Hygienic evaluation of materials for the production of elastomers in contact with drinking water

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SUMMARY
Materials intended for use in contact with drinking water have to meet specific requirements for the protection of human health. In Germany, these requirements are laid down in the Drinking Water Ordinance and are legally binding. Where elastomer products are concerned, their hygienic assessment can alternatively be based on the Federal Environment Agency (UBA) Elastomer Guideline, which mainly addresses the evaluation of starting substances and their migration. This paper discusses the specific requirements and the principles of the assessment.

INTRODUCTION
Legally binding requirements for materials in contact with water intended for human consumption are laid down in the German Drinking Water Ordinance (Trinkwasserverordnung) of 2001 [1]. Section 17 “Requirements for installations for the obtention, treatment or distribution of drinking water” firstly specifies general requirements:

• compliance with the generally recognised codes of practice
• protection of human health from direct or indirect risk
• no change to the odour or taste of drinking water
• no substances to be leached into the drinking water in quantities larger than those inevitable when the generally recognised codes of practice are complied with.

In Section 17, the Federal Environment Agency (Umweltbundesamt, UBA) is mandated with stipulating an assessment basis for materials that come into contact with drinking water. This will be legally binding after a period of two years following its publication.

For the hygienic assessment of elastomer products in contact with drinking water, the Federal Environment Agency’s Elastomer Guideline [2] can be used. This guideline is a recommendation and not an assessment basis as stipulated in Section 17. It represents the current state of scientific and technical knowledge. However, it may be assumed that elastomers in contact with drinking water which meet the requirements of the Elastomer Guideline will also satisfy the hygiene requirements of the Drinking Water Ordinance 2001.

The Elastomer Guideline lays down requirements for the hygienic suitability of elastomers in contact with drinking water. These include the listing of starting substances used for manufacturing elastomers (positive list), the test method (migration test) and the limit values in the form of DWPLL (Drinking Water Positive List Limit) values.

POSITIVE LIST IN THE ELASTOMER GUIDELINE
A number of chemical substances are required for manufacturing elastomers. The main ingredient is rubber, which is made of monomers, polymerisation aids such as catalysts and additives such as stabilisers. Crosslinking agents, such as peroxides, are used for vulcanising rubber. Various additives, such as fillers, plasticisers, processing aids and anti-ageing agents, are needed to
achieve specific elastomer properties. The properties of elastomer products are determined by the formulation of the rubber compound and the manufacturing process.

The Elastomer Guideline’s positive list contains substances that can be used to manufacture elastomers, and is divided into three parts:

- Part 1 contains substances that have already been assessed toxicologically by the European Food Safety Authority (EFSA).
- Part 2 lists substances for which no conclusive toxicological assessment is currently available. The UBA has been provided with information on the use of these substances, possible reactions during vulcanisation, estimation of their migration potential and references to existing toxicological data. Based on the available information, the UBA has decided to accept these substances on to the positive list for a limited period.
- Part 3 contains the typical rubbers used for elastomers in contact with drinking water. The starting substances required for manufacturing rubbers are listed in parts 1 or 2 of the positive list. Part 3 is for information only.

Parts 1 and 2 are divided into monomers, fillers, plasticisers, anti-ageing agents, processing aids, crosslinking agents, colorants and aids to polymerisation for rubber, according to their technological function.

The substances are shown in the positive list with their CAS number (CAS: Chemical Abstracts Service), the PM Ref. No. (EEC Packaging Material Reference Number) from Regulation (EU) No. 10/2011, their chemical name and their restriction. The restrictions can be requirements relating to the specification of the listed substance, requirements in the form of DWPLL values according to their toxicological evaluation.

Through vulcanisation, starting substances may occasionally give rise to new substances which can also migrate into drinking water. The Elastomer Guideline also lays down DWPLL values for these substances in the different categories under the additional requirements, for example “primary aromatic amines”.

The DWPLL value is a human-toxicologically derived temporary drinking water limit for material-specific substances. It is generally derived from the TDI (tolerable daily intake) value using Equation (1):

$$\text{DWPLL} = \frac{\text{TDI} \cdot 60 \text{ kg BW}}{2 \text{ l/d}} \cdot 0.1$$

(1)

It is assumed for this calculation that the body weight (BW) of a person is approximately 60 kg and that the person consumes approximately 2 litres of drinking water per day. The total exposure to a substance via the drinking water pathway must be no more than 10%, since drinking water is indispensable. It is also possible to calculate the DWPLL value from a specific migration limit (SML) from Regulation (EU) No 10/2011 using Equation (2):

$$\text{DWPLL} = \frac{1}{20} \cdot \text{SML}$$

(2)

The very conservatively derived DWPLL value is a precautionary limit which covers possible lifelong exposure to a substance via the drinking water pathway.

SPECIFICATION OF DWPLL VALUES

The number and concentration of substances transferred into drinking water from elastomer products in contact with drinking water must be as low as possible. The total organic carbon content (TOC), which is one of the basic requirements of the Elastomer Guideline, is used as a measure of the migration of organic compounds into water from an elastomer product. The “DWPLL\textsubscript{TOC}” value is 0.5 mg/l carbon. The TOC value is not a toxicologically based value but is well established as a useful and important parameter from the old KTW recommendations (German Guideline for Hygienic Assessment of Organic Material in Contact with Drinking Water) and the Guidelines of the Federal Environment Agency. It shows the extent to which organic substances – regardless of their chemical structure and properties – can migrate into drinking water. The TOC parameter also covers non-intentionally added substances (NIAS).

If specific substances can be expected to migrate, it must be guaranteed that the consumer is not put at risk. Migration limits for the individual substances are therefore stipulated in the positive list in the form of DWPLL values according to their toxicological evaluation.

PRINCIPLES IN ASSESSING SUBSTANCES FOR INCLUSION IN THE POSITIVE LIST OF THE ELASTOMER GUIDELINE

A stepwise procedure has already been established for the inclusion of substances in the positive list for plastics in contact with food from Regulation (EU) No. 10/2011. In particular, this avoids any unnecessary animal testing and allows proper use of resources. The extent of toxicological data required is dependent on the level of mass transfer. For most substances evaluated by the EFSA, only low levels of migration into food are acceptable.

This evaluation procedure is also used for assessing new substances in the Elastomer Guideline. This seems appropriate, since the evaluated substances in Part 1
of the Elastomer Guideline’s positive list have already been assessed by this procedure.

The petitioner has to submit a dossier for the substance being assessed, which should contain the information required in the questionnaire of the EFSA Note for Guidance [3]. The dossier should contain reliable information on the use of the substance and on the nature and quantity of mass transfer including impurities, breakdown products and reaction products. The level of any mass transfer determines the extent of the toxicological data required.

For food contact materials there are three levels of possible migration into food:
- migration < 0.05 mg/kg of food
- migration of 0.05 – 5 mg/kg of food
- migration of 5 – 60 mg/kg of food

In line with the derivation of limit values for drinking water materials from the specific migration limits for food contact materials via Equation (2), the toxicological study data requirements for the different migration limits are obtained as shown in Table 1.

### CONTENTS OF THE APPLICATION FORM IN THE RULES OF PROCEDURE

The assessment of substances for the manufacture of drinking water materials is based on the European Commission’s questionnaire for the evaluation of substances for use in food contact materials. The Federal Environment Agency has published its own Rules of Procedure [4] for maintaining the positive lists for organic materials in contact with drinking water. The questionnaire has been adapted to be more specific and consists of eight sections:

- Section 1: Identity of the substance
- Section 2: Physical and chemical properties of the substance
- Section 3: Intended use of the substance
- Section 4: Authorisation of the substance
- Section 5: Data on migration of the substance
- Section 6: Data on residual content of the substance
- Section 7: Microbiological properties of the substance
- Section 8: Toxicological data

The first section should contain information describing the substance, such as its chemical name, CAS number and trade name(s) including its purity and data on impurities associated with its production. However, impurities may vary according to the manufacturer and production process. Any impurities are not usually included in the positive list. It should be demonstrated in the dossier that these impurities do not contribute to migration into drinking water.

In the second section, the physical and chemical properties of the requested substance should be described, with a particular emphasis on water solubility and possible hydrolysis of the substance, its impurities or any decomposition products and the stability of the substance.

Section 3 requires information on the substance for use in the product coming into contact with drinking water in terms of the technological function of the requested substance and its possible reactions in the product, e.g. the formation of oligomers from the monomer being assessed or of degradation products of a stabiliser in the case of additives. Possible applications of products that can be manufactured with the substance should be described, e.g. hoses at public festivals or seals in domestic installations.

Oligomer fractions below 1000 Da are relevant to the toxicological assessment of polymers since they can also be metabolised. It is assumed that oligomers over 1000 Da pass through the gastrointestinal tract without being absorbed and are excreted.

The fourth section calls for information on the acceptance of the requested substance in other countries, e.g. authorisation of the substance or of a product containing this substance in another EU Member State.

The fifth section defines the basic criteria for estimating possible consumer exposure to the requested substance,

<table>
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<tr>
<th>Migration of substances into drinking water</th>
<th>Toxicology data required</th>
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<tr>
<td>&lt; 2.5 µg/l</td>
<td>• Tests to rule out mutagenicity</td>
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<td>2.5 – 250 µg/l</td>
<td>• Tests to rule out mutagenicity</td>
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<td>• 90-day test</td>
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<td>• Data to demonstrate the absence of accumulation of the substance in man</td>
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<tr>
<td>&gt;250 µg/l</td>
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<td>• Data to demonstrate the absence of accumulation of the substance in man</td>
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<td></td>
<td>• Study on chronic toxicity and carcinogenicity</td>
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its impurities, oligomers or reaction products through drinking water. Data should be provided for any mass transfer, taking into account the worst case for the planned application. In some cases, for example, the intended temperatures (warm-water or hot-water applications) are relevant. Very long periods of use are assumed for products in contact with drinking water. The migration test should therefore demonstrate any long-term mass transfer that may be expected. This test is to be performed in accordance with the Elastomer Guideline Annex 3 (DIN EN 12873-1 [5]). The test results are to be given in the format of Tables 4 and 5 of Annex 3 of the Elastomer Guideline. Instead of the total migrate, the Elastomer Guideline requires the TOC to be analysed as NPOC (Non Purgeable Organic Carbon according to DIN EN 1484).

In section 6, possible residual contents of the requested substance, its impurities and its reaction and breakdown products should be provided, with a discussion of whether the substance itself is modified, e.g. incorporated into the polymer skeleton and therefore unavailable for migration into drinking water, or is intended to break down into other constituents. Information on the levels of the substance in the product is essential for a mathematical estimate of the migration of the substance into drinking water.

The seventh section is only relevant if the requested substance is intended for use as a biocide. Biocidal additives in elastomers in contact with drinking water should only be used for in-can preservation. It should be borne in mind that in order to meet the requirements of DVGW (German Technical and Scientific Association for Gas and Water) Code of Practice W270 relating to the microbiological suitability of elastomers, the surfaces of elastomer products must not have a biocidal action.

In section 8, the toxicology studies available for the substance should be reported and submitted as original studies. They should also be summarised in the questionnaire. Alternatively, a final assessment from another authority, such as the EFSA, may be accepted. Regardless of the toxicology studies required, all known toxicological information on the requested substance, its impurities and its possible reaction and breakdown products should be reported.

BASIC CONSIDERATIONS AND PROCEDURES FOR DETERMINING POSSIBLE TRANSFER OF SUBSTANCES FROM ELASTOMERS INTO DRINKING WATER

Information on possible mass transfers is essential in assessing the requested substance. Not only the substance itself has to be assessed but also other relevant migrants, such as impurities in the substance as well as the reaction and breakdown products that are expected in the manufacture or processing of the product for the requested application.

Since it is not possible to predict all of the real-world applications, models have been developed in order to provide a conservative estimate of migration. For food contact materials it is assumed that 6 dm$^2$ of packaging comes into contact with 1 kg of food. The different products/components in drinking water installations are tested with a surface to volume ratio (S/V ratio) of 5 dm$^{-1}$, which is close to the model for food contact materials.

For pipes that are tested by filling, the S/V ratio is much greater for small internal diameters. For instance, for a pipe with an internal diameter of 10 mm used in a drinking water installation, the S/V ratio is 40 dm$^{-1}$. As the internal diameter of the pipe increases, the S/V ratio decreases. An S/V ratio of 5 dm$^{-1}$ correlates to an internal pipe diameter of 80 mm. Pipes of this size are generally used outside of buildings, which illustrates the fact that pipes in a drinking water installation have the greatest effect on drinking water quality.

Various approaches are possible for describing the transfer of substances from elastomer products into drinking water. However, it is essential to prove that there is no harmful migration into drinking water in the planned use. Possible consumer exposure is estimated from the level of migration, which determines the extent of toxicological data required. The determination of mass transfer is therefore central to the application procedure.

In determining mass transfer, model conventions are used which can under- or overestimate the actual amount of substance transferred. The petitioner should select a level that is as close as possible to that in the real world. In the migration test according to DIN EN 12873-1 or -2, possible effects of organic materials on drinking water should be modelled, taking into account the following conditions:

- selection of a specimen for the migration test
- treatment of the specimen prior to testing
- surface to volume ratio
- operating range/temperature

A product representing a typical application in water distribution should be manufactured using the requested substance, based on the assumption that pipes and hoses have the greatest effect on drinking water quality because of their large S/V ratio. As far as possible, the specimen should undergo the same processes as the finished product, taking account of any after-treatments that may be necessary, such as post-curing of peroxide-cured products, which should also form part of the considerations.

An S/V ratio of 5 dm$^{-1}$ is generally assumed in migration tests. This is a convention and is adequate for components (items of equipment) in water distribution. When considering pipes and hoses which are to be tested by filling, the S/V ratios are significantly higher (5 - 40 dm$^{-1}$), depending on the internal diameter of the pipe or hose.
The temperatures for the migration test depend on the planned use:

- testing at (23 ± 2)°C – cold water test (supply pipes)
- testing at (60 ± 2)°C – warm water test (drinking water installation)
- testing at (85 ± 2)°C – hot water test (water heaters)

The temperature selected in a migration test has a considerable effect on the level of migration. However, it is necessary to consider/focus on the end use described in the dossier. Not all materials are suitable for use at elevated temperatures, such as the migration test at 85°C for hot-water applications. Each product is developed for a specific purpose and it is therefore unreasonable to require a warm or hot water test for every application. A migration test for cold water must always be carried out.

If mass transfer cannot be determined experimentally, it can be calculated theoretically based on an assumption of complete transfer or can be estimated mathematically with the aid of diffusion models in accordance with the Modelling Guideline [6]. In this case, it is essential to provide data on the residual content in the product (cf. Section 6 of the questionnaire “Note for Guidance”).

The analytical methods used, including their validation, should be described in the dossier as set out in the questionnaire.

PROCEDURE FOR DETERMINING THE TRANSFER OF SUBSTANCES FROM ELASTOMERS INTO DRINKING WATER

The European Commission questionnaire was developed for plastics in food contact. More specific information is therefore needed to assess substances for the production of elastomers in contact with drinking water.

The migration test must be performed in accordance with the specifications in the Guideline and in the migration standard DIN EN 12873. The test parameters (product group, S/V ratio, temperature) should be selected according to the real-world application. However, the mass transfer values obtained from the test should not underestimate those of the foreseeable real-world applications.

For an elastomer coating of a drinking water container, cold-water testing is sufficient while cold and warm water tests should be performed for the various components of a drinking water installation. The conditions of the migration test selected in the application must be clearly justified by the petitioner.

Any impurities resulting from the production of the requested substance, possible oligomers and other reaction and breakdown products must be described in the dossier and should be given the same consideration as the requested substance itself. For the assessment of crosslinking agents, e.g. peroxides, the application procedure can focus on the intentionally obtained reaction and recombination products. For a substance to be included in a positive list, an evaluation procedure is always necessary even if the substance itself is not detected in the migrate.

Screening processes, e.g. GC-MS screening according to prEN 15768, can be used to detect various substances. It must be ensured that the relevant migrants to be analysed can be recorded by the screening method.

CONCLUSIONS

The substance evaluation procedure described provides a transparent process which has been well established for food contact materials for many years and is recognised by the industry. It is already used successfully to evaluate starting substances for organic coatings in contact with drinking water under the Epoxy Resin Guideline, which was published as long ago as 2003 and was replaced by the Coating Guideline in 2005.

At the European level, this procedure for the evaluation of substances for inclusion in the common positive lists has been approved as part of the 4MS initiative for harmonising the requirements for materials in contact with drinking water [7]. Substance evaluations under the Elastomer Guideline can therefore also be included in the process for the mutual recognition of substances for inclusion in the “4MS Core List”. This has the advantage for the industry concerned that an application for a substance to be evaluated for inclusion in a material-specific positive list need only be submitted for the requested substance in one of the Member States participating in the 4MS process.

For assessing substances for the production of organic materials in contact with drinking water, the tried and tested procedure for food contact materials is used, which already benefits from ten years of positive experience. This procedure has the additional advantage that all of the substances included in the positive list, including those evaluated by the EFSA, are assessed according to the same principles.

REFERENCES

3. Note for Guidance for Petitioners presenting an Application for the Safety Assessment of a
Substance to be used in Food Contact Materials prior to its Authorisation, EFSA document, 30.07.2008

4. Rules of Procedure of the Federal Environment Agency for maintaining the positive lists of starting substances for organic materials in contact with drinking water, UBA Rules of Procedure (Geschäftsordnung), 06.02.2014


7. Approval and Harmonisation – 4MS Initiative, UBA publication, 08.08.2013

UBA information on materials in contact with drinking water is available in German at http://www.umweltbundesamt.de/themen/wasser/trinkwasser/trinkwasser-verteilen and in English at http://www.umweltbundesamt.de/en/topics/water/drinking-water/distributing-drinking-water.