# REACH Practical Guide on Exposure Assessment and Communication in the Supply Chains
# Part III: Mixtures under REACH

**March 2010**

**Important note to the reader**

This document has been prepared by a VCI working group as part of the joint Cefic/VCI project to develop tools and guidances for industry – in respect of Chemical Safety Assessments, Chemical Safety Reports and Exposure Scenarios.

It is Part III of the REACH Practical Guide on Exposure Assessment and Communication in the Supply Chains. It describes the status of development as per Q1 2010. Many activities, both in industry working groups as within ECHA are still ongoing. The guide is therefore not to be regarded as complete, but as a status overview.

The Practical Guide comprises five several parts. An overview is given in the preface of Part I.

The structure and the contents of the REACH Practical Guide are described on the following web sites:

VCI: http://www.vci.de/default~cmd~shd~docnr~125022~lastDokNr~102474.htm

All related documents can be downloaded from this site. In addition you find here information on related issues and actual developments.

CEFIC: http://cefic.org/templates/shwPublications.asp?HID=750

# REACH Practical Guide on Exposure Assessment and Communication in the Supply Chains

Part III: Mixtures under REACH

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# 1 Introduction

The safe use of chemicals is one of the main objectives of REACH. Therefore, chemical safety assessments (CSA) of substances are of central importance. In the CSA the whole life cycle of a substance has to be evaluated.

In many cases substances are used in mixtures during their life cycle. Therefore this use has to be evaluated in the CSA. On the other side the use of substances in mixtures implies often changes of the conditions of use. These changes may be relevant for the operational conditions and risk management measures.

Most chemical products are mixtures, which are usually formulated or produced directly in order to change certain properties and effects of substances or to achieve specific effects of the product. Mixtures may be formulated from substances or other mixtures but they are often a result of a production process e.g. if a substance is manufactured in a solution.

The following sections are dealing with tasks and obligations of the different actors who handle mixtures.

# 2 Supply chains and mixtures

A typical **supply chain** starting with the manufacturer of substances and ending with the final downstream user who applies a mixture in an industrial or professional application is illustrated in Fig. 1. The structure of the supply chain can vary according to the different mixtures. It can be shorter or longer, and can involve distributors between each step. However, the main elements shown in figure 1 are relevant for most mixtures.[1]

The different actors shown in figure 1 have different obligations under REACH regarding mixtures:

- **Manufacturers of substances** have to register each substance and to elaborate a CSA for those substances which they produce in quantities of 10 tonnes or more per year per registrant.
- **Formulators** produce mixtures by formulating substances or other mixtures. If they do not manufacture or import the substances, they are only acting as downstream users under REACH.

[1] In order not to overload the figure, importers of a substance or a mixture are not included. Details on the role of this actor and his obligations are given in the ECHA Guidance for downstream users chapter 15, p. 126ff.

Mixtures from the first formulator can be used by a second formulator as a raw material for his mixtures. Several formulators can be involved until the end-use mixture is supplied to the final downstream user[2].

- **Final downstream users of chemical products**. They are applying mixtures in industrial, professional applications and have specific obligations under REACH. Private users have no obligations since they are not downstream users under REACH.

**Distributors** can be involved several times in the supply chain, they are no downstream users.

[2] Consumers are not considered as downstream users under REACH.

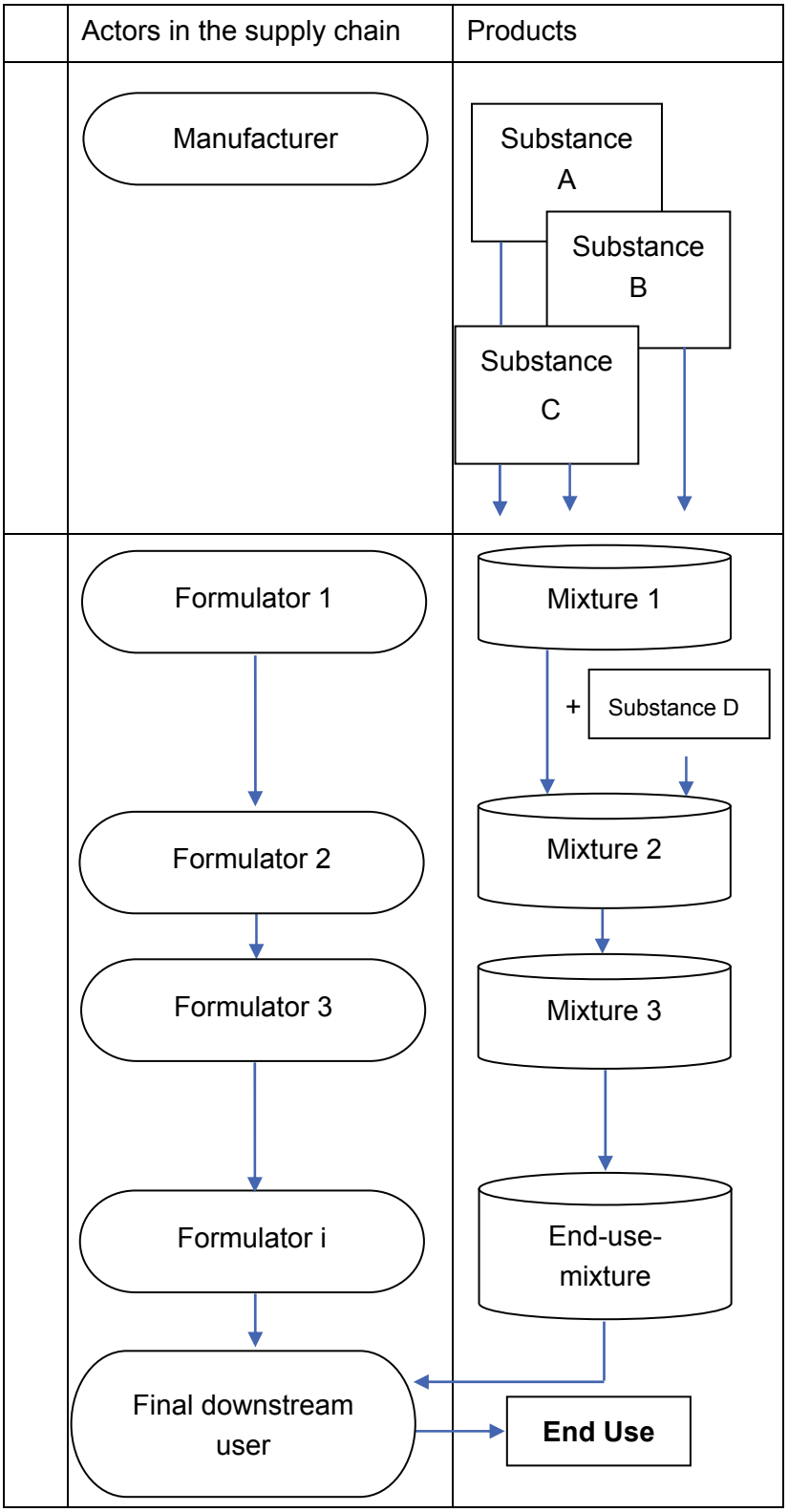


Figure 1 Supply chain and mixtures

# 3 REACH obligations for actors dealing with substances in mixtures and mixtures themselves

REACH obligations for manufacturers, formulators and the final downstream user differ according to their role and are described in more detail in this chapter. Before it is helpful to get an overview which kind of documents related to a dangerous substance and which documents related to a mixture can be expected to be handled from the different actors in the supply chain.

(Please note: Not all of these documents are obligatory for each substance; e.g. chemical safety reports are only required for substances subject to registration produced in quantities of 10 tonnes or more per year and per registrant; DU chemical safety reports are only required for uses which are not covered by the ES of the supplier and if exemptions can not be applied).

*REACH documents that have to be prepared for the registration by the manufacturer/ importer (M/I) related to a dangerous substance:*

- registration dossier;
- chemical safety report[3] (CSR), which documents the chemical safety assessment (CSA) of the substance. It is part of the registration dossier;
- exposure scenarios (ES) for the identified uses of the substance (part of the CSR);
- extended Safety data sheet (eSDS), with one or more exposure scenarios as annexes to the eSDS, only if the substance is placed on the market in the EU.

*REACH documents that may be prepared or forwarded by downstream users related to a mixture classified as dangerous:*

- extended safety data sheet for the mixture;
- exposure scenarios for substances in the mixture, if required according to REACH Art. 31.7 and/or REACH Art. 37.4.;
- exposure scenario for the mixture as part of own assessment or eSDS (option according to REACH Art. 31.2);
- downstream user notification to ECHA of uses not covered by exposure scenarios he received from his suppliers according to REACH Art. 38.;
- downstream user Chemical safety report (DU CSR) for one or more dangerous substances in the mixture (Art. 37,4 REACH) (if their use is not covered by the ES of the supplier or if his supplier advises against this use);

[3] A chemical safety report is required for substances with a production volume of 10 t/year and more per manufacturer/importer and is part of the registration dossier

- downstream user Chemical safety report (DU CSR) for the mixture (Art. 31,2 REACH)[4] (optional).

Nearly all REACH obligations are related to substances as such or as part of a mixture – but not to mixtures themselves. In regard of mixtures, Title IV of REACH sets requirements for the communication in the supply chain including safety data sheets for mixtures.

Three main obligations are important for actors handling substances in mixtures:

*1. Chemical safety assessment of substances (M / I)*

The chemical safety assessments prepared have to cover production of the substances and all identified uses during the complete life cycle including being part of the mixture (REACH Art. 14.4 and Annex I).

This requirement only refers to manufacturers and importers who have to register substances. (In certain cases, downstream users may develop their own CSA, if their uses are not covered by the exposure scenarios which they received from their suppliers – see Part I of this Practical Guide, chapters 4, 5 and 7).

Chapter 4.4 of this document deals with the question how the registrant can take into account that his substance becomes part of mixtures when he performs the chemical safety assessment.

*2. Check of downstream user (DU) whether his uses are covered by the exposure scenario*

The obligation to assess whether own uses and the uses of customers (if applicable) are covered by exposure scenarios which have been received applies to **any** downstream user of a substance on its own or in a mixture throughout the whole supply chain (see figure 2). This includes the first actor who is producing a mixture as well as following formulators and finally the (industrial or professional) user of the end-use mixture.

A downstream user has to check the compliance of his uses with the conditions of use as described in the exposure scenarios which he receives (REACH Art. 37.4).(This check of compliance made by the downstream user refers to the exposure scenarios which the downstream user receives. In the figures in this guidance it is called in short “DU check conditions of use”. Please be aware that this assessment of the downstream user has nothing to do with the compliance check of the European Chemicals Agency related to registration dossiers).

If his use is not covered and he could not implement the conditions of use described in the exposure scenario, he has four options:

- contact the supplier to have the use included;

[4] REACH Art. 37.4 describes in which cases a downstream user chemical safety report is not required (see chapter REACH Practical Guide, chapter4.2).

- prepare his own CSA;
- change the supplier;
- find a substitute for the substance.

The downstream user assessment whether his uses are covered, its consequences and the related time frames are described more detailed in Part I of the Practical Guide, chapters 7.2; 7.4–7.6.[5]

*3. Inclusion of information in safety data sheets (SDS) (M/I, DU)*

Any downstream user shall include (or be consistent with) relevant information from received exposure scenarios, and use other relevant information, from the safety data sheets supplied to him when compiling his own safety data sheet for identified uses (REACH Art. 31.7, 2nd sentence).

This requirement refers to everybody who receives safety data sheets and is required to develop a safety data sheet for his substance or mixture for identified uses. This is especially the case for formulators producing mixtures and supplying them together with the corresponding safety data sheets to the customers. The following figure 2 describes the main tasks for formulators and final downstream users. Final downstream users of an end-use mixture do not prepare safety data sheets and therefore are not affected by this obligation.

The task of preparing an SDS for a mixture is illustrated in figure 3. It is described in detail in chapter 6 of this document.

[5] A downstream user has six months to prepare a notification for uses which are not covered and to send it to ECHA. He has one year to perform his own chemical safety assessment (in both cases starting from the reception of an safety data sheet with a registration number and an exposure scenario).

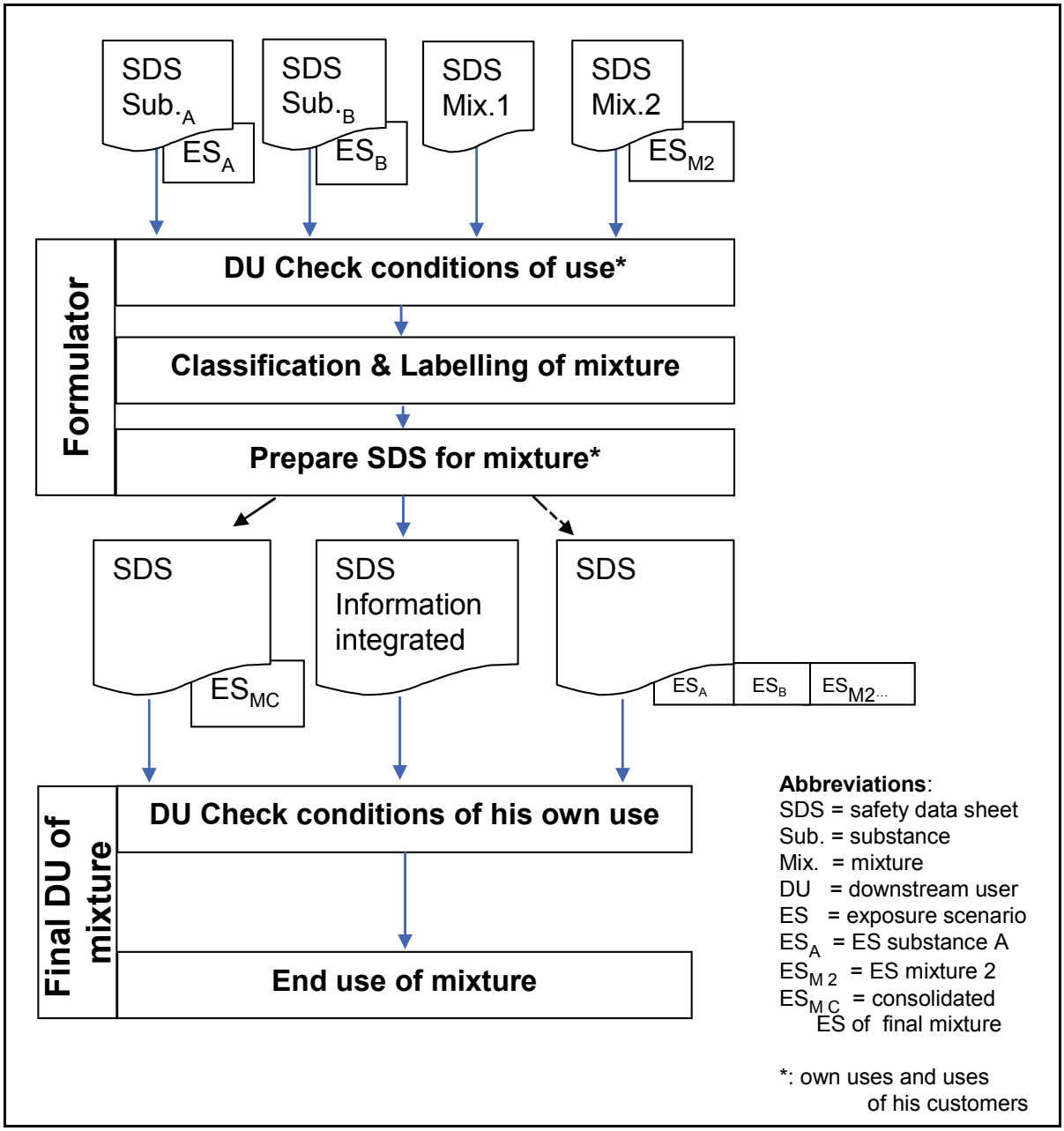


Figure 2 Main tasks for a formulator and final downstream users receiving safety data sheets. Both actors (the formulator and the final downstream user of the mixture) have to implement the operational conditions (OCs) and the risk management measures (RMMs) related to their own uses. The second part of the figure illustrates three options to include information from safety data sheets of substances into the safety data sheet of the mixture. See chapter 5 for details.

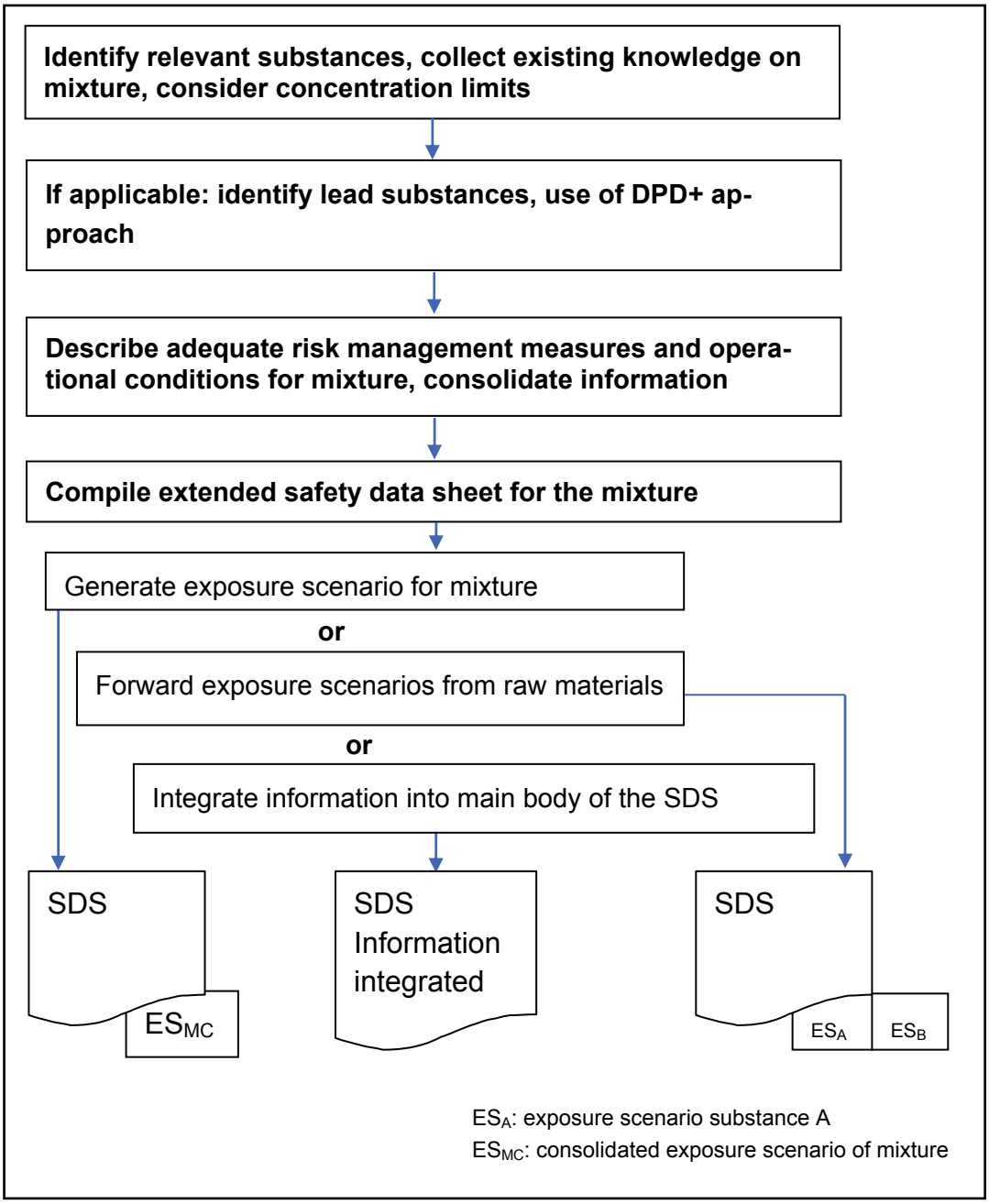


Figure 3 Main tasks for a downstream user preparing a safety data sheet for a mixture. The second part of the figure illustrates three options to include information from safety data sheets of substances into the safety data sheet of the mixture. Remark for the second option: it might be necessary to modify exposure scenarios of substances before forwarding them. See chapter 5 for details.

# 4 REACH and formulators

Formulators, who do not import or manufacture substances, but produce mixtures from substances, are downstream users under REACH. Therefore they have to fulfil the obligations which REACH defines for downstream users.

Some of these obligations are identical for all downstream users, independently of whether they are formulators or users of a mixture. Some obligations are specific to formulators.

## 4.1 Tasks for formulators that still continue under REACH

Formulators who produce mixtures by formulating many raw materials (substances or mixtures) have the following specific tasks and obligations within the supply chain:

- Classify and label the mixtures: assess the hazardous potential of their products and describe operational conditions and risk management measures to handle their products in a safe way[6].
- to review the hazard assessment as soon as new information on their substances is received.
- to prepare safety data sheets for products if supplied to customers. These safety data sheets contain all the information necessary to handle the mixtures safely.

Under REACH, like in the past, SDSs for mixtures are required only if mixtures are classified as dangerous according to the Dangerous Preparations Directive (REACH Art. 31.1 (a)). In addition, SDSs for mixtures are required if the mixture contains at least one dangerous or PBT/ vPvB[7] substance in concentrations above the limits defined in REACH Art. 31.3 or if it contains a substance for which a Community workplace exposure limit exists.[8] (Note: PBT assessment is a new requirement under REACH).

In addition, safety data sheets do not need to be supplied where dangerous substances or mixtures offered or sold to the general public are provided with sufficient information to enable users to use them safely (REACH Art. 31.4).

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[6] The Dangerous Preparations Directive (DPD) and the Regulation on Classification, Labelling and Packaging define the legal obligations for the hazard assessment of mixtures apart from REACH.

[7] PBT: persistant, bioaccumulative, toxic; vPvB: very persistant, very bioaccumulative.

[8] REACH Art. 31.3 refers to safety data sheets which have been requested by the customer.

## 4.2 New obligations for formulators under REACH

REACH defines new obligations for formulators and partly changes the conditions for existing and continuing tasks.

**Formulators have to do a check whether their – and their customers' – uses are covered by the exposure scenarios which they receive.**

Future eSDS supplied to formulators will contain exposure scenarios. The new task of formulators is to assess whether their uses and the uses of their customers are covered by the exposure scenarios of the substances (for detailed information see Part I of the Practical Guide, chapters 7 and 7.2). If the exposure scenarios described in the eSDS of the supplier do not match with the operational conditions of the identified uses significant differences in the exposure situations can result.

If the exposure scenarios of the substances do not cover the conditions of use of the mixtures yet, the formulator has several possible follow-up tasks. In any case at least one actor in the supply chain has to do the exposure assessment, the risk characterization and the identification of the conditions of safe use. The downstream user has the right to communicate his use to the supplier to make it an identified use (REACH Article 37.2.)[9]

**Formulators will receive more information on their substances under REACH and will have to check whether classification & labelling was changed. SDS will anyway need to be modified to fit with new Annex II requirements and CLP classification.**

More information on the hazardous properties of substances will become available due to the registration of substances. Classification and labelling of substances may change due to new information or change of regulation (CLP Regulation, see Part I of this Practical Guide, chapter 2.6).

More information on the safe use of substances will be communicated in the supply chain, especially safe limit values (DNEL, PNEC) for the substances. To an increasing degree, safety data sheets for substances will contain exposure scenarios as annexes describing the conditions of safe use. Later on, extended safety data sheets of mixtures classified as dangerous will be supplied.

[9] For reasons of protection of human health or the environment, the registrant can decide not to include it as an identified use (REACH Art. 37.3). In this case, he shall inform ECHA and the downstream user and may not supply the substance to any DU without informing on the rationale.

**Formulators shall include (or be consistent with) relevant information from exposure scenarios received and use other relevant information from the safety data sheet supplied to them when compiling the safety data sheet for their product (REACH Art. 31.7).**

This requirement refers to all actors of the supply chain which are compiling safety data sheets. It is of specific relevance for formulators because they have to handle information from all of the substances that they use to make their products.

Chapter 5 deals with the question on how to include the information from exposure scenarios of substances into the safety data sheet of a mixture.

## 4.3 Tips to cope easier with the obligations under REACH

- Perform a downstream user check whether your use is covered only if concentrations of substances in a mixture are above the limit concentrations of REACH Art. 14.2.
- When compiling a SDS for a mixture:
  - Use limit concentrations of REACH Art. 14.2 to focus on relevant substances of a mixture.

**!** As a general rule, for substances contained in mixtures in concentrations below 0.1% (e.g. T+, T, CMR Cat 1 or 2, N) or 1% (Xn, C, Xi sensitising, CMR Cat.3), it **is not required** to perform a chemical safety assessment (Art.14.2).**!** Exemptions from this general rule: for a particular substance, specific concentration limits can be defined in the Dangerous Preparations Directive (Directive 1999/45/EC) and in the CLP Regulation (EC) No. 1272/2008 (the CLP Regulation also includes the classification and labelling inventory). In this case, if the concentration in the mixture is lower than the lowest substance-specific concentration limit (see REACH Art. 14.2), a CSA is not required (see Annex I of this guidance for details).

  - Concentrate on the lead substances for the specific properties of the mixture (see chapter 7).
  - Decide which of the different ES received are relevant for the use and the use conditions of the mixture supplied.
  - Decide if a new ES for the mixture is necessary or more appropriate.

  **Note:** at the beginning, only partial information will be available to the DU as eSDS of substances will be received gradually. Case-by-case decisions will have to be made to decide when to update SDS of mixtures.
- Information on substances should be carefully assessed and compiled by the supplier. If identical substances are supplied by different suppliers, classification and labelling and hazard data (DNEL, PNEC) should be identical (in practice this is often not the case today; with the joint registration approach, it is reasonable to expect that this

situation will improve in the future). This requires a careful check if such data are used by the next actor in the supply chain for his own assessments (see also chapter 9.2). A plausibility check of the received ES data on raw materials – substances and mixtures – by the DU is very important and part of the legal obligations set in the Dangerous Preparations Directive/ CLP Regulation for the assessment of mixtures.

- In chapter 15 of the SDS, it must be made clear whether a CSR has been made or not. In addition, it should state if an exposure scenario has been prepared. For mixtures, it is helpful to document for which substances in the mixture CSR and ES (or/and the CSR/ES for the mixture as such) have been prepared.
- Information in the ES for substances (used as substances for a mixture) is structured in a modular way which helps to select relevant modules for the ES of the mixture.
- ES of substances already covers the use of the substance in mixtures.
- Registrants give guidance to formulators on how to show that a use is covered, even if individual conditions of this use differ from the exposure scenario (this procedure is called “scaling”, if simple calculations are used. It is described in detail in Part I, chapter 7.7 of the Practical Guide).
- Input parameters, applied methodology and results of the exposure assessment used in ES are documented in a transparent way to support the check of the next downstream user whether he is covered by the exposure scenario. Reference can be given to a site where these data are available (e.g. http://reach-guide.oeko.info/L_REACH_Input_ECETOC_TRA.pdf, http://reach-guide.oeko.info/L_REACH_Results_ECETOC_TRA.pdf, http://reach-guide.oeko.info/L_REACH_environment_water.xls)
- ES of mixtures should clearly indicate the risk-/ RMM-determining substances of the mixture for the different exposure routes and the related risk characterisation ratios. While the latter is not a legal requirement, it is an essential element to allow downstream user to check whether their uses are covered and assessments of the next uses of the mixtures throughout the whole supply chain. In the standard format of exposure scenarios section 3 is foreseen for information on prediction of exposure (see Part II, chapter 9.2 of the Practical Guide).
- ES of substances only contain information relevant for the downstream user describing safe use and supporting the check whether the uses of the downstream user are covered. It is not required to list all information from the CSR in the ES. If additional information is required, e.g. on marine ecosystems, it can be given in more detail on a publicly available site (e.g. http://reach-guide.oeko.info/L_REACH_Input_ECETOC_TRA.pdf, http://reach-guide.oeko.info/L_REACH_Results_ECETOC_TRA.pdf, http://reach-guide.oeko.info/L_REACH_environment_water.xls).

## 4.4 Information to be given by formulators for the risk assessment of substances in mixtures

The chemical safety assessment of a substance should cover its whole life cycle. It has to consider the different exposure routes, the operational conditions and the risk management measures applied to the uses which have been identified.

In many cases, a registered substance is used by formulators for manufacturing of mixtures. In general the registrant does not know the recipes of the mixtures in which his substance will be used further downstream in the supply chain. Therefore, he cannot take into account potential changes of the determinants of exposure for his substance if used in mixtures.

In general, the registrant assumes that the use of a substance in a mixture can be seen primarily as a dilution of the substance by other substances. Apart from the diluting effect, the other substances are considered to be inert.

If substances with the same hazards and / or effect profile are formulated together the synergistic or antagonistic effects have to be considered e.g. as described in the DPD. If the manufacturer of the substance does not know about this (as will be often the case), he is not able to assess these additive effects. Then it is the task of the formulator to take his specific knowledge on the mixture into account.

However, if for specific uses it is well known that the substance behaves differently in a mixture (synergistic or antagonistic effects), this should be considered in the chemical safety assessment of the substance. An increase of the solubility of a substance due to presence of a carrier in a mixture or the decrease of the irritating potential of mixtures of different surfactants are examples for this case.

In most cases, these changes are intended by the formulator. They are used to achieve specific functional properties of the mixture. If such changes are foreseeable and influence the exposure, the formulator should inform his supplier. In this case the registrant can consider these changes in the chemical safety assessment of the substance used for mixtures.

The following recommendations aim to support the communication between suppliers of substances and formulators:

- Exposure scenarios for substances used in mixtures should state which concentration range is covered by the conditions of use. These conditions of use can be specified for different concentration ranges. Thereby it is ensured that the ES of a substance covers a broad range of uses. Furthermore it should be clear that these ranges only relate to mixtures, in which the other components are inert and have no influence on the hazards or the other exposure determinants.
- If certain parameters have to be tested with the mixture (e.g. the flammability), it can be that different RMMs have to be applied depending from the test result. In this case these RMMs should be described in the ES of the substance.

- Classification of a mixture can be different from the classification of its substances (e.g. a mixture with a content of 2% diethyl ether is not classified as flammable, whereas ethyl ether is classified as highly flammable). The supplier can describe specific risk management measures and operational conditions for different results of classification of the mixture. This makes it easier for a formulator to identify the appropriate conditions of use for his mixture.

Any downstream user has the right to make uses of a substance known to its suppliers[10].

The following information should be given to the supplier by the formulator:

- The substance is used in mixtures.
- Maximum concentration of the substances in mixtures or relevant concentration ranges, if the substance can occur in different concentrations in mixtures (as a consequence, the registrants could recommend specific sets of operational conditions (OCs) and risk management measures (RMMs) for these concentration ranges.
- Changes in the determinants of exposure due to the use of the substance in mixtures, if relevant.

Normally, this information is communicated as part of the exchange on general conditions of use. Use of a substance in a mixture can be considered as a specific condition of use of the substance.

- Information should be part of the mapping of main uses. In many cases, the product categories already indicate that substances are used in mixtures.
- Representative exposure information within different industry sectors should be collected by sector groups (see Part II, chapter 10 of the REACH Practical Guide).

## 5 Exposure scenarios of mixtures

Exposure scenarios for mixtures are one of several possibilities to include information on substances into extended safety data sheets of mixtures. (In REACH there is no formal obligation for any actor of the supply chain to prepare an exposure scenario of a mixture).

If a registrant prepares an exposure scenario for a substance used in the supply chain, it is obligatory for him to communicate this exposure scenario. For downstream users, who pre-

[10] The information given should be in a way that a CSA is possible. REACH guidance provides a Use Descriptor System (UDS) which allows describing sector of uses, processes, product and article categories in a harmonized way. Additional information on operational conditions and risk management measure are of big value. Assignment of uses to the UDS is often called mapping (see for details Part II, chapters 9 and 10 of the REACH Practical Guide).

pare their own safety data sheets there is no legal obligation to prepare own exposure scenarios as long as their uses are covered by the exposure scenarios of their suppliers. For them it is compulsory to **include** information which they have received in their own safety data sheets (REACH Art. 31.7, see chapter 2). They can do this in several ways[11] :

1. **Forwarding** the exposure scenarios for each substance to the customers without consolidation.

Note: Forwarding is only possible if the pieces of information in the exposure scenarios are in line to each other and if there are no contradictions to the information in the SDS. Therefore in many cases it will be necessary to modify one or more of the received exposure scenarios of substances according to the specific conditions of use of the mixture. The modified exposure scenarios of the substances can be attached to the SDS of the mixture.

2. **Consolidating** the received exposure scenarios for substances into a new exposure scenario for the mixture ("mixture exposure scenario") annexed to the SDS of the mixture.
3. **Extracting** the relevant information on risk management measures and operational conditions from the received ES, summarizing and including them in the related sections of the SDS for the mixture.

(If the immediate downstream user is the formulator of a product to be offered or sold to the general public, he can use another option. He can extract, summarize and include the relevant information on risk management measures and operational conditions in the information for the general public. This is a fourth option).

It depends on the specific situation of an actor in the market which option will be the most appropriate one for him and his customers. It also depends on the number of hazardous substances in the mixture and the type of effects.

The first option, just forwarding received exposure scenarios, seems to be simple. Especially in cases of mixtures containing only a very limited number of dangerous substances this option might be of relevance. However, it has to be ensured that information in the exposure scenarios is consistent with the information in the safety data sheet of the mixture themselves. In addition, it is possible that the ES for the substances have to be modified in order to cover the specific properties of the mixture (see chapter 6.3).

If the same route of exposure is relevant for several substances in the mixture, it is advisable to cover them in one exposure scenario for this route for a mixture. It is very unlikely that in practice downstream users will implement conditions of safe use distributed in several exposure scenarios.

[11] See ECHA Guidance on information requirements and chemical safety assessment, Chapter G, Extending the safety data sheet (in version May 2008: p. 18ff).

It is a company decision which of these options will be most appropriate for them. It may depend on its customers. Some aspects play a role in this decision:

1. If the mixture is an end-use product which is used under different conditions (e.g. adhesives), consolidation of information into new exposure scenarios for the different uses can be the best option. Here use-specific risk management measures for each use are necessary. They might be described in use-specific ES, while the main body of the SDS contains the information which is relevant for all users.
2. For a mixture which is an end-use product with a well-defined user group, integration of information into the main body of the SDS might be the best way. Risk management measures and operational conditions can be described which are appropriate for this specific use. In such a case it is not necessary to define different RMM and OC for different conditions of use. In addition it is not necessary to describe scaling possibilities because the conditions of use are more or less fixed.
3. As long as mixtures are further "processed" in the supply chain, in particular when used in other mixtures, supplying information in form of an ES helps the following actor in his task of identifying and including the relevant information for the substances which he receives in his own safety data sheet.
4. If use of scaling possibilities plays an important role for the downstream user, at present it is easier to provide this information in the exposure scenario than in the main body of the SDS.
5. If an ES is attached, it should be ensured that information in chapter 1 – 16 of the SDS are consistent with the information given in the ES.
6. If industrial users with experience in workplace exposure control are interested primarily in the substance specific data given in the main body of the safety data sheet, inclusion of information seems more appropriate.
7. In addition, the safe use of substances and mixtures will be considered more likely if the necessary information for this is provided in a structured way. This makes it easier for a downstream user to check whether he complies with the conditions of use which have been assessed as being safe. Chances of implementation by professional users as handicraftsman increase if the advices on safe use are presented in a short annex – instead of being distributed in several pages of an SDS.

Remark: Annex II gives an overview on the contents of an exposure scenario and the corresponding section of the safety data sheet. This provides guidance on how a downstream user may integrate the information from ES into the safety data sheet of his mixture if this option is chosen by him.

# 6 Preparing exposure scenarios and extended safety data sheets for a mixture

Mixtures often consist of many substances. The task of including the relevant information from the exposure scenarios of the substances into the extended safety data sheet (eSDS) of the mixture can be made easier if it is possible to concentrate on substances which determine the hazardous properties and/or the Risk Management Measures (RMM) of the mixture – and to sort out substances which are not relevant for the operational conditions and the RMM.

In this context, for substance-rich mixtures, the following points are important:

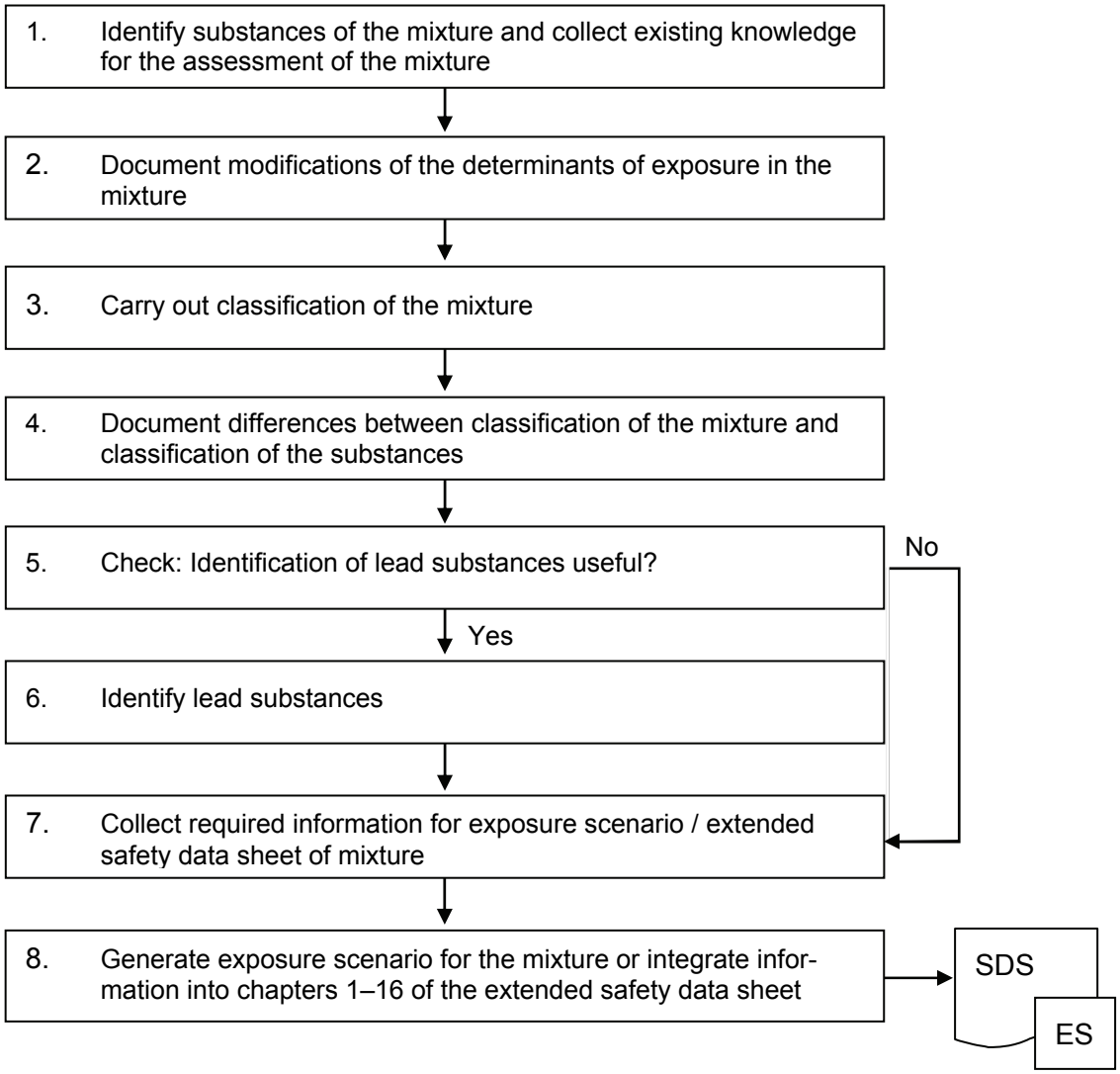
1. Information from exposure scenarios only have to be included for substances present in the mixture in concentrations above the concentration limits set in Art. 14(2).
2. If they are relevant the decision which ES of a CSA for a specific substance in a mixture is relevant should be reflected on the question “does it require risk management measures (RMMs) and operational conditions (OCs) for the mixture itself” and on the question “are the RMM not already triggered by other substances or the mixture itself (regardless if ES for these components are available)”. Tools are being developed which help to identify the risk-determining substances (lead substances, critical components, priority substances) for specific exposure routes.

The basic assumption is that if the risk associated with the lead substance is adequately controlled for a particular endpoint, risks from other substances for the same endpoint will also be controlled adequately.

## 6.1 The process and its main steps

The main steps in preparing the extended safety data sheet (eSDS) of a mixture are shown in flowchart 1. It includes the use of existing knowledge, the requirements for the classification and labelling of a mixture and also the new obligations under REACH. Flowchart 1 shows the whole process from the identification of the substance profile of the mixture and its hazard assessment until the preparation of the safety data sheet of the mixture.

**Flow chart 1: Assessment of a mixture and generation of eSDS**




In table 1, more details on the working steps are given. Step 1–4 refer to the hazard assessment of the mixture, step 5–8 to the generation of the safety data sheet for the mixture, including the option to generate an exposure scenario for the mixture.

This table refers to the case that the formulator not only forwards exposure scenarios which he has received, but consolidates or integrates the information (see chapter 7.6). Some of the steps are described in the next subchapters, as indicated in the table. For the formulator these steps require more time for a new mixture than for a product which is already used in the supply chains.

Table 1 Explanation of the working steps for assessing the hazard of a mixture and for preparing its safety data sheet.

| Step | Task | Comments |
|---|---|---|
| **1** | **Identify substances of the mixture and collect existing knowledge** | |
| 1.1 | Document existing SDS of the mixture and related product information. | Examples for such information are existing safety data sheets, technical information, information on the label, further information (e.g. from existing laws, sector specific information on adequate risk management measures). |
| 1.2 | Document recipe of the mixture | |
| 1.3 | Compile list of raw materials (substances and mixtures) used for the mixture. | This table of raw materials (List A1) contains substances as well as mixtures. |
| 1.4 | Compile substances, content (%) and classification (R phrases). List substances according to concentration in the mixture (start with the major compounds) | This step leads to a table of substances in the mixture (List A2).<br>Non-hazardous substances need not to be communicated in the safety data sheet. Therefore the full composition of the substances is not available in most cases. |
| 1.5 | Identify substances which are in general not relevant because:<br>(1) below concentration limits of DPD / REACH (0.1%, 1% or substance specific limit values, see REACH Art. 14.2)<br>(2) non dangerous / non PBT- / non vPvB- substances | Classify the substances in your list “(1)”, “(2)” |
| 1.6 | Consequences of step 1.3–1.5: How many substances are relevant for assessment of the mixture? Exclude non dangerous substances and substances below threshold. | This table (List A3) shows the substances relevant for the assessment of the mixture. |
| 1.7 | Expert judgement: check whether substances identified as non-relevant might influence the properties of the mixture / check list of relevant substances (List A3) | If required: modify the list of relevant substances. Result: List A4 |
| **2** | **Document modifications of the determinants of exposure of the mixture** | |
| 2.1 | This step requires expert judgement on the characteristics of the mixture (Physicochemical properties, human health properties, environmental properties). | Clarify: Is the assessment of the mixture based on testing of the mixture itself or is it based on properties of the substances? |
| 2.2 | Check: Do you know of interactions between the substances resulting in reduced or increased exposures? Do you know about additivity or other interactions of substances for specific endpoints? These interactions can take place on purpose to build up the specific functionality of the mixtures. They are important for the assessment of the mixture. | In most cases this knowledge is restricted to intentional interactions. See chapters 8.3 and 11 for more details.<br>Consider these findings in the assessment of the mixture. |
| **3** | **Carry out classification and labelling (C&L) of the mixture** | |
| | C&L has to be done according to DPD until 1st June 2015. C&L according to CLP Regulation is obligatory from 1st June 2015 on, but can be done voluntarily already before. | See Part I of this Practical Guide, chapter 2.6 for details on the time lines. This legal requirement is set by DPD / CLP Regulation. For C&L of a mixture according to DPD, the pH value of the mixture (if relevant) has to be considered. Furthermore, all properties of the mixture which might have relevance for the safe use have to be considered (see also chapter 8.3 and 11). |

| Step | Task | Comments |
|---|---|---|
| **4** | **Document differences between classification of the mixture and classification of substances used as raw materials for the mixture.** | |
| | Such differences indicate that information from exposure scenarios of the substances can not be used directly to compile the exposure scenario of the mixture, but need modification. See chapter 6.3 for details. | |
| **5** | **Check: Identification of lead substances useful?** | |
| | The lead substance approach is useful for substance-rich mixtures if the hazard assessment of the mixtures is based on data of the substances. If the hazard assessment is based on testing of the mixture (e.g. for physicochemical hazardous properties) or on expert knowledge, identification of lead substances is not required. | See chapter 7 for details on the appropriate approach, e.g. expert judgement, DPD+ method. In addition, companies might have own experiences in assessing lead substances at workplace which should be taken into account. |
| **6** | **Identify lead substances** | |
| | Identification of lead substances, if appropriate use of DPD+. | Chapter 7 describes the identification of lead substances and the required control steps in detail. |
| **7** | **Collect required information for exposure scenario of the mixture / for the safety data sheet of the mixture** | |
| 7.1 | Collect the SDS and ES for the lead substances and (for control purposes) also for the other relevant substances. | Information might be analysed and stored in company-specific IT systems (see chapter 9 |
| 7.2 | Analysis of data base<br>Clarification on need for further data | |
| 7.3 | Filling of data gaps: According to the timelines for registration set by REACH, exposure scenarios for many substances will not be available within the next few years. If no exposure scenarios are supplied for the lead substances of the mixture, additional data sources should be used for RMMs and OCs.<br>Starting points should be safety data sheets of the substances or current SDS of mixtures. Safety assessment should have been done already under current legislation according to the existing SDS requirements and according to the Chemical Agents Directive. They can be used as information sources.<br>Further information can be taken from existing sector-specific guidances on the use of the substances and mixtures. RMMs and OCs can be determined by using exposure assessment tools as COSSH essential / EMKG, see Annex III. If necessary, the supplier can be contacted for missing information ( e.g. use of sector-specific information).<br>Be aware that availability of ES at the supplier depends on the different REACH registration deadlines of the substances. ES of the lead substance may be received in 2013 or 2018 only if the lead substance is a low volume chemical. | |
| **8** | **Generate exposure scenario for mixture or integrate information into chapter 1–16 or Annex of the eSDS** | |
| 8.1 | Compile relevant RMM and OC | It might be that information from exposure scenarios of substances has to be adapted to the specific conditions of use in the mixture. See chapter 6.3 for details. |
| 8.2 | Consolidate the RMMs and OCs | |
| 8.3 | Check whether RMM cover all substances | Control steps are described in chapter 7.3 |
| 8.4 | Decide on scaling guidance and – if yes – develop this guidance | Details on scaling are given in Part I of the Practical Guide, chapter 7.7. |
| 8.5 | Decide in which form the information should be included in the safety data sheet of the mixture | Downstream users have several options to include information in the SDS. See chapter 5. |
| 8.5A | Structure the information as ES for a mixture<br>**or** | Structure and contents of an ES are described in Part II of the Practical Guide, chapter 9.2. |
| 8.5B | Integrate the information into the chapters 1–16 of the SDS | See chapter 5 and Annex II for details. |

The complete sequence of working steps has been elaborated in the case study of an adhesive consisting of two components (see Part V of the Practical Guide).

## 6.2 Compiling data from exposure scenarios of substances

Figure 4 gives an example of how a formulator can use the result from the identification of lead substances (using the DPD+ method described in chapter 7–7.2) to compile the information he needs for the exposure scenario of the mixture.

The example refers to a mixture composed of five substances. Three of these substances are lead substances: they are triggering the risk management measures and operational conditions of the mixture, due to their hazardous properties and their concentrations in the mixture:

- BADGE (Bisphenol A – diglycidylether) is the lead substance for dermal exposure, eye exposure and exposure of the aquatic environment;
- Xylene is triggering the risk management measures for inhalative exposure;
- Isophorone diamine is the lead substance for oral exposure.

The remaining two substances in the preparation – benzene alcohol and ethanol – are no lead substances; it is assumed that risks from these substances are adequately covered by the conditions of use identified for the lead substances.

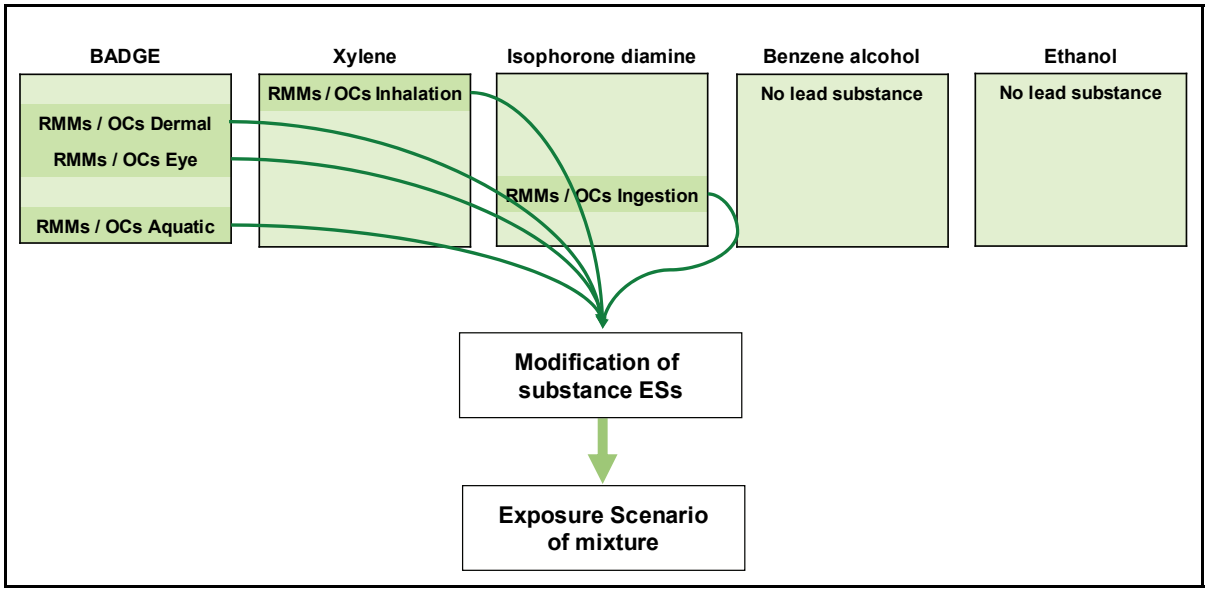



Figure 4 Compiling information from exposure scenarios of substances. By using the DPD+ approach, three substances have been identified as lead substances.

Based on this result of the application of the DPD+ method, the formulator takes the relevant pieces of information on risk management measures and operational conditions from the

exposure scenarios of the three lead substances. E.g.: for inhalative exposure, he uses the information for this exposure route from the exposure scenario of xylene, which has been identified as the lead substance for inhalative exposure.

## 6.3 Modification of substance-specific exposure scenarios

In the mixture some determinants of exposure can be different from the assumptions in the exposure scenarios of the raw materials. In this case it can be necessary for the formulator to adapt the information from the exposure scenarios of substances before he can use it for the exposure scenario of the mixture (or before integrating them in chapter 1–16 of the safety data sheet of the mixture). An example for this is shown in Table 2.

The registrant of the substance assumed that the substance is used as such. In the mixture it is used in a concentration of 60%. In addition, the registrant estimated that 10% of the substance is emitted to waste water (emission factor to water: 0.1). The formulator has additional measurements which show that for the uses of his customers emissions are below this value and only 2% are emitted (emission factor to water: 0.02). If the exposure assessment is made using a concentration of the substance in the mixture of 60% and an emission factor to water of 0.02, the amount of the product which can be used per day is calculated to 16.7 kg. This and the related input values are documented in the exposure scenario of the mixture.

Table 2 Modification of data from exposure scenario for a substance. Parameters which have been modified are underlined.

| Parameter | ES substance | ES mixture |
|---|---|---|
| C: concentration of the substance in the product | 1 | 0.6 |
| f water: emission factor to water | 0.1 | 0.02 |
| f abatement: efficiency of an abatement | 0 | 0 |
| f STP: removal of substance in sewage treatment plant | 0.15 | 0.15 |
| T emission: duration of emission [d/year] | 365 | 365 |
| CAPACITY: water treated in STP [$m^3$/d] | 2,000 | 2,,000 |
| DILUTION: dilution factor in the receiving water body | 10 | 10 |
| RCR: risk characterization ratio | 1 | 1 |
| M safe: amount of the product which can be used resulting in a RCR of 1 [kg/d] | 2 | 16.7 |

*Abbreviations: ES = exposure scenario*

The following formula has been used to calculate the maximum amount of the mixture which can be used safely taking the information from table 2 (see table 2 for abbreviations):

$$\mathbf{Msafe}_{\text{Mixture}} = \mathbf{Msafe}_{\text{Substance}} \times \frac{\mathbf{C}_{\text{ES substance}}}{\mathbf{C}_{\text{Mixture}}} \times \frac{\mathbf{f}_{\text{water, ES substance}}}{\mathbf{f}_{\text{water, Mixture}}}$$

# 7 Identification of lead substances

## 7.1 Introduction

As mixtures may consist of numerous individual substances a downstream user formulating mixtures may use substances or mixtures as raw materials. Hence, he may receive from his supplier (s)

- SDS for a substance/s and/or
- SDS for a mixture/s.

In the transitional period until all phase-in substances will be registered (until June 2018), he may receive substance SDSs with or without ES. For substances produced or imported in quantities below 10 tonnes per year only, there will be no exposure scenario even after this date.

Especially for complex mixtures, it will be difficult to manage the wealth of information on human health and environmental hazards obtained with the individual SDS. Some safety data sheets contain exposure scenarios, others not. Not for all substances limit values as DNELs and PNECs will be available.

In this case, it is helpful to identify those substances, which require specific operational conditions and/or are triggering the risk management measures. These so-called “critical components” (see ECHA Guidance for downstream users, 2008) or “lead substances” (see DPD+ methodology, below) may be endpoint- and pathway-specific, i.e. there may be different lead substances for

- oral exposure of humans;
- inhalative exposure of humans;
- dermal exposure of humans;
- Emission to the environment and exposure of the environment.

Two approaches have been discussed to identify these lead substances: The critical component approach (CCA) and the DPD+ methodology.

The **critical component approach** as outlined in the ECHA Guidance for downstream users (ECHA 2008) relies on DNEL and PNEC for all substances, their concentrations in the mixture (C) and substance- and use-specific availability parameters (A) indicating their potential

for exposure. A risk indicator RI = C x A/(DNEL, resp. PNEC) would indicate the relative contribution of an individual substance to the overall risk of the mixture.

The critical component approach has not been developed in detail yet. First ideas how to determine the availability parameters (A) and the risk indicators (RI) have been described. The principles of the approach have been presented as a concept in the European discussion process on exposure scenarios[12]. The CCA approach was considered difficult to implement, because it requires

- availability of DNEL and PNEC for all substances in the mixture (these values will be unavailable for many phase-in substances before June 2018 and for substances to be registered in quantities below 10 tonnes/a even thereafter);
- knowledge on the detailed composition of mixtures obtained from other suppliers (for all substances with DNEL, irrespective of whether they are above or below the concentration limits for classification of the mixture), which often would be considered confidential information.

Therefore, other ways were sought to identify lead substances in a mixture. An alternative method, which was developed by industry, is the **DPD+ metho**d [13]. The method is based on the current legislation for classification of mixtures as laid down in Directive 1999/45/EC ("**D**angerous **P**reparations **D**irective", DPD), amended ("**plus**") by consideration of the volatility of substances.

If for a substance identified as a lead substance no exposure scenario is available, information on adequate risk management measures and operational conditions for this substance should be identified from other sources, e.g. existing safety data sheets (see table 1, section 7.3).

## 7.2 DPD+ Methodology

*Principle*

The Dangerous Preparations Directive (DPD, Directive 1999/45/EC) requires a mixture to be classified, if endpoint-specific concentration limits are exceeded by a component of the mixture, which itself is classified based on its toxicological and/or ecotoxicological properties. The DPD+ method makes use of these rules of the DPD by comparing the concentration limits, which lead to classification of a mixture as hazardous, with the concentrations of the

[12] A presentation on the CCA approach has been given during the Workshop on exposure scenarios for preparations and generic exposure scenarios, 19-20 May 2008, Varese, Italy. The principles of the CCA approach have been described in brief in the ECHA Guidance for Downstream Users. There is no description of the CCA method available which could be used in practice.

[13] A description of the method is available at http://cefic.org/templates/shwPublications.asp?HID=750.

substances in the mixture. Therefore in DPD+ all substances classified according to Directive 67/548/EEC are taken into account.

Depending on the classification of the substance, either the general concentration limit from Annexes II, III and V of DPD for a specific R phrase is used or, if available, a substance specific concentration limit according to Annex VI of Regulation (EC) No 1272/2008 ("CLP Regulation").[14] These concentration limits are used as an indicator of the hazard associated with the substance and are compared to the concentration of the substance in the mixture. In Annex I of the methodological description of DPD+, generic concentration limits from DPD for all R phrases are listed and assigned to exposure pathways. The ratio calculated from substance concentration $C_i$ and concentration limit $C_L$ is called Lead Substance Indicator (LSI).

$$LSI = C_i/C_L$$

For the inhalation exposure, the vapour pressure VP is introduced to take into account the differences in volatility between substances

$$LSI = VP \times C_i/C_L$$

LSI are to be calculated separately for inhalation, dermal, oral and eye exposure and for the aquatic environment. The substance with the highest LSI per pathway is selected as lead substance. In the methodological description, it is emphasized that when LSIs of two substances differ by less than 10%, both substances should be considered lead substances. Moreover, when two or more substances with the same health endpoint are contained in a mixture, which may lead to additive effects, the total amount of these substances should be taken into consideration, when identifying adequate risk management measures. (Note: Expert judgement is needed in this case to decide whether the sum of the risk characterisation ratios has to be used in the assessment).

*Required input data*

The following minimum information is required for application of DPD+:

- Identity and concentration of hazardous substances in a mixture
- Classification of substances (R phrases)
- Specific concentration limits for substances, if available
- Vapour pressure of substances

General concentration limits for classification of mixtures according to Annexes II, III and V of the Dangerous Preparations Directive or substance specific concentration limits from Annex VI of the CLP Regulation are used as an input for $C_L$.

[14] Higher priority is given to substance-specific concentration limits compared to general limits as laid down in DPD.

*Applicability and Limitations of DPD+*

DPD+ has not been developed to assess physicochemical hazards. As Directive 1999/45/EC requires manufacturers of a mixture to determine the physicochemical properties of the mixture experimentally[15], identification of a lead substance is not necessary for this type of hazards.

Also, for some human health endpoints, such as skin irritation, information may be available from testing the mixture itself. In these cases, the mixture data should be used to identify suitable risk management measures and identification of a lead substance for the respective pathway is not necessary. Nevertheless, in such a case DPD+ is applicable for the other pathways.

Substances, which are carcinogenic, mutagenic or reprotoxic (category 1 or 2, according to Directive 67/548/EEC) or respiratory sensitizers or are identified PBT-, or vPvB-substances, are not covered by the DPD+ method. Mixtures containing such substances in safety-relevant concentrations require advanced considerations for identifying the substances triggering the RMM. Also, corrosiveness or applications leading to formation and inhalation of aerosols trigger additional evaluation steps beyond the application of DPD+.

Consideration of environmental effects is not as differentiated as toxicological effects as only few risk phrases for the environment exist in the current classification system. In addition, as the DPD does not contain concentration limits for R phrases R54 to R57 (toxic to fauna, flora, soil organisms, or bees), the scope of DPD+ is limited to effects on the aquatic environment.

When applying the method, its limitations should be clearly kept in mind:

- Any interactions between components of the mixture cannot be assessed by DPD+.
- Physicochemical hazards have to be judged separately.
- For considering the extent of inhalation exposure, the vapour pressure of the individual substances is included. No specific provision is foreseen to deal with high exposures due to specific application techniques such as spraying. Therefore, aerosol exposures have to be dealt with separately.
- With respect to substances, which require advanced evaluations (CMR substances category 1 or 2, respiratory sensitizers, PBT or vPvB substances, endocrine disrupting chemicals and non-biodegradable substances, see Chapter 8), the method can not be applied. Additional steps are required then to make sure that adequate risk management measures are identified to cover also these critical substances (to differentiate them from the lead substances identified by DPD+ in the following these substances are called “priority substances”). A work flow including these steps is proposed below.

[15] See Directive 1999/45/EC, Art. 5, No 2 to 4 and CLP Regulation Annex I, section 2.6.4 for exemptions from this requirement.

The possibilities of advanced evaluations of mixtures are described in chapter 8. This chapter also considers specific conditions of use, e.g. formation of aerosols.

*Experience with DPD+ and recommendations*

Within its applicability range, the method works well and is easy to use. Required input data are generally available and application of the method and identification of lead substances is straightforward. The method can be easily implemented electronically. Within the ES modifier (see Part I of the Practical Guide, chapter 7.7.2) a module with an implementation of DPD+ based on Excel® worksheets is available. Therefore, DPD+ can be considered a pragmatic, ready-to-use approach to identify lead substances.

From experience gained so far, it can be expected that in most cases risk management measures required due to the presence of CMR category 1 or 2 substances will also provide safe use conditions for the lead substance and, hence, for the whole mixture. But note that such considerations are pathway-specific. For example, nickel salts are classified as carcinogenic (category 1) after inhalation exposure only, and risk management measures for other exposure pathways may be driven by other substances within the mixture.

DPD+ can be applied to mixtures containing skin sensitizers and corrosive substances, but the widely differing potencies of substances with respect to these endpoints should be taken into consideration. When more than one substance per endpoint is present in a mixture, chosen RMM should be checked for their appropriateness for each of them.

*Further developments*

As already mentioned, intensity of (inhalation) exposure is dealt with by inclusion of the vapour pressure as the weighting factor. As the vapour pressure of the individual substances is only a rough indicator for inhalation exposure to the mixture (e.g. process temperature is not considered in this approach) further developments may use other parameters, but still the balance between accuracy and (easy) applicability has to be obeyed.

With the implementation of the new Globally Harmonised System for Classification and Labelling (GHS) by CLP Regulation (EC) No. 1272/2008 the transition to GHS has started. For continued application of DPD+, the method should be translated into the new system, which should be possible without any principle changes in methodology.

By using rules from DPD, selection of lead substances is mainly ruled by short-term effects on human health and the environment (e.g. acute toxicity, skin irritation and sensitisation, short-term aquatic toxicity). Substances having the same R-Phrase lead to the same LSI value, independently from their potency and long-term effects. In the next few years, substances with DNELs and PNECs will be increasingly available, which aim at providing safe levels for chronic exposure. It should be kept in mind that substances having the same R-Phrase (e.g. R48/20/22 or R63) may have very different DNELs. Also, for dermal exposure, scope is widened to systemic effects after repeated exposure, with skin penetration varying

widely between chemicals. In the future, means should be sought to integrate various and different substance specific levels of information in the identification of the lead substances.

*Rules for using (substance-specific) concentration limits*

Some hazard classifications of a substance lead to different classifications of the mixture, depending on substance concentration. For example, a corrosive compound (R 34) leads to classification of the mixture as irritating (R 36/38), if the concentration is ≥ 5%, but to classification as corrosive (R 34), if the concentration is ≥ 10%.

DPD+ uses the lowest concentration for each R phrase, which triggers any classification of the mixture, even when a different R phrase results (in the example above 5% would be used for calculation of the LSI).

The same principle applies to substance-specific concentration limits. The evaluator has to identify the concentration limits related to a specific R phrase.

Examples for application in DPD+ and the identification of the lead substances are given in table 3 A and B.

Table 3 Example for application of DPD+ to a mixture (two component adhesive) containing 5 components

*A: compilation of input data*

| **Overall Composition** | | **Vapour pressure (hPa at 25°C)** | **R-phrase** | | | | | **default concentr. limit (%)** | **specific concentr. limit (%)** |
|---|---|---|---|---|---|---|---|---|---|
| Component | % | | inhalation | dermal | eye | ingestion | aquatic | | |
| BADGE | 60.00% | low | | R38 | | | | 20.00% | 5.00% |
| BADGE | 60.00% | low | | | R36 | | | 20.00% | 5.00% |
| BADGE | 60.00% | low | | R43 | | | | 1.00% | |
| BADGE | 60.00% | low | | | | | R51/53 | 2.50% | |
| Xylene | 10.00% | 10.65 | R20 | | | | | 25.00% | 12.50% |
| Xylene | 10.00% | 10.65 | | R21 | | | | 25.00% | 12.50% |
| Xylene | 10.00% | 10.65 | | R38 | | | | 20.00% | |
| Isophorone diamine | 18.00% | 0.0258 | | R21 | | | | 25.00% | |
| Isophorone diamine | 18.00% | 0.0258 | | | | R22 | | 25.00% | |
| Isophorone diamine | 18.00% | 0.0258 | | R34 | | | | 5.00% | |
| Isophorone diamine | 18.00% | 0.0258 | | | R34 | | | 5.00% | |
| Isophorone diamine | 18.00% | 0.0258 | | R43 | | | | 1.00% | |
| Isophorone diamine | 18.00% | 0.0258 | | | | | R52/53 | 25.00% | |
| Benzyl alcohol | 10.00% | 0.13 | R20 | | | | | 25.00% | |
| Benzyl alcohol | 10.00% | 0.13 | | | | R22 | | 25.00% | |
| Ethanol | 2.00% | 78.91 | | | | | | | |

*B: Identification of lead substances (highest LSI per pathway in bold and grey shades)*

| Overall Composition | inhalation | | dermal | | eye | | ingestion | | aquatic | |
|---|---|---|---|---|---|---|---|---|---|---|
| Component | R-phrase | LSI | R-phrase | LSI | R-phrase | LSI | R-phrase | LSI | R-phrase | LSI |
| BADGE | | | R38 | 12,0 | | | | | | |
| BADGE | | | | | R36 | **12.0** | | | | |
| BADGE | | | R43 | **60.0** | | | | | | |
| BADGE | | | | | | | | | R51/53 | **24.0** |
| Xylene | R20 | **8.5** | | | | | | | | |
| Xylene | | | R21 | 0.8 | | | | | | |
| Xylene | | | R38 | 0.5 | | | | | | |
| Isophorone diamine | | | R21 | 0.7 | | | | | | |
| Isophorone diamine | | | | | | | R22 | **0.7** | | |
| Isophorone diamine | | | R34 | 3.6 | | | | | | |
| Isophorone diamine | | | | | R34 | 3.6 | | | | |
| Isophorone diamine | | | R43 | 18.0 | | | | | | |
| Isophorone diamine | | | | | | | | | R52/53 | 0.7 |
| Benzyl alcohol | R20 | 0.05 | | | | | | | | |
| Benzyl alcohol | | | | | | | R22 | 0.4 | | |
| Ethanol | | | | | | | | | | |

*Abbreviations:* *BADGE = Bisphenol A – diglycidylether*
*LSI = Lead substance indicator*
*R-phrase = risk phrase*

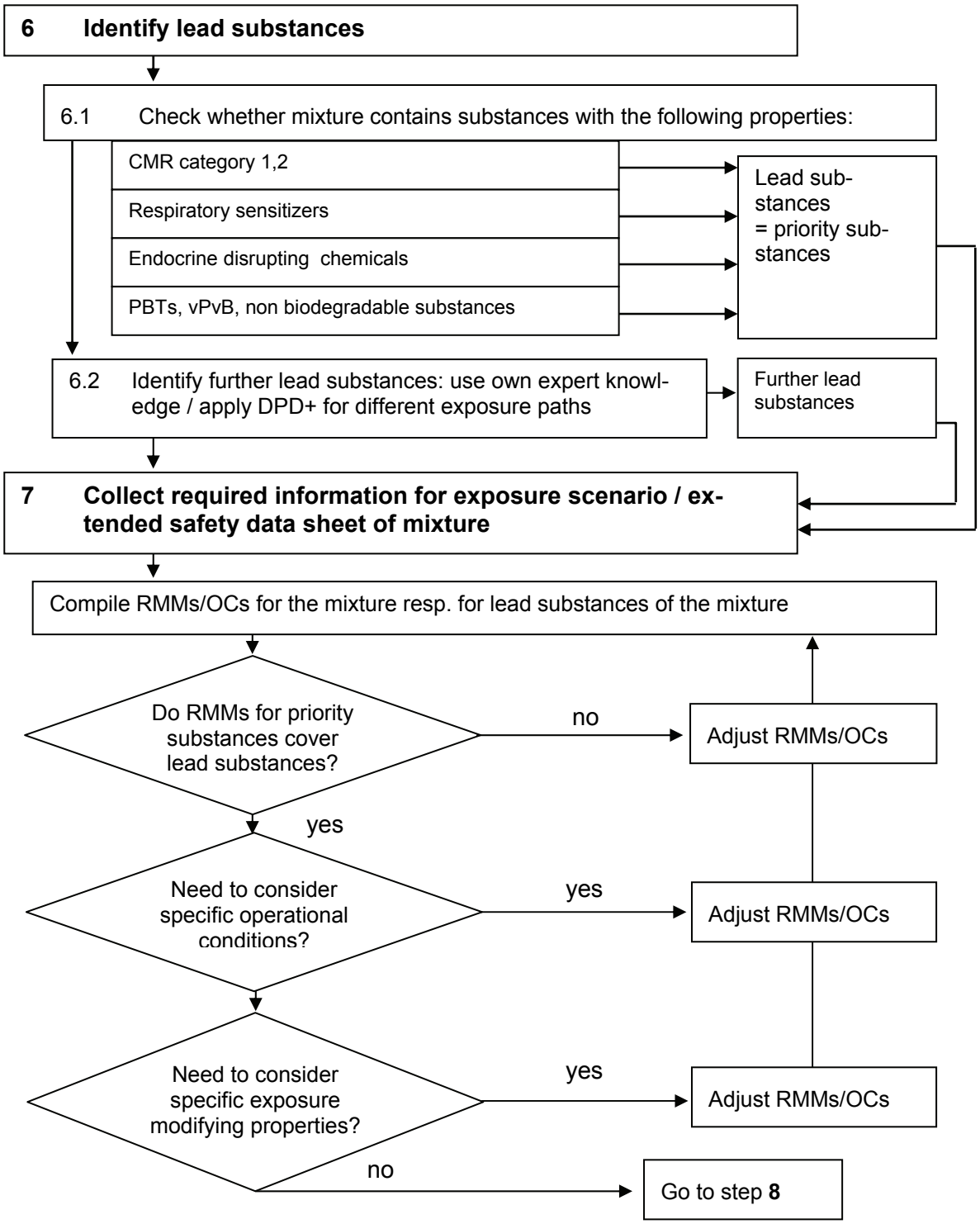
## 7.3 Workflow to identify lead substances based on the DPD+ method

The working steps for the determination of lead substances are given in more detail in Flow Chart 2.

The analysis starts with the identification of substances which require an advanced evaluation (e.g. substances classified as carcinogenic, category 1 or 2). If such “priority” substances are present in the mixture in relevant concentrations, adequate risk management measures for these substances are identified first.

In the next step, additional lead substances are identified using the DPD+ method. After this, it is determined if the risk management measures for the priority substances allow an adequate control of all identified lead substances. If not, additional risk management measures have to be identified covering all identified lead substances.

**Flow chart 2: Working steps to identify lead substances (step 6) and to compile adequate risk management measures (step 7)**

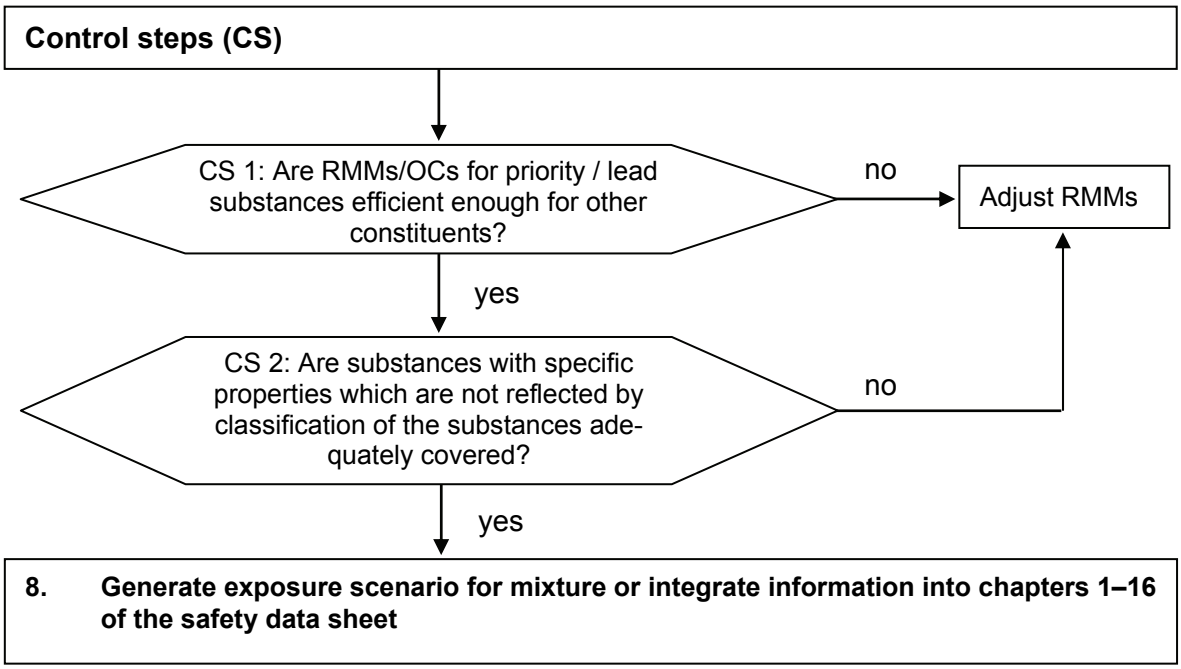



CMR category 1,2: carcinogenic, mutagenic or reprotoxic category 1 or 2
PBTs: Persistent and bioaccumulative and toxic substances
vPvB: very persistent and very bioaccumulative substance

** Endocrine disrupting chemicals with equivalent level of concern with CMR level 1 and 2*

Priority and lead substances generally require the most stringent risk management measures. However, if these measures are substance-specific (e.g. a precipitation step), it is possible that they do not control adequately other substances of the mixture with different physicochemical properties. Therefore it is recommended to apply control steps to ensure that the recommended risk management measures are really adequate for the mixture. These steps are shown in Flow Chart 3.

**Flow chart 3: Control steps**




Abbreviations:
RMMs: Risk Management Measures
OCs: Operational Conditions

**Control step 1** aims to ensure that risk management measures for lead and/or priority substances cover also the other substances in the mixture. Possibly, the substance-specific measure removes the lead substance very efficiently (e.g. precipitation of remaining sulphide concentration in the waste water with iron hydroxide). However, the precipitation has no effect on any surfactant existing in the mixture. In this case risk management measures for the surfactant (as proposed in the respective safety data sheet) have to be considered for inclusion.

Another example is substances in mixtures, which require specific gloves for sufficient protection against dermal exposure. The gloves required for lead substances, however, do not

necessarily ensure skin protection against further substances contained in the mixture. Protection against these substances may necessitate other gloves.

In practice, it is recommended to screen the substances' safety data sheets as well as its exposure scenarios with regard to prescriptions on substance-specific risk management measures. If such measures are prescribed therein, it may become necessary to adjust those measures identified for lead substances.

**Control step CS 2** refers to substances causing risks to humans or the environment, which is indicated by other information such as available DNELs, OELs (occupational exposure limits) or PNECs even if they don't fulfil the classification and labelling criteria. REACH requires an assessment of the risks caused by the use of substances.

If for substances in the mixture low threshold values (e.g. OELs) or DNELs/PNECs are documented in the safety data sheet, it should be checked that these substances are adequately covered by the proposed RMMs and operational conditions. Proposed RMMs and OCs should be in line with sector-specific recommendations.

It should be systematically checked, whether exposure scenarios of substances provide specific risk management measures and operational conditions for impact areas and exposure routes, which are not related to the classification of the substances. It has to be ensured that this information is included adequately when compiling the SDS of the mixture. In these cases it might be that a modification of the recommended RMMs and OCs is required.

Note: There is no need for a comprehensive study of all relevant information. Control steps 1 and 2 intend to take into account additional substance specific information which is available. This can be done by a screening of the exposure scenarios which have been received from the supplier.

# 8 Advanced evaluation of mixtures

## 8.1 Specific intrinsic properties of substances

As discussed above, some groups of substances are not covered by the DPD+ approach. The most prominent of these groups are substances classified as carcinogenic, mutagenic or toxic to reproduction (CMR substances, category 1 or 2). The occurrence of one or more CMR category 1 or 2 substances in a mixture above their classification limits triggers an advanced evaluation to make sure that adequate risk management measures are identified to cover these critical components.

The European Occupational Safety and Health Legislation (among them Directive 2004/37/EG), requires – if substitution is not possible – strict exposure reduction and control measures. In general, it is plausible to assume that risk management measures triggered by

the presence of a CMR, category 1 or 2, substance would also lead to adequate control measures for other substances at the workplace. But for some substances, CMR properties are associated with a particular exposure pathway. For example, nickel compounds are classified as R49 ("may cause cancer by inhalation") and risk management measures would tend to control inhalation exposure only. In such cases, pathway-specific consolidation of measures triggered by both the CMR substance and the identified lead substance is compulsory.

The same principles apply to other substances with specific health hazards such as respiratory sensitizers or PBT or vPvB substances, which are also not within the scope of DPD+. For some known respiratory sensitizers such as toluene di-isocyanates (TDI) or diphenylmethan-4,4'-diisocyanate (MDI) sector-specific guidance is available, which can be used for an advanced evaluation. For example, the European Diisocyanate and Polyol Producers Association provides valuable safety and health information on its website (www.isopa.org). The German Technical Rule for Hazardous Substances TRGS 430 provides guidance on hazard and exposure assessment and identification of risk management measures for workplaces where isocyanates are used.

For PBT and vPvB substances it is necessary to implement and recommend risk management measures which minimise exposures and emissions as far as possible (REACH Annex I, 6.5). For these substances a quantitative risk characterisation is not possible. Further guidance is given in chapter R11 of the ECHA Guidance on information requirements and chemical safety assessment (ECHA 2008).

At present, no generally harmonized and agreed testing strategy exists to identify endocrine active chemicals and to asses whether they lead to adverse effects (endocrine disruption). This has to be examined case by case.

For the identification of adequate risk management measures existing experience with the management of substances classified e. g. as toxic for reproduction (according to Directive 67/548/EEC) can be used as starting point – as long as no further information is available from the CSA of these substances.

**Advanced evaluation in the case of CMR substances – the borate example.**

With the first "Adaptation to technical and scientific progress" (ATP) to Regulation (EC) No 1272/2008 („CLP-Regulation") borates like disodium tetraborate has been classified as reproductive toxins (Repr. Cat. 2; R60-61) and in consequence mixtures containing ≥4.5% of this substance have to be classified as toxic for reproduction (category 2).

For disodium tetraborate a NOAEL with regard to reprotoxic effects can be identified in reliable experimental studies, which then allows the derivation of a DNEL. As a consequence, the specific concentration limit for classification is significantly higher (4.5%) than the default classification limit of 0.5% for R60-61. This DNEL can be used to perform a

substance-specific evaluation for inhalative and dermal systemic effects. RMMs identified in this evaluation can be compared with RMMs relevant for the lead substances as identified by the DPD+ method for all pathways and endpoints

## 8.2 Specific conditions of use

Specific forms of application of mixtures require considerations which are beyond the "individual substance" scope generally applied. For example, spraying leads to generation of substantial amounts of aerosols. Independently of the hazardous properties of the substances contained in the aerosol, inhalation of large quantities of particles in the respiratory tract may affect the capability of human lungs for self-cleaning and regeneration. Furthermore, the increased surface area during spraying leads to accelerated release of volatile compounds. Therefore, many EU countries have established occupational exposure limits (OEL) for dust and/or fine dust (diameter < 10 µm) even for inert materials like iron or aluminium. Germany adopted a general fine dust OEL of 3 mg/m³ (respirable fraction). According to BG rule 231 (of the German Institution of statutory accident insurance and prevention) the analytical limit of detection of 1.45 mg/m³ can be used for evaluating risks from exposure to paint aerosols. It is evident that paint aerosol concentrations in operators' respiratory environment may easily exceed either of these concentration limits, making respiratory protection equipment mandatory even when effective ventilation is provided.

Other examples for conditions of use, where risk management measures are triggered by considerations other than substance-specific health hazards, are generation of fine dusts and fumes in processes in the metal industry and other industrial surroundings. Also during service life of many products (e.g. coatings), processes such as grinding, sanding, or polishing and also during recycling of coated objects specific exposure conditions such as dust generation may occur, which have to be considered specifically.

## 8.3 Interactions between substances of a mixture

Hazard assessment of formulations may differ from substance-based hazard assessment, as some properties will change significantly. Hazards associated with dustiness and surface properties of particles (silicogenic particles, nanoparticles) are negligible as long as these particles are integrated into a polymer matrix. Flammability of solids (aluminium, nitro cellulose) is not relevant below specific concentrations. Corrosiveness of organic acids and amines is lost due to buffering mechanisms of the formulation (antagonism). Classification derived from flash point may be overruled for water-based materials.

On the other hand, under specific conditions, harmful properties may be enhanced in mixtures (synergism). Some substances, such as dimethyl sulfoxide may enhance skin penetrations of others, thus leading to higher toxicity after dermal exposure.

Evaluation of specific properties of mixtures relies heavily on the expert knowledge of the formulator, as the effects of a multitude of possible combinations of substances in a mixture cannot be anticipated. More details on different properties of mixtures are given in section 11.

# 9 IT support for the compiling of safety data sheets for mixtures

Many companies generate SDSs for their chemical products in an automated process. This is especially the case for companies producing hundreds or thousands of products. Often SDSs are generated in more than 30 languages.

REACH requires including additional information from exposure scenarios of substances into the SDSs of mixtures. For an effective implementation of this requirement, it is necessary that it can also be done to a large extent automatically. “Manual” application of expert judgement should be minimized as much as possible. (At least for a final check of the result of the automatic compilation process expert judgement is needed).

The tasks described above to generate an extended safety data sheet for a mixture can be supported by IT systems. This is easier to do if the additional information in the exposure scenarios is structured in a uniform and modular way. The principal approach of generating extended safety data sheets in an automated process is illustrated in figure 5[16].

[16] The following three figures have been elaborated from Mr. Morabito, DuPontCoatings. They are based on the system which is used in this company.

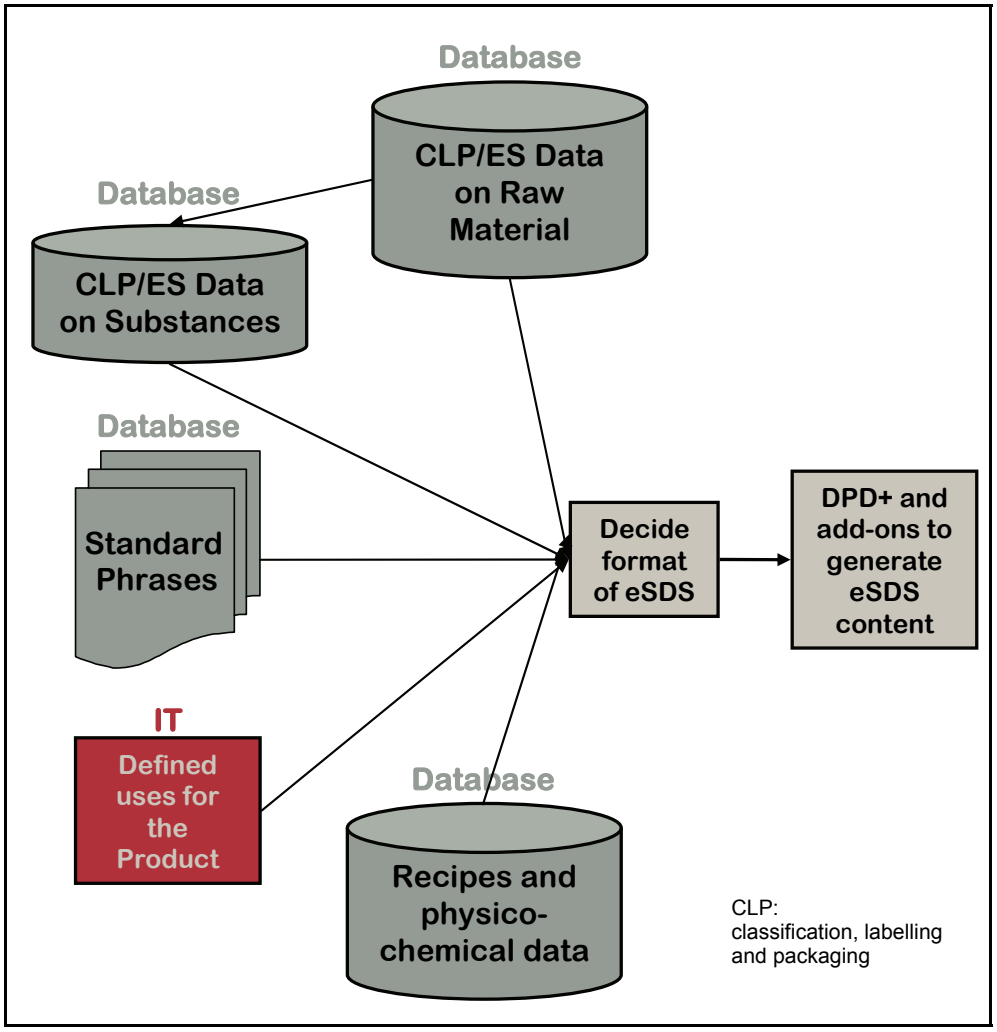



Figure 5 Elements of an IT system for the generation of extended safety data sheets (eSDS).

Information on classification, labelling and packaging (CLP data) and exposure scenarios of raw materials are stored in a specific database (these raw materials are substances or mixtures). From this database information on substances is extracted and stored in a second data base. Further databases contain standard phrases used for safety data sheets, description of the uses of the products, appropriate risk management measures, recipes and physicochemical data of the mixtures.

The extended safety data sheet for the mixture is generated based on the composition and physicochemical data of the mixture.

Even today, the application of the Dangerous Preparation Directive to classify and label a mixture is done automatically in many cases. In a similar way, additional assessment steps such as the selection of lead substances can be implemented in existing IT systems for the generation of SDSs of mixtures.

In addition, expert judgement which is needed for an advanced evaluation can be integrated if it refers to standard situations, e.g. substances with defined properties like CMR1 and CMR2 (see chapter 8.1). These properties can be clearly identified from the results of the classification of the substance. In addition, further risk management measures for specific conditions of use (e.g. spray applications with aerosol formation) can be added automatically if this is indicated for a specific use in the underlying database.

Examples for a decision tree which can be implemented in an IT system are given in the following figures 6 and 7. These figures aim to illustrate the possibility to use IT systems for the generation of extended safety data sheets. It refers to an existing system in a company manufacturing coating products. Therefore the decision trees show the principal structure and company-specific elements, e.g. modules for spray applications.

It depends on the internal organisation and the products of a company how such a decision tree is structured in detail.

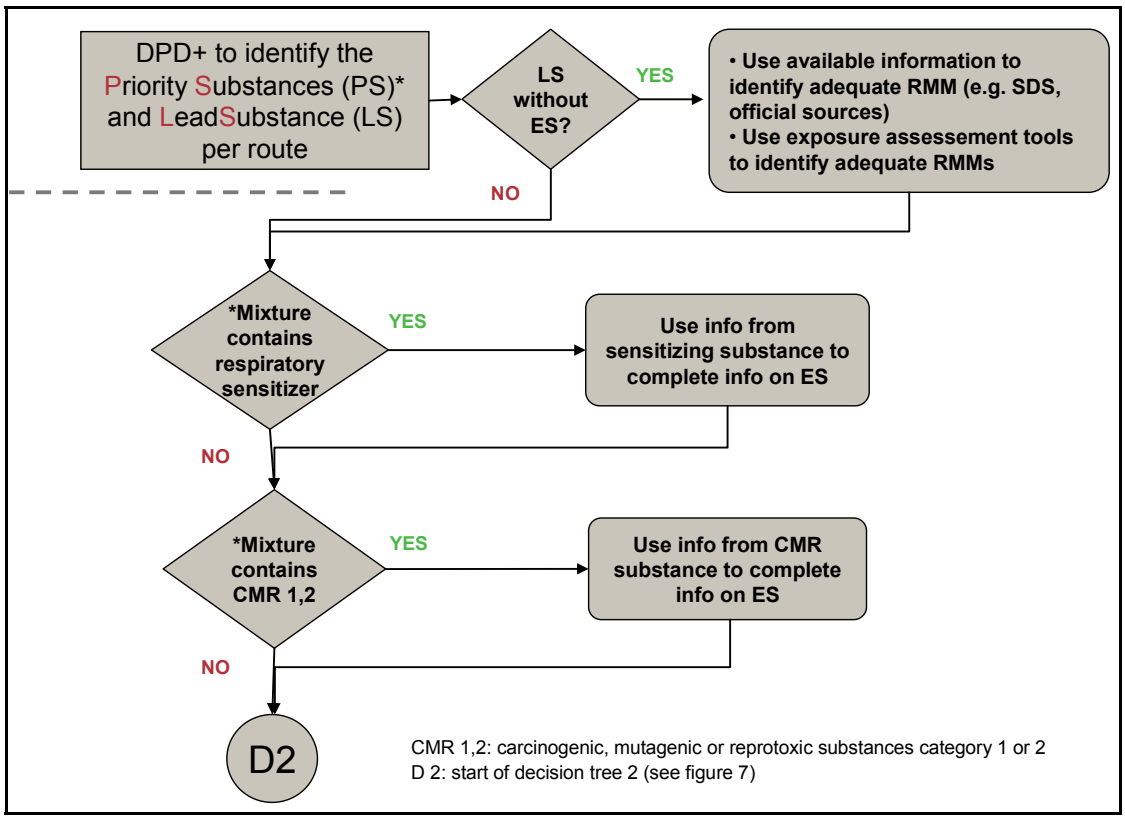



Figure 6 Decision tree for implementation of an advanced evaluation of mixtures in an IT system. Focus is set on the specific properties of substances.

Starting point of the decision tree in figure 6 are the results of the application of the DPD+ method. It leads to the identification of priority substances and lead substances. The first question which can be answered automatically is whether for the lead substances exposure scenarios are available. If this is not the case, information from other sources has to be used to find adequate risk management measures. Sources which can be used here are existing safety data sheets or exposure tools which propose risk management measures (e.g. EMKG, see chapter 6.1, table 1, section 7.3 and Annex III). Tests showed that in most cases suppliers are willing to give additional information on their products.

Figure 6 shows two additional questions which can be answered automatically: does the mixture contain respiratory sensitizers or substances classified as carcinogenic, mutagenic or toxic to reproduction category 1 or 2? In both cases it is necessary to adjust the risk management measures in the exposure scenario addressing these specific intrinsic properties.

Specific conditions of use can change the exposure situation. Therefore they have to be taken into account if the safety data sheet of a mixture is prepared. The decision tree in figure 7 refers to three specific situations: use of high temperature, use of mixtures as part of 2 component systems and uses which include spraying.

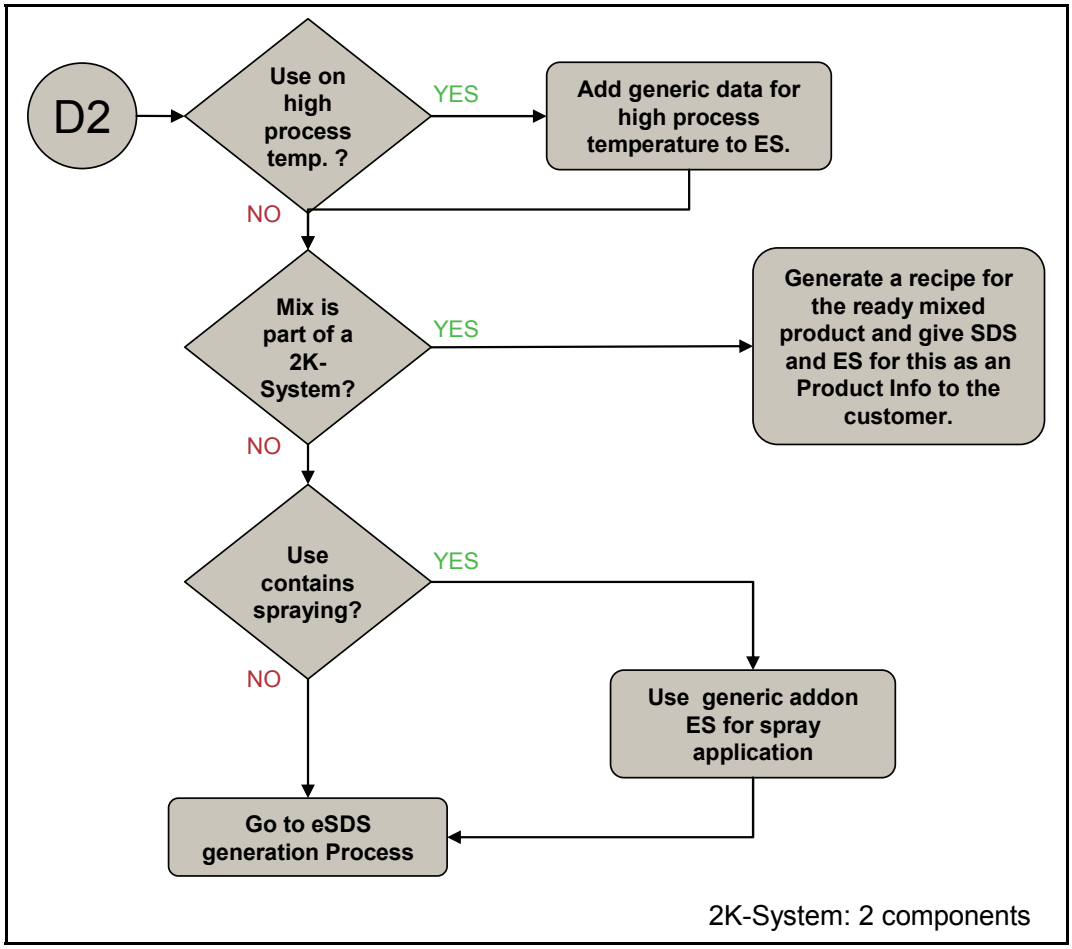



Figure 7 Decision tree for implementation of an advanced evaluation of mixtures in an IT system. Focus is on specific conditions of use.

In case of processes at high temperature and processes with spray applications additional specific risk management measures are described in the extended safety data sheet of the mixture. For these cases generic descriptions are available and replace the substance specific data, evaluated before.

In case of mixtures used as part of a two component system, additional product information is generated. It refers to the recipe of the ready mixed product (which can be introduced into the same IT system). This additional document describes the appropriate risk management measures for the ready mixed product.

## 10 Downstream User Chemical Safety Assessment for a mixture

The hazardous properties and other exposure determinants of a mixture can deviate from the properties of the substances it contains (see chapter 8.3 and 11). When several substances in a mixture are used outside the conditions described in the related exposure scenarios, the downstream user has to carry out chemical safety assessments for each of these substances (see Part I, chapter 7.8 of the REACH Practical Guide).

As an alternative option, the downstream user can perform a chemical safety assessment for the mixture as a whole. A CSA for a mixture is voluntary – however, it can be more efficient than several assessments related to single substances in the mixture. The downstream user includes the results from the assessment in his safety data sheet and attaches an exposure scenario. The safety data sheet of the mixture has to be consistent with the CSA of the mixture (instead of including information from the CSAs of the substances of the mixture).

If a mixture contains many substances it is possible to concentrate the work on the substances which determine the risks of the mixture instead of assessing all substances in the mixture.

The main steps in making a CSA for a mixture are[17]:

- Develop the exposure scenario for the mixture – describe the conditions of use. These conditions are the same for all substances in the mixture.
- Check if the exposure scenario should be based on the properties of the mixture or on the properties of specific critical substances or lead substances (see chapter 7).
- If one or more risk determining substances in the mixture are selected assess their safety. For these substances, exposure assessments and risk characterisations have to be made.
- Specifying adequate risk management measures and operational conditions which ensure a safe use of the risk determining substances.
- Controlling that the recommended conditions of use cover the potential exposure from all substances in the mixture and from the mixture as such.

The results of a CSA for a mixture are documented in a chemical safety report (CSR). The downstream user chemical safety report for a mixture is structured according to REACH Annex XII and Annex I.

- In the report, the hazard data for the substances in the mixture and the references are given (e.g. taken from the SDS of the substances). In addition, the hazard data of the mixture should be given.

[17] In the ECHA Guidance for downstream users (ECHA 2008) a description is given how to perform a CSA for a mixture (Chapter 7.13, (p. 79ff, fig. 7.5 in the version of May 2008).

- If risk determining substances have been identified, the substances and the method used for identification are documented (results, reasoning).
- The exposure scenario which is part of the report covers all substances in the mixture; results of the exposure assessment and the risk characterization are documented separately for each of the risk determining substances, but as well for the mixture as such.
- It is documented that the recommended conditions of use cover all substances in the mixture and the mixture as such.

The downstream user CSA (for a mixture or for a substance) has not to be sent to ECHA. However, the downstream user has to inform ECHA about substances for which the conditions of use are not covered by the exposure scenario of its supplier.

In section 15 of the safety data sheet, the downstream user indicates that a CSA has been made. He documents which substances of the mixture have been covered by this assessment.

Further details on how to do a downstream user CSA for a mixture are given in the ECHA Guidance for downstream users chapter 7.13, p. 79ff, figure 7.5 (ECHA 2008). A short introduction is given in the same document in chapter 7.1 (p. 62) and 7.2.2 (p.65).

# 11 Differences between properties of mixtures and properties of their raw materials

Chapter 7.3 described how interactions between substances of a mixture can be taken into account in the advanced evaluation of mixtures. The following part gives some additional information why this point is of importance for the assessment of mixtures.

Mixtures can have properties which are quite different from the properties of the substances used as raw materials. The hazardous potential of a substance in a mixture can be lowered (e.g. by dilution of a substance classified as corrosive below the concentration which triggers this characteristic). On the other hand hazardous properties can be enhanced: e.g. a specific additive can increase the solubility of a substance in the mixture or its bioavailability.

Risk management measures which are adequate for the safe use of substances are communicated with the related safety data sheets. Due to the above described differences between the properties of substances and mixtures, in many cases it will not be appropriate to recommend the risk management measures of the substances directly for the mixtures. Adequate risk management measures for mixtures have to be identified based on the knowledge about the properties of the mixture.

Depending on the complexity of the mixtures, their properties can be difficult to predict. Therefore, in any case, existing knowledge regarding the function and possible interactions between substances have to be taken into account when assessing a mixture.

An example for a mixture with a limited number of substances is given in the next table. It refers to a real spray oven cleaner for private use. It shows a moderate degree of complexity and consists only of five substances including water. The case studies in the project cover mixtures with a wide range of complexity. They also include mixtures used as performance coatings consisting of more than 20 substances.

Table 4 Recipe of a spray oven cleaner intended for private households.

| Nr. | Raw material | Comments | Concentration of pure substance | Classification & Labelling |
|---|---|---|---|---|
| 1 | Water | | 91.50 | Non hazardous |
| 2 | Sodium hydroxide 33% | | 2.50 | C – R 35 |
| 3 | Sodiumethylhexyl-sulfate | (43% in water)<br>Anion. tenside | 4.00 | Xi – R 38, R41 |
| 4 | Lithium Sodium Magnesium Silicate | | 1.90 | non hazardous |
| 5 | Xanthan Gum | | 0.10 | non hazardous |

Nevertheless, even a mixture such as the oven cleaner with only two substances classified as hazardous can show important factors regarding exposure estimation. The size of the particles which are released during the use of the product is mainly determined by the non-hazardous ingredient xanthan gum. This substance is used in the mixture as a thickener. Even in low concentrations it considerably increases the size of the particles and minimizes the number of inhalable particles. An assessment of the mixture which only considers the hazardous compounds of the mixture would overlook this effect and lead to a wrong estimation of the exposure situation. The oven-cleaner formula refers to a foam – and not to an aerosol with inhalable droplets. Therefore an exposure scenario for spray applications is not applicable in this case.

Therefore, for the assessment of the mixture's properties and the exposure, four factors can play an important role:

- properties of the substances in the mixture used as raw materials;
- concentration of the substances in the mixture;
- interactions between substances of the mixtures (some of them might be intended for the function of the mixture);
- operational conditions of use of the mixture (e.g. increased volatility of substances in a mixture if the mixture is used at higher temperatures).

Already before REACH, the Dangerous Preparations Directive (DPD) set legal requirements on how to assess the hazardous potential of a mixture in order to classify and label it. For some properties of mixtures, e.g. physicochemical properties such as the flash point, a direct testing of the mixture may be required. For some phisico-chemical-properties calculation is allowed, example given flash point. For other properties, e.g. human health hazards, DPD describes calculation methods which allow a classification and labelling of the mixture based on the properties of substances and their concentrations.

If mixtures have specific properties with relevance for the exposure situation, it is likely that they require an advanced evaluation (see chapter 8.3 on advanced evaluation).

In case a mixture has specific properties, information should be given by the formulator to his supplier of substances in order to ensure that these properties are covered by the registration – see chapter 4.4.

# 12 Glossary

| | |
|---|---|
| **AC** | Article category |
| **BREF** | Best Available Technique (BAT) Reference Notes |
| **CAD** | Chemical Agents Directive 98/24/EC |
| **CLP Regulation** | Regulation on classification, labelling and packaging of substances and mixtures, Regulation EC No 1272/2008 |
| **CMR** | Substances which are carcinogenic, mutagenic or of reproductive toxicity |
| **Conditions of use** | Conditions of use are operational conditions (OC, e.g. duration of activity) and risk management measures (RMMs, e.g. local exhaust ventilation) |
| **ConsExpo** | Model for exposure estimation and risk description for exposures of consumers |
| **COSHH** | Control of Substances Hazardous to Health. Approach from Great Britain for the derivation of risk management measures for workplace. |
| **CSA** | Chemical safety assessment |
| **CSR** | Chemical safety report |
| **DNEL** | Derived No-Effect Level |
| **DPD** | Dangerous Preparation Directive, Directive 99/45/EC |
| **DPD+ methodology** | Method to identify lead substances in mixtures based on the Dangerous Preparation Directive |
| **ECETOC-TRA** | Model for exposure estimation and risk description. TRA: “Targeted |

| | |
|---|---|
| | Risk Assessment” |
| **EDC** | Endocrine disrupting chemical |
| **EMKG** | “Einfaches Maßnahmenkonzept Gefahrstoffe” (“Easy-to-use workplace control scheme for hazardous substances”). Generic model for exposure estimation at the workplace worked out by the BAuA. |
| **ES** | Exposure Scenario |
| **sSDS** | Extended Safety Data Sheet |
| **ERC** | Environmental Release Category. Categories for release of chemical substances into the environment. |
| **ESIG** | European Solvents Industry Group |
| **ESVOC** | European Solvents Volatile Organic Compounds |
| **EUSES** | Generic model for environmental-related exposure assessment. |
| **Exposure** | Exponere (lat): to be set out; contact between a chemical substance or a physical or biological agent on the one hand and an organism or an environmental compartment on the other. |
| **GHS** | Globally Harmonized System of Classification and Labelling. It is implemented in Europe by the CLP Regulation. |
| **OC** | Operational condition (of use) such as duration and frequency of substance use, application temperature, state of aggregation of the substance |
| **OEL** | Occupational Exposure Limit |
| **PBT** | Persistent, bioaccumulative and toxic (substance) |
| **PC** | Product category |
| **PEC** | Predicted Environmental Concentration |
| **PNEC** | Predicted No-Effect Concentration |
| **PROC** | Process category |
| **RCR** | Risk Characterisation Ratio |
| **RMM library** | Library of risk management measures. Compilation of risk management measures for exposure assessments with data on the efficiency of the measures (http://www.CEFIC.org/files/downloads/RMM%20Library%20.xls 'Individual Measures'!A1). |
| **RMM** | Risk management measure (e.g. local exhaust, closed equipment, gloves of a certain specification, instructions). For details, see Part I of the Practical Guide, chapter 6.3. |
| **SDS** | Safety data sheet |
| **Scaling** | Here: Use of simple arithmetic operations, in order to be able to calculate with exposure estimates based on one’s own specific input values. |

| | |
|---|---|
| | This is simple where there is a linear dependence between the exposure level and the input. (Example: with a doubling of the receiving waters volume, the calculated concentration of a substance which can be expected there, if the other input parameters remain equal, is halved.) |
| **SU** | Sector of use |
| **SVHC** | Substances of very high concern |
| **Use Descriptor System** | System for the short description of uses. The abbreviations specified in this system can be used in the short title of an exposure scenario, in order to give a first indication, in which industries a substance is used, to which type of product it belongs, during which processes it is used and – if of importance – in which products it can appear later on. |
| **vPvB** | very Persistent and very Bioaccumulative (substance) |

# Annex I: Concentrations limits for substances in mixtures according to REACH Art. 14.2

1. Substance specific concentrations limits. These concentration limits are given in an agreed entry in the classification and labelling inventory referred to in Article 42 of Regulation (EC) No 1272/2008 or specific concentration limits that have been set in Part 3 of Annex VI to Regulation (EC) No 1272/2008 (CLP Regulation))
2. For substances classified as hazardous to the aquatic environment, if a multiplying factor („M-factor“) has been set in Part 3 of Annex VI to the CLP Regulation, the cut-off values in table 1.1 of Annex I to the CLP Regulation apply. The concentration limits are the same as the values given in table A.1
3. For substances of acute aquatic toxicity and for substances with are very toxic to the aquatic environment and may have long term adverse effects on aquatic organisms (classified as very toxic for the aquatic environment) concentration limits depend on the toxicity of the substances (if these concentration limits are below the applicable concentrations defined in the table of Article 3.3 of the Dangerous Preparations Directive) – see the following tables A.1–A.2

Table A.1: Values for acute aquatic toxicity and long-term adverse effects of substances classified as “very toxic to the aquatic environment” and corresponding concentration limits for the classification of mixtures containing these substances (Annex III Part B of the Dangerous Preparations Directive).

| LC50 or EC50 value (‘L(E)C50’) of substance classified as N, R50-53 (mg/l) | Classification of the preparation | | |
|---|---|---|---|
| | N, R50-53 | N, R51-53 | R52-53 |
| 0,1 < L(E)C50≤ 1 | Cn ≥ 25 % | 2,5 % ≤ Cn < 25 % | 0,25 % ≤ Cn < 2,5 % |
| 0,01 < L(E)C50≤ 0,1 | Cn ≥ 2,5 % | 0,25 % ≤ Cn < 2,5 % | 0,025 % ≤ Cn< 0,25 % |
| 0,001 < L(E)C50≤ 0,01 | Cn ≥ 0,25 % | 0,025 % ≤ Cn < 0,25 % | 0,0025 % ≤ Cn < 0,025 % |
| 0,0001 < L(E)C50≤ 0,001 | Cn ≥ 0,025 % | 0,0025 % ≤ Cn < 0,025 % | 0,00025 % ≤ Cn< 0,0025 % |
| 0,00001 < L(E)C50 ≤ 0,0001 | Cn ≥ 0,0025 % | 0,00025 % ≤ Cn< 0,0025 % | 0,000025 % ≤ Cn < 0,00025 % |

For preparations containing substances with a lower LC50 or EC50 value than 0,00001 mg/l, the corresponding concentration limits are calculated accordingly (in factor 10 intervals).

Table A.2: Values for acute aquatic toxicity of substances classified either as N, R50 or as N, R50-53 and corresponding concentration limits for the classification of mixtures containing these substances (Annex III Part B of the Dangerous Preparations Directive)

| LC50 or EC50 value ('L(E)C50') of substance classified either as N, R50 or as N, R50-53 (mg/l) | Classification of the mixture N, R50 |
|---|---|
| 0,1 < L(E)C50 ≤1 | Cn ≥ 25 % |
| 0,01 < L(E)C50 ≤ 0,1 | Cn ≥ 2,5 % |
| 0,001 < L(E)C50 ≤ 0,01 | Cn ≥ 0,25 % |
| 0,0001 < L(E)C50 ≤ 0,001 | Cn ≥ 0,025 % |
| 0,00001 < L(E)C50 ≤ 0,0001 | Cn ≥ 0,0025 % |

For preparations containing substances with a lower LC50 or EC50 value than 0,00001 mg/l, the corresponding concentration limits are calculated accordingly (in factor 10 intervals).

4. For all other substances the general applicable concentrations are relevant as defined in the table of Article 3.3 of the Dangerous Preparations Directive 1999/45/EC, see the following table A.3.

Table A.3 Applicable concentrations defined in Art. 3 par. 3 of the Dangerous Preparations Ddirective

| Category of danger of the substance | Concentration to take into consideration for gaseous mixtures | |
|---|---|---|
| | gaseous mixtures % vol/vol | other mixtures % w/w |
| Very toxic | ≥ 0,02 | ≥ 0,1 |
| Toxic | ≥ 0,02 | ≥ 0,1 |
| Carcinogenic Category 1 or 2 | ≥ 0,02 | ≥ 0,1 |
| MutagenicCategory 1 or 2 | ≥ 0,02 | ≥ 0,1 |
| Toxic for reproduction Category 1 or 2 | ≥ 0,02 | ≥ 0,1 |
| Harmful | ≥ 0,2 | ≥ 1 |
| Corrosive | ≥ 0,02 | ≥ 1 |
| Irritant | ≥ 0,2 | ≥ 1 |
| Sensitising | ≥ 0,2 | ≥ 1 |
| Carcinogenic Category 3 | ≥ 0,2 | ≥ 1 |
| Mutagenic Category 3 | ≥ 0,2 | ≥ 1 |
| Toxic for reproduction Category 3 | ≥ 0,2 | ≥ 1 |
| Dangerous for the environment N | | ≥ 0,1 |
| Dangerous for the environment ozone | ≥ 0,1 | ≥ 0,1 |
| Dangerous for the environment | | ≥ 1 |

5. The concentration limits given in Annex II Part B of the Dangerous Preparations Directive are not relevant because they are always higher than the limits set by Art. 3 (3) of the Dangerous Preparations Directive.

# Annex II: Integration of information from an exposure scenario in the main body of a safety data sheet

The following table A-2 gives an overview on the contents of an exposure scenario and the corresponding section of the safety data sheet. This provides guidance on how a downstream user may integrate the information from ES into the safety data sheet of his mixture if this option (see option 3 in chapter 5) is chosen by him.

**NOTE**: By integration of ES information into the main body of the SDS it can become more difficult for the following downstream user to check whether his uses (and the uses of his customers, if applicable) are covered by the exposure scenario. (In chapter 5 the different options have been described in detail).

Table A-2 Content of the exposure scenario and the corresponding sections in the safety data sheet.[18,19]

| Title of section in the exposure scenario (referring to OC and RMM for individual uses or groups of uses) | | Include in chapter ….. of SDS or check consistency |
|---|---|---|
| 1. [1] | Short title of Exposure Scenario | Ensure consistency with 1.2 and eventually 7.3 |
| 1. [2] | Description of activities/process(es) covered in the Exposure Scenario | At present no inclusion in main body / **Proposal**: include in section 1.2 |
| 2. [3] | Operational conditions and risk management measures | |
| 2. [3.1] | Duration and frequency of use for which the ES ensures control of risk | Ensure consistency with DNEL provided in section 8.<br>Include in 8, where applied to control risk.<br>Consider also handlings, conditions to avoid, instructions. |
| 2. [4.1] | Physical form of product in which the substance is contained | Ensure consistency with 9; include in summary in 8.2, where applied to control risk. |
| 2. [4.1a] | Surface area per amount of article containing the substance (if applicable) | Include in summary in 8.2, where applied to control of risk. |

[18] Source: ECHA Guidance on information requirements and CSA, part G, p. 15, table G.2, with modifications regarding information which are at present not included in the main body of the SDS. These modifications are underlined). Numbers of section refer to the proposed new structure of ES (4 sections, subsections of section 2 depend on the format chosen). Numbers of sections in brackets refer to the earlier structure of the ES [9 sections].

[19] Please be aware that this format is the current version. At present the format of the ES is under review and it is expected that the TGD IR/CSA will be revised according to the decision on the new ES format.

| | | |
|---|---|---|
| 2. [4.2] | Concentration of substance in mixture or article | Ensure consistency with 3; include in summary in 8.2, when applied to control risk. |
| 2. [4.3] | Amount used per time or per activity for which the RMM, in combination with other operational conditions of use ensure control of risk (if applicable) | Include in summary in section 8.2, where applied to control risk. |
| 2. [5] | Other operational conditions determining exposure, e.g. temperature, capacity of receiving environment (water flow; room size x ventilation rate), emission or release factors to the relevant compartments, and other | Include in summary in chapter 8.2, where applied to control risk. |
| 2. [6] | Risk Management Measures that, in combination with the operational conditions of use, ensure control of risk related to the different target groups | |
| 2. [6.1.1] | Occupational measures following the hierarchy of Directive 98/24/EC: type and efficiency of single options or combination of options on exposure to be quantified; options to be phrased as instructive guidance | Include in summary in section 8.2.1. |
| 2. [6.1.2] | Consumer-related measures: type and efficiency of single options or combination of options on exposure to be quantified; options to be phrased as instructive guidance | Include in summary in section 8.2.3 |
| 2. [6.2] | Environment-related measures: type and efficiency of single options or combination of options on exposure to be quantified; options to be phrased as instructive guidance | Include in summary in section 8.2.2 |
| 2. [7] | Waste-related measures needed to ensure control of risk at the different life cycle stages of the substances (including mixtures or articles at the end of service life) | Ensure consistency with 13. |
| 3. [8] | Prediction of exposure resulting from the conditions described above (entries 3-6) and the substance properties (to be quantified based on exposure assessment in the CSA); make reference to the exposure assessment tool applied | At present no inclusion in main body text / **Proposal**: include in chapter 16. |
| 4. [9] | Guidance to DU to evaluate whether he works inside the boundaries set by the ES | At present no inclusion in main body text / **Proposal**: include in chapter 16. |

*Explanation of SDS sections:*
*1.2 (use of substance); 7 (Handling and storage); 7.3 (specific uses); 8 (Exposure controls); 13 (waste related measures).*

The following table A-3 shows the link between sections of the safety data sheet and the content of the exposure scenario.

Table A-3 Content of the exposure scenario and the corresponding sections in the safety data sheet. Source: own compilation based on Table A-1.

| Sections of the safety data sheet | | Sections of the ES with relevant information for the section of the SDS |
|---|---|---|
| 1. | IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY / UNDERTAKING | |
| 1.1 | Identification of the substance or preparation | |

| | |
|---|---|
| 1.2 Use of the substance/preparation | Ensure consistency with section 1. [1] Short title of Exposure Scenario<br>Proposal: include here section 1. [2] Description of activities/process(es) covered in the Exposure Scenario (at present no inclusion in main body) |
| 1.3 Company/undertaking identification | |
| 1.4 Emergency telephone | |
| 2. HAZARDS IDENTIFICATION | |
| 3. COMPOSITION/INFORMATION ON INGREDIENTS | 2. [4.2] Concentration of substance in mixture or article |
| Substances presenting a health or environmental hazard in concentrations above the concentration limits according to REACH Annex II, Art. 3.2.a | |
| Substances for which there are Community work-place exposure limits | |
| PBT and vPvB substances | |
| Substances in preparations not classified (see REACH Annex II, Art. 3.3) | |
| Classification of the above substances | |
| Name, registration number, EINECS or ELINCs number, if available, of the above substances. CAS Number and IUPAC name may also be helpful. | |
| 4. FIRST AID MEASURES | |
| 5. FIRE-FIGHTING MEASURES | |
| 6. ACCIDENTAL RELEASE MEASURES | |
| 7. HANDLING AND STORAGE | |
| 7.1 Handling | 2. [3.1] Duration and frequency of use for which the ES ensures control of risk |
| 7.2 Storage | |
| 7.3 Specific use(s) | Ensure consistency with section 1. [1] Short title of Exposure Scenario |
| 8. EXPOSURE CONTROLS/PERSONAL PROTECTION | 2. [3.1] Duration and frequency of use for which the ES ensures control of risk |
| 8.1 Exposure limit values | 2. [3.1] Duration and frequency of use for which the ES ensures control of risk |
| 8.2 Exposure controls | 2. [4.1] Physical form of product in which the substance is contained<br>2. [4.1a] Surface area per amount of article containing the substance (if applicable)<br>2. [4.2] Concentration of substance in mixture or article<br>2. [5] Other operational conditions determining exposure, e.g. temperature, capacity of receiving environment (water flow; room size x ventilation rate), emission or release factors to the relevant compartments, and other |
| 8.2.1 Occupational exposure controls | 2. [6.1.1] Occupational measures following the hierarchy of Directive 98/24/EC: type and efficiency of single options or combination of options on exposure to be quantified; options to be phrased as instructive guidance |

| | | | |
|---|---|---|---|
| | Consumer related exposure controls | 2. [6.1.2] | Consumer-related measures: type and efficiency of single options or combination of options on exposure to be quantified; options to be phrased as instructive guidance |
| 8.2.2 | Environmental exposure controls | 2. [6.2] | Environment-related measures: type and efficiency of single options or combination of options on exposure to be quantified; options to be phrased as instructive guidance |
| 9. | PHYSICAL AND CHEMICAL PROPERTIES | 2. [4.1] | Physical form of product in which the substance is contained |
| 9.1 | General information | | |
| 9.2 | Important health, safety and environmental information | | |
| 9.3 | Other information | | |
| 10. | STABILITY AND REACTIVITY | | |
| 10.1 | Conditions to avoid | 2. [3.1] | Duration and frequency of use for which the ES ensures control of risk |
| 10.2 | Materials to avoid | | |
| 10.3 | Hazardous decomposition products | | |
| 11. | TOXICOLOGICAL INFORMATION | | |
| 12. | ECOLOGICAL INFORMATION | | |
| 12.1 | Ecotoxicity | | |
| 12.2 | Mobility | | |
| 12.3 | Persistence and degradability | | |
| 12.4 | Bioaccumulative potential | | |
| 12.5 | Results of PBT assessment | | |
| 12.6 | Other adverse effects | | |
| 13. | DISPOSAL CONSIDERATIONS | 2. [7] | Waste-related measures needed to ensure control of risk at the different life cycle stages of the substances (including mixtures or articles at the end of service life) |
| 14. | TRANSPORT INFORMATION | | |
| 15. | REGULATORY INFORMATION | | |
| 16. | OTHER INFORMATION | 3. [8] | Prediction of exposure resulting from the conditions described above (entries 3-6) and the substance properties (to be quantified based on exposure assessment in the CSA); make reference to the exposure assessment tool applied (at present no inclusion in main body of the safety data sheet) |
| | | 4. [9] | Guidance to DU to evaluate whether he works inside the boundaries set by the ES (at present no inclusion in main body of the safety data sheet) |

In the SDS the focus is on information related to the risks posed by the substances. The ES contains additional information on exposure and exposure assessment. In addition, the ES contains guidance on scaling. Therefore, there is no direct correspondence between the following information from the ES and sections in the SDS at present:

- Section 2: Description of activities/process(es) covered in the ES.
- Section 8: Prediction of exposure.
- Section 9: Guidance to downstream users to evaluate whether he works inside the boundaries set by the ES.

The following recommendation has been discussed in the project how to include the above mentioned information from the ES into the following chapters of the SDS:

- Section 1, Title: Description of activities/process(es) covered in the ES: chapter 1.2 of the SDS. Concern: Section 1 should not become a long list of use descriptors (since activities/processes in the ES will consist of descriptors). We are trying to avoid this.
- Section 3: Prediction of exposure: chapter 16 of the SDS.
- Section 4: Guidance to downstream users to evaluate whether he works inside the boundaries set by the ES chapter 16 of the SDS (e.g. compliance with certain specifications like “no skin contact”).

**Note 1:** If an exposure scenario has been integrated into the main body of the safety data sheet, the following remark should be given in the SDS:

“This safety data sheet contains an ES in an integrated form. Contents of the exposure scenario have been included into sections 1.2, 8, 9, 12, 15 and 16 of this safety data sheet. The check of the downstream user whether his uses (and the uses of his customers, if applicable) are covered by the ES has to take into account this information.”

**Note 2:** For new information in chapter 1–16 of the main body of the safety data sheet additional standard phrases are necessary (see Part I, chapter 5.2 of the Practical Guide).

# Annex III: EMKG

A methodology has been developed by the German Federal Institute for Occupational Safety and Health (BAuA)[20] for the assessment of chemical substances at the workplace in the context of EU framework Directive 89/391/EEC and related directives and the German Hazardous Substance Ordinance. The EMKG (“Einfaches Maßnahmenkonzept Gefahrstoffe”) uses a banding approach similar to the COSHH (Control of Substances Hazardous to Health Regulations) in the United Kingdom[21]. An electronic exposure estimation tool, called EMKG

[20] A methodological description and all currently existing Schutzleitfäden is available (currently in German only): http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/EMKG/EMKG__content.html

[21] http://www.coshh-essentials.org.uk/, see also for English versions of control guidance sheets.

expo-tool[22] was developed in parallel and is explained in detail in Part IV of the Practical Guide, “Exposure Estimation”.

The EMKG aims at identifying appropriate risk management measures for inhalation and dermal workplace exposures for substances (with and without occupational exposure limits).

With EMKG, no lead substances need to be identified. Rather, with few input data (see below) and an easy-to-follow assessment strategy, the method leads to so called control guidance sheets (in German: Schutzleitfäden), which consist in comprehensive descriptions of technical risk management measures for specific activities. Control guidance sheets are available at three levels.

100 series: describe basic occupational hygiene standards

200 series: describe technical measures for various industrial activities such as filling and emptying containers

300 series: describe solutions for applying closed systems for various activities such as use of glove boxes and pumping of liquids.

Most of these guidance sheets are available in both German and English.

EMKG was developed as a method to carry out assessments at the workplace according to the occupational safety and health regulation, but may easily be adapted to REACH requirements. The control guidance sheets focus on technological risk management measures and may be helpful to identify suitable RMMs especially in cases where lead substances may not easily be identified. They do not provide information to identify suitable personal protection measures. Control guidance sheets for relevant industrial activities such as spray application of liquids are missing, but may be developed in the near future.

Activities are planned to adapt the method to specific REACH requirements, provide guidance and means for easy application (electronic implementation).

**Input information for application of EMKG to mixtures:**

- **R phrases (for assigning the mixture to a hazard group);**
- **amount used per activity (broad categories, semi-quantitative)**
- **exposure-related information: Boiling point and process temperature for assessing release (broad categories, semi-quantitative); dustiness in case of solids;**
- **exposed skin area and dermal exposure time for assessing dermal exposure (broad categories, semi-quantitative).**

**Example: Electrolyte mixture for industrial galvanic treatment, containing 23% chromium (VI) trioxide: supplementing galvanic bathes with electrolyte mixture.**

[22] http://www.reach-clp-helpdesk.de/en/Exposure/Exposure.html__nnn=true

**Input data:**

Classification of CrO3: Carc. Cat. 1; R45 – Muta. Cat. 2; R46 – Repr. Cat. 3; R62

Amounts used per activity: medium (kg range, for adding electrolyte mixture to galvanic bathes)

Duration of activity: < 15 min per event

Volatility: low (component is solid, in liquid mixture)

Skin contact area: large (contact to hand surface possible)

Skin contact duration: long (> 15 min/day)

**Output:**

Recommendation for inhalation exposure: seek advice, check existence of sector-specific guidance (for “high hazard” substances such as those classified with R45 EMKG will always come up with the recommendation for specific advice and advanced evaluation).

Recommendation for dermal exposure: “Increased requirement for action” (Control Guidance Sheet (Schutzleitfaden) 250)

Sector-specific guidance:

For use of chromium (VI) trioxide in Germany there exists BG Information 790-16 (Information 790-16 of the Institutions of statutory accident insurance and prevention) which provides recommendations for the evaluation and identification of RMMs for galvanic and anodising processes.