

BASF comments to the
Annex XV dossier
PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS a SVHC

N,N-Dimethylformamid (DMF)
EC# 200-679-5 CAS# 68-12-2

Submitted by: European Chemicals Agency on request of the European Commission
(Version: August 2012)

General comments

page	Dossier XV text or dossier assumptions	Comments or suggestions
7 ff	<p>1.2 Volumes</p> <p>The production volume in the EU was in the range of 50000 to 100000 tonnes per year in 2001 (OECD, 2001)</p> <p>In Asia the production volume was 100000 to 500000 tonnes per year</p> <p>General remark</p>	<p>The volumes do not at all reflect the development of the DMF-market in the last 10 years. OECD-data (from 2001) should be removed. Instead current data as reported in CEH Marketing Research Report on DMF in 2010 should be used.</p> <p>EU production volume is certainly too high. Current values are available to ECHA and should be used.</p> <p>Asian production volumes are much higher today.</p> <p>EU DMF Production and consumption is less than 10% of the world market.</p> <p><i>See confidential part of BASF comment for additional data.</i></p> <p><i>Actual data are available in CEH Marketing Research Report on DMF in 2010.</i></p>
8	<p>2.1 Uses according to the literature</p>	<p>1) Suggestion: change title to "Global Uses according to the Literature".</p> <p>2) The differentiation between global uses and European uses should be made clearer as main uses in the EU clearly differ from global or Asian main uses.</p> <p><i>Actual data are available in CEH Marketing Research Report on DMF in 2010.</i></p> <p>3) Differentiation of uses is very important</p>

	<p>As a solvent used in synthesis, DMF....</p>	<p>for the choice of the best and correct RMO (which is likely to be rather a restriction than authorization, based on described risks form articles).</p> <p><i>See confidential part of BASF comment for additional data.</i></p> <p>Use for chemical synthesis, fibre spinning and artificial leather needs to be separated:</p> <p>1) Residual DMF after use in chemical synthesis can be expected to be below 0.1 %.</p> <p>2) Used for synthesis of pharmaceuticals DMF has even to be below 0.08%.</p> <p>3) DMF use in fibre manufacturing is not synthesis, but processing of a polymer solution during the spinning-process.</p> <p>4) Residual amount in the raw fibre is expected to be comparable to DMAC (average of 0.2%; CAS 127-19-5) or even lower due to the higher vapour pressure of DMF. Correct numbers may be provided by CIRFS (European Man-made Fibres Association).</p>
9	<p>2.2 Uses according to ECHA's dissemination database of registered substances</p> <p>SU 22: Professional uses. Public domain e.g. tradesmen, services....</p>	<p>Registered uses do cover > 90 % of the European DMF market. These are industrial uses which do not pose a risk to the workers.</p> <p><i>See confidential part of BASF comment for additional data.</i></p> <p>The only professional use registered is laboratory use. It was added to cover use for research at university (education) and use in analytical laboratories. It can be expected that well-educated personnel using the necessary PPE handles the substance. The necessary technical equipment for control of exposure (e.g. fume cupboard) is in place. The volume used is expected to be quite low. Consequently in practice there is almost exclusively industrial use.</p>
9ff	<p>2.3 Identified uses in the EU....</p> <p>DMF is also used as a feedstock for syntheses of aldehydes, acetals, amides, esters and heterocyclic substances.</p>	<p>To our knowledge, DMF is almost exclusively used as solvent in chemical synthesis. The use as synthesis feedstock seems to be very limited.</p>

	<p>In a study by the French Antipoison centers, 84 products have been found to contain DMF in concentrations varying between 0.3 and 100% (Comité de Coordination de Toxicovigilance, 2011). From the information available, it is difficult to know the nature of the products and articles that contain DMF.....</p>	<p>Intermediate use is a standard use of a chemical with no additional data requirements. BASF added this exposure scenario even without any notice from a downstream user. As the nitrogen of DMF is fully substituted there are practically no meaningful reactions one can think of.</p> <p>It is necessary to allocate product classes and DMF concentration in the product to identify the products that may pose a risk.</p> <ol style="list-style-type: none">1) DMF content below 1% in a product is unlikely to have any function, but is rather a possible residual amount in an article or product.2) DMF content < 0.5 % may even mean that DMF is not present in the product any longer. The figure is only cited because DMF was used in a preceding manufacturing step and to show now that it is below the relevant concentration limit (e.g. article or pure chem. substance).3) To distinguish between substances, articles and residual amounts when talking about products is very important for the choice of the best and correct RMO, which may be rather a restriction than authorization, for risks from residuals or from articles (e.g. imported artificial leather).4) Consumer use of substances or preparations is not allowed for CMR 1a/b substance according to Annex XVII entry 30 Reach already.5) The use in pesticides is not within the scope of REACH as pesticides do have their own authorization procedure. However, DMF is not allowed in pesticides being authorized or re authorized after 2009 by Regulation 1107/2009.6) The use in medicine and veterinary medicine is also not within the scope of REACH as pharmaceuticals do have their own authorization procedure (see as well BASF confidential comments).
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	<p>The Swiss products register (July 2001)...</p> <p>The SPIN database indicated that there was a very probable exposure of consumers (at low concentrations, below 0.5%) and that the range of use of DMF in applications was very wide in Denmark, Norway, and Sweden in 2010.</p> <p>The Danish product register (August 2001)..... Among the products there were 5 products for consumer/private use.</p> <p>In the Swedish product register in 2008.... Among them 3 consumer products</p>	<p>Switzerland is not an EU country and EU regulations do not apply. Beyond this, 2001 is likely to be out-dated.</p> <p>Again: Consumer use of substances or preparations is not allowed for CMR 1a/b substance according to Annex XVII entry 30 Reach already.</p> <p>The relevant concentration limit for DMF was 0.5% in 2010 and earlier. For contents of <0.5% see comment above. 0.5 %DMF has no function and is rather a residual. It may just be a precautionary notification to the SPIN data base if DMF impurity in the product is possible.</p> <p>To distinguish between substances, articles and residual amounts when talking about products is very important for the choice of the best and correct RMO (which may be rather a restriction than authorization, for risks arising from residuals or from articles).</p> <p>The concentration 0.5% given to SPIN database is expected to decline to 0.3 % with the CLP labelling being binding for mixtures in 2015 for the reasons given above.</p> <p>Again: Consumer use of substances or preparations is not allowed for CMR 1a/b substance according to Annex XVII entry 30 Reach already.</p> <p>The products used by consumers and their DMF-content should be listed to define if and which RMOs or enforcement procedures are appropriate and necessary to improve protection of consumers (chemical products vs. articles).</p> <p>See comment on Danish product register</p>
11	<p>2.4 Conclusion on uses</p> <p>...use as a cleaning solvent, e.g. in textile and plastics industries and laboratories...</p>	<p>BASF is not aware of DMF being used as cleaning agent for finished textiles.</p> <p>DMF is used as cleaning agent for reactors or pipelines in industrial settings in some cases. The systems are closed (same conditions as</p>

	<p>use for the formulation of mixtures e.g. paints, adhesives, coatings, pesticides and medicines,</p>	<p>for the reactions done before) and DMF is incinerated after use. If alternatives are available, they are used already (see as well BASF confidential comments). Water is no alternative (even if steam/pressure was used) since a large amount of contaminated waste water would be generated which cannot be incinerated.</p> <p>1) To our knowledge DMF is not used in industrial paints, mastics and glues.</p> <p>2) BASF is not aware of coating formulations.</p> <p>Again: The use in pesticides and in medicinal or veterinary products is not within the scope of REACH as these products do have their own authorization procedure (see comment above on identified EU uses).</p>
12ff	<p>3.2 Occupational exposure</p> <p>An inventory of used CMR substances in France (2005), cited in the INRS report, shows that 16000 employees are theoretically exposed to DMF in the chemical, pharmaceutical and textile finishing industries.</p> <p>In 1998 Wrbitzky and Angerer investigated the external and internal exposure to DMF of 126 workers from a factory producing synthetic fibres...</p>	<p>The number of 16.000 employees being theoretically exposed is clearly overestimated. Exposure of workers in France is regulated (OEL) and personnel handling DMF in industry is well educated. Real exposure levels as measured at BASF in Germany even show values far below the OEL (s. table below). Since RMM-measures in industry are standardized, these values are expected to be representative also for chemical industry in France.</p> <p>This demonstrates that DMF exposure is not a real workplace issue.</p> <p>This study is about 15 years old and does not reflect current exposure of workers in the fibre industry.</p> <p>This is proven by an ECHA health surveillance study of 2005 cited in the Annex XV dossier, in which urine analysis was not able to distinguish between exposed and not exposed workers.</p> <p>Urine analysis is giving an estimation of total exposure of the worker (inhalative + dermal exposure). Exposure in the range of the human no effect level based on internal exposure (German BAT) is easily detectable</p>

	<p>In the Safety Data Sheet for DMF by Taminco (2010)...</p>	<p>by urine analysis. Consequently there is not any health risk for workers in fibre industry.</p> <p>Exposure was determined by using ECTOC TRA. ECETOC TRA tends to overestimate exposure. Vapor pressure of DMF is 3.77 hPa at 20 ° C. ECTOC TRA uses a 10 hPa substance for estimating exposure in this case. BASF SE Measurement data: see table below.</p>
<p>13</p>	<p>Table 9: National occupational exposure limits within Europe</p>	<p>There are much more European OELs available for DMF than given in the annex XV dossier.</p> <p>Beyond this, the value given for UK is incorrect. UK changed Dec. 2011 to IOEL.</p> <p>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 updated their OELs in 2011 and 2012. The IOEL of directive 2009/161 was introduced in all member states that recently up-dated their OEL.</p> <p>20 of the 27 member states do comply with the IOEL. It was not possible for BASF SE to obtain OEL information of Cyprus and Malta within the commenting period. Only 5 member states.</p> <p>Member states 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.</p> <p>It is expected that these member states are currently updating their national OEL as demanded by COMMISSION DIRECTIVE 2009/161/EU.</p> <p>See complete OEL list in the annex of this document.</p>

14	<p>3.3 Consumer exposure</p> <p>Danish survey (2005) demonstrated emission of DMF (0.4% of the emitted VOCs) from one slimy toy (14 products tested).</p>	<p>Citations from the OECD of 2001 document have to be considered carefully:</p> <ol style="list-style-type: none"> 1.) Data may be out dated 2.) Data includes non-EU uses (especially NAFTA uses) <p>Available information from SPIN database should be used to indicate which consumer-products may contain an amount of DMF posing a risk to consumers.</p> <p>Residual DMF-content in articles (e.g. slimy toy) and emissions thereof could be topic of further or other regulation (restriction).</p> <p>The source of DMF emission is an article that might also be imported from a non EU country. This is a clear case for restriction.</p>
	<p><u><i>The chapter of Consumer exposure is mainly a repetition of the Chapter 2.3 Identified uses in the EU and consequently following comments are mainly repetitions of comments provided in the text above.</i></u></p> <p>In a study by the French Antipoison centers, 84 products have been found to contain DMF in concentrations varying between 0.3 and 100% (Comité de Coordination de Toxicovigilance, 2011).</p>	<p>It is important to separate and to identify the products that pose a risk. They are candidates for a restriction on DMF (Paint, lacquers and varnishes)</p> <p>It is necessary to allocate product classes and DMF concentration in the product to identify the products that pose a risk.</p> <ol style="list-style-type: none"> 1) DMF content below 1% in a product is unlikely to have any function, but is rather a residual amount in an article. 2) DMF content < 0.5 % may even mean that DMF is not present in the product any longer and the figure is only cited because DMF was used in a preceding manufacturing step and to show now that it is below the relevant concentration limit (e.g. article or pure chem. substance).

The Swiss products register (July 2001)...

This is again a repetition in the Annex XV dossier and consequently a repetition of comments

The SPIN database indicated that there was a very probable exposure of consumers (at low concentrations, below 0.5%) and that the range of use of DMF in applications was very wide in Denmark, Norway, and Sweden in 2010.

This is a repetition in the Annex XV dossier and consequently a repetition of comments

3) To distinguish between substances, articles and residual amounts when talking about products is very important for the choice of the best and correct RMO, which may be rather a restriction than authorization, for risks from residuals or from articles).

4) Consumer use of substances or preparations is not allowed for CMR 1a/b substance according to Annex XVII entry 30 Reach already.

5) The use in pesticides is not within the scope of REACH as pesticides do have their own authorization procedure. However, DMF is not allowed in pesticides being authorized or re authorized after 2009 by Regulation 1107/.

6) The use in medicine and veterinary medicine is also not within the scope of REACH as pharmaceuticals do have their own authorization procedure (additional information see BASF confidential comments).

Switzerland is not an EU country and EU regulations do not apply. Beyond this, 2001 is likely to be out-dated.

Again: Consumer use of substances or preparations is not allowed for CMR 1a/b substance according to Annex XVII entry 30 Reach already.

The relevant concentration limit for DMF was 0.5% in 2010 and earlier. For contents of <0.5% see comment above. 0.5 %DMF has no function and is rather a residual. It may just be a precautionary notification to the SPIN data base if DMF impurity in the product is possible.

To distinguish between substances, articles and residual amounts when talking about products is very important for the choice of the best and correct RMO (which may be rather a restriction than authorization, for

	<p>The Danish product register (August 2001)..... Among the products there were 5 products for consumer/private use.</p>	<p>risks from residuals or from articles).</p> <p>The concentration 0.5% given to SPIN database is expected to decline to 0.3 % with the CLP labelling being binding for mixtures in 2015 for the reasons given above.</p> <p>Again: Consumer use of substances or preparations is not allowed for CMR 1a/b substance according to Annex XVII entry 30 Reach already.</p> <p>The products used by consumers and their DMF-content should be listed to define if and which RMOs or enforcement procedures are appropriate and necessary to improve protection of consumers (chemical products vs. articles).</p>
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For additional question, please feel free to contact:

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Evaluation of Substances called most “promising alternatives” in the Annex XV dossier

page		Conclusion
XXX as alternative		
15	Toluene, white-spirit, alcohol	These solvents are flammable. The solvation properties are not comparable to DMF. Therefore those solvents are no suitable alternatives for DMF.
	DMSO	Though DMSO may be an alternative in analytical applications, it is not a suitable alternative for major applications of DMF.

Overall conclusion: BASF is not aware of a suitable alternative for major DMF-applications.

Table solvent properties: Solubility parameters (Polarity(x), H-bonding (y)) demonstrate that solvents with similar properties to DMF are either drugs (GBL = date rape drug) or reprotoxicants (NMP, DMAC) and consequently in practice no real alternatives. Toluene white spirit and usually alcohols as well, are clearly less polar than THF and therefore not visible in the figure below.

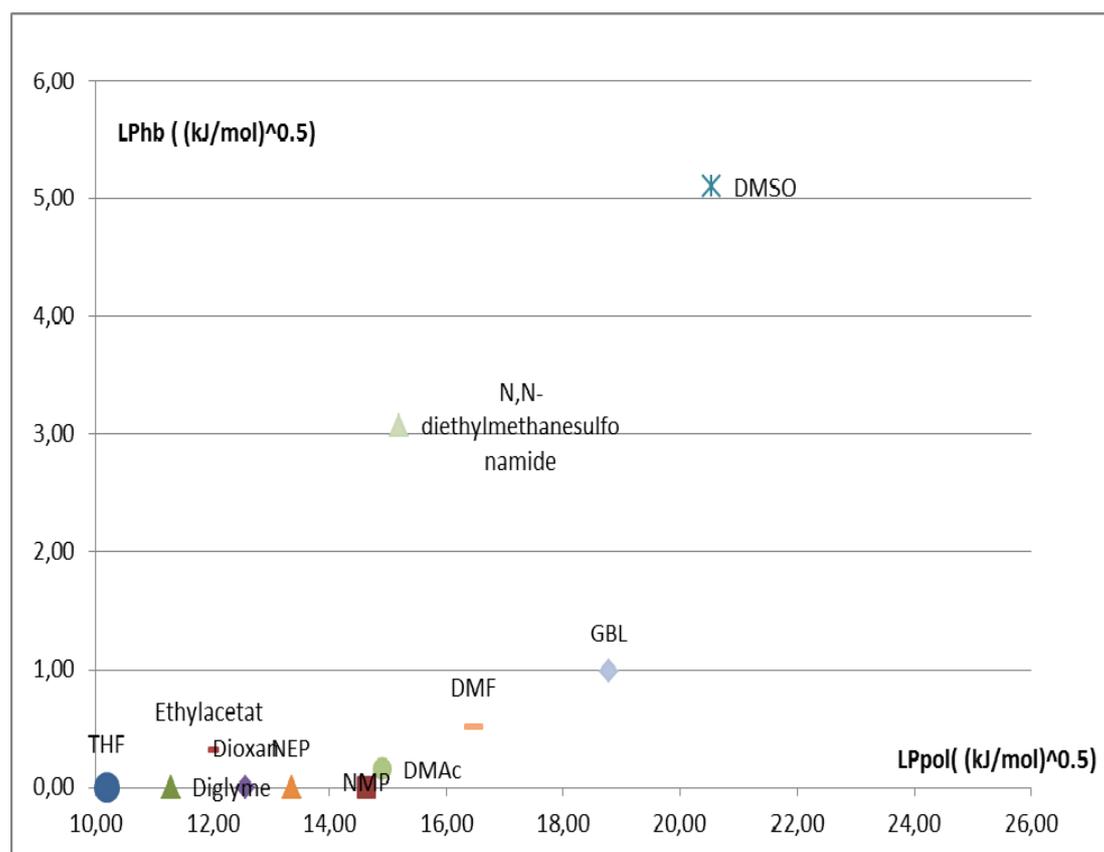


Table: BASF SE Workplace measurements

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/m ³ Personnel shift mean value	Routine OEL Measurement of BASF (<u>not detectable</u> 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/m ³ Personnel shift mean value	Routine OEL Measurement of BASF (<u>not detectable</u> 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/m ³ Personnel shift mean value	Routine OEL Measurement of BASF (<u>not detectable</u> in 9 measurement between 2005 and 2010)
Filling - PROC 8b: Transfer of substance or preparation (charging/ discharging) from/to vessels/large	0,189 mg/m ³ 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/m ³ Personnel shift mean value	Routine OEL Measurement of BASF (<u>not detectable</u> in 10 measurement between 2005 and 2010; no newer data)
Use for industrial cleaning (Ludwigshafen) Includes Proc 1,2, 3, 4, 8a, 8b	< 0.11 - < 0.12 mg/m ³	Routine OEL Measurement of BASF (<u>not detectable</u> in 3 measurement between 2005 and 2010; no newer data)
Use for industrial cleaning (Ludwigshafen) Includes Proc 1,2, 3, 4, 8a, 8b	4.2 -6.9 mg/m ³ Personnel shift mean value	Routine OEL Measurement of BASF (<u>detectable</u> 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/m ³ Stationary	Routine OEL Measurement of BASF (<u>detectable</u> in 10 measurement between 1998 and 2001)
Use for industrial cleaning (Antwerp) Includes Proc 1,2, 3, 4, 8a, 8b	< 0.2 mg/m ³ Stationary	Routine OEL Measurement of BASF (<u>not detectable</u> 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/m ³ Personnel shift mean value	Routine OEL Measurement of BASF (<u>not detectable</u> in 19 measurement between 2001 and 2011)

Table : EU OEL

Country	Year		TWA [mg/m ³]	STEL [mg/m ³]
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	2001	OEL	30	60
Denmark	2011	MAK	15	30
Estonia	2011	OEL	15	30
Finland	2005	OEL	15	30
France	2006	OEL	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
Lithuania	2011	OEL	15	30
Luxemburg	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