³]	STEL [mg/m³]
EU	**2009**	**2009/161 EU**	**15**	**30**
Austria	**2011**	**MAK**	**15**	**30**
Belgium	**2011**	**OEL**	**15**	**30**
Bulgaria	**2001**	**OEL**	**30**	
Cyprus	**No information**			
Czech Republic	**2012**	**OEL**	**15**	**30**
Denmark	**2011**	**MAK**	**15**	**30**
Estonia	**2011**	**OEL**	**15**	**30**
Finland	**2005**	**OEL**	**15**	**30**
France	**2012**	**OEL**	**15**	**30**
Germany	**2012**	**OEL**	**15**	**30**
Greece	**2001**	**OEL**	**30**	**60**
Hungary	**2011**	**OEL**	**15**	**30**
Ireland	**2011**	**OEL**	**15**	**30**
Italy	**2009**	**OEL**	**15**	**30**
Latvia	**2011**	**OEL**	**15**	**30**
Lithunia	**2011**	**OEL**	**15**	**30**
Luxenburg	**2011**	**OEL**	**15**	**30**
Malta	**No information**			
Netherlands	**2011**	**OEL**	**15**	**30**
(Norway)	**2011**	**OEL**	**15**	**30**
Poland	**2011**	**OEL**	**15**	**30**
Portugal	**2004**	**OEL**	**30**	**-**
Romania	**2006**	**OEL**	**10**	**30**
Slovakia	**2012**	**OEL**	**15**	**30**
Slovenia	**2010**	**OEL**	**15**	**30**

Spain	**2012**	**OEL**	**15**	**30**
Sweden	**1987**	**OEL**	**30**	**45**
UK	**2011**	**OEL**	**15**	**30**

COMMISSION DIRECTIVE 2009/161/EU of 17 December 2009 established the IOEL for DMF to be 15 mg/m³ (TWA) and 30 mg/m³ (STEL). *Article 4 (*1) of this Directive states that "Member States shall bring into force the necessary laws, regulations and administrative provisions to comply with this Directive by 18 December 2011 at the latest." Due to this fact many member states up-dated their OELs in 2011 and 2012.

The IOEL of directive 2009/161 was introduced in all member states that recently up-dated their OEL.

Member state that do not comply with the IOEL have not up-dated their OEL for 7 or more years. This means that these member states established their national OEL before 2009 in which the IOEL was settled.

It is expected that these member states are currently updating their national OEL as demanded by COMMISSION DIRECTIVE 2009/161/EU.

Information source: Ariel data base for SAP EH&S module:
http://msds.3ecompany.com/files/Ariel_Solutions_SAP_Final.pdf