ANNEX XV INVESTIGATION REPORT

Investigation of the available analytical methods to measure content and migration of polycyclic aromatic hydrocarbons, limit values in rubber and plastic articles in paragraphs 5 and 6 of Entry 50 of Annex XVII to REACH, and alternative low-PAH raw materials

SUBSTANCE NAME: Polycyclic aromatic hydrocarbons (PAHs)

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CONTACT DETAILS OF THE REPORT AUTHOR: EUROPEAN CHEMICALS AGENCY

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About this report

This report has been prepared at the request of the Commission. A call for evidence to gather relevant information took place between 1 June and 31 July 2017.

ECHA submitted a draft report to the Commission in November 2017. Subsequently, the Joint Research Centre (JRC) published its final report on the *Migration of Polycyclic Aromatic Hydrocarbons (PAHs) from plastic and rubber articles* on 8 August 2018 and ECHA agreed to update its draft report to take it into account.

The final report takes comments and information received after November 2017 from the Commission, the JRC and industry into consideration.

Summary

Paragraphs 5 and 6 of entry 50 of Annex XVII to the REACH Regulation ((EC) No 1907/2006) restrict the placing on the market and supply to the general public of polycyclic aromatic hydrocarbons (PAHs) in articles and toys (including activity toys and childcare articles). Rubber and plastic components of articles and toys that come into direct and prolonged or short-term repetitive contact with human skin or the oral cavity under normal or reasonably foreseeable conditions of use are covered by the restriction.

The restriction applies:

- to consumer articles if the components contain more than 1 mg/kg of any of the eight PAHs (listed in the left column of entry 50); and
- to toys if the components contain more than 0.5 mg/kg of the PAHs.

On the basis of the provisions included in paragraph 8 of entry 50, the European Commission has asked ECHA to prepare an evaluation report to assist them in their review of paragraphs 5 and 6 of entry 50 of Annex XVII to REACH on PAHs.

Specifically, the Commission has requested ECHA to:

1. examine the availability of validated analytical methods to establish content as well as migration of individual PAHs;
2. evaluate analytical performance parameters of these methods including limits of quantification;
3. investigate the availability of analytical methods in commercial laboratories, including their practicality and cost;
4. review the availability of alternative low-PAH raw materials, in particular, carbon black and extender oils used to manufacture rubber articles;
5. advise on possible more stringent content limits for PAHs in articles covered in paragraphs 5 and 6 in light of new scientific information.

In response to the Commission's requests, ECHA has concluded that:

1. An analytical methodology to determine the **content** of PAHs (listed in entry 50) in articles at a very low level is available. Although not validated, the method has been developed by the JRC in the context of the STANPAH[1] project and their limit of quantification is in a range between 0.6 and 3.6 ng/ml, with a sample-specific limit of 0.001 to 0.007 mg/kg for a 500 mg sample.

   This methodology allows significantly lower concentrations of PAHs to be tested (up to two orders of magnitude lower) than any other methods currently used[2].

[1] Information provided in Section 2.4.3 of this document.

[2] The most widely used method to determine the content of PAHs in plastics and rubbers was developed by German AfPs in 2014. This method has been recently updated in 2019 (see Section 2.4.4. of this document for additional information) and it has a limit of quantification of 0.2 mg PAH/kg material. Other methods are also available to measure the content of PAHs in specific materials (see Section 2.2. of the JRC report for more information).

The in-house validated method developed by the JRC to measure **migration** of PAHs (listed in entry 50) from plastic and rubber matrices showed a good performance although high variability was observed in the inter-laboratory comparison study attributed to the fact that the determination of PAHs is close to the limit of quantification.

Tests were performed by the JRC on the same rubber and plastic specimen (representative of most common commercial articles) using both artificial saliva (to assess migration in the oral cavity) and 20 % ethanol solution (to assess migration to skin) as migration media. Migration was observed only when 20 % ethanol was used as migration media, while no migration was observed in artificial saliva. Therefore, it has been concluded that the use of 20 % ethanol as migration media can be considered as a conservative approach to assess both migration to skin and in the oral cavity.

2. Methods developed by the JRC to determine the **content** and **migration** of PAHs are considered sufficiently reliable, easily available in all Member States and also outside the EU.

   Costs of content testing seem to be acceptable to industry. Minor shortcomings of the JRC method for determining the content of PAHs could be addressed by the ongoing development by CEN of a harmonised method for determining PAH content in rubbers and plastics upon the mandate by the Commission[3]. In relation to the method to measure the migration of PAHs from articles, the JRC has identified possible actions (not implemented in the method) that may contribute to reducing the variability.

   These methods (content and migration) can be easily deployed in commercial laboratories and the testing costs can be considered comparable with the costs of the method used for PAH quantification.

3. Information obtained in the call for evidence is not sufficient to identify **alternatives** to currently used PAH-containing substances. However, information in the Annex XV restriction report from Germany (2010) and information obtained from industry show that alternatives are available to high PAH-containing materials. Such alternatives include low-PAH carbon black and low-PAH extender oils as well as carbon black/extender oil-free alternatives that can be used to produce consumer articles (e.g. thermoplastic elastomers, and PAH-free plasticisers). However, some of these alternatives may pose health-related concerns and availability issues in applications where high quantities of extender oils are used.

4. In relation to the **content limits**, based on the German report on migration of PAHs from articles (2017), actual content limits may not guarantee a low level of migration of PAHs from consumer articles and safe use for all types of plastic and rubber matrices. Germany has, therefore, recommended that the current limits are kept or even reduced. A similar conclusion was drawn by RIVM, in their study on the

[3] https://ec.europa.eu/growth/tools-databases/mandates/index.cfm?fuseaction=search.detail&id=579

assessment of PAH content limits in rubber articles (2016). More recently, the JRC (2018) showed that detectable migration of PAHs from plastic and rubber matrices was only observed in rubbers with high-PAH content. The JRC also concluded that there is no linear relationship between PAH content in the article and their migration.

Mandated by industry, the Fraunhofer Institute (2017) studied the migration of PAHs from articles made from recycled tyres. Based on the tests performed on a number of commercial articles, showing very low migration of PAHs from analysed articles, the Fraunhofer Insitut concluded that the contact area and not the PAH content in the article, determines the extent of migration.

Based on this study, Professor Hoffman (University of Mainz) published (in June 2020) an expert opinion commissioned by industry on the toxicological risk assessment of PAHs in rubber articles and safety slabs made of granulate from recycled rubber tyres. In his opinion, Professor Hoffman concluded that toxicological effects of PAHs in rubber tiles do not depend on the quantity of PAHs present in the article, but on the quantities that migrate from the contact area of the article to the human body through the skin. Professor Hoffman also concluded that, in the case of the tiles (considered in his study), the migration of PAHs was very low and did not pose any additional risk to human health. Based on available information, ECHA concludes that the current content limits for PAHs in plastic and rubber articles are still considered effective as risk management measure to control consumer exposure. However, work done by the JRC along with other literature information have provided better knowledge on the migration behaviour of PAHs from articles compared to the Annex XV restriction report from Germany (2010). Although some uncertainties still exist in the determination of the influence of certain parameters on the migration of PAH content in articles (e.g. thickness of the material, use pattern and deterioration), reliable methods are available to measure migration.

Overall, taking all available information into account, ECHA is of the opinion that it is necessary to perform a risk assessment to conclude if a migration limit could be set in addition to or as an alternative to the content limit. However, if the Commission requests, ECHA is ready to assess the risks for consumers from migration of PAHs from plastic and rubber articles and to analyse whether a migration limit could be established to control risk and, in addition, if the current content limit value is protective enough against risks from exposure to PAHs.

Background

To enable the Commission to review paragraphs 5 and 6 of entry 50 of Annex XVII to REACH, ECHA investigated methodologies available to establish the content of PAHs in articles and to measure their migration from articles, the availability of alternatives with low-PAH content and any new information which could lead to a review of the PAH content limits in articles.

ECHA's considerations included in this report are based mostly on:

- the outcome of the 2018 project from the JRC (the STANPAH project) on the development of the methodology for assessing the migration of PAHs;
- the conclusions of the 2017 German monitoring programme on PAHs in consumer articles and toys;
- the information gathered from the call for evidence launched by ECHA between June and July 2017 to collect information on the presence of PAHs in consumer articles and toys, methods used for their quantification and availability of alternatives; and
- the Annex XV restriction report from Germany (2010) on PAHs in consumer articles.

Analytical methods for content and migration measurement

Analytical methods to measure the PAH **content** in certain materials aim to extract, to the extent possible, all PAHs from the material using solvents and to analyse the amount of extracted PAHs. Analyses are usually performed using gas chromatography-mass spectrometry (GC-MS).

Solvent extraction is followed by a purification step to remove non-PAH substances (e.g. phthalates) that are also extracted.

A standardised method for quantification of PAH content in plastic and rubber materials is not available, therefore the JRC performed, in the context of the STANPAH project, a review of available methods and developed their own method for determining PAH content.

Existing methods are mostly based on Soxhlet extraction using toluene or other substances (e.g. acetone, cyclohexane or 2-propanol) as a solvent. These methods have a limit of quantification (LoQ) generally reported at 0.2 mg/kg for each PAH (see Section 2.4.2.2. of this report for additional details).

The method developed by the JRC, based on Randall hot extraction using toluene as a solvent, allows the content of the eight PAHs (listed in entry 50 of Annex XVII to REACH) to be determined in plastic and rubber materials at a very low level (i.e. 0.001 to 0.007 mg/kg for 500 mg sample).

Measurement of PAH **migration** aims to quantify the amount of PAHs that migrate, during a certain time, into a media with characteristics similar to human skin or the oral cavity (simulant). A migration test typically consists of the following steps: placing the material into the simulant over a defined period of time, extracting the PAHs from the simulant (e.g. using solid phase cartridges) and analysing the amount of extracted PAHs with GC-MS.

Testing methods to measure the migration of hazardous substances from plastic matrices have been in use for many years for food contact materials that are subject to specific regulatory requirements.

As part of the STANPAH project, the JRC analysed existing methods to measure the migration of PAHs and developed its own technique to measure the migration of the eight PAHs included in entry 50 of Annex XVII to REACH, from custom-made plastic and rubber test pieces containing different type of carbon blacks and extender oils (both known as the main sources of PAHs).

A variety of migration media were used with the aim of better representing the conditions of the human skin and mouth. The method was further subject to an inter-laboratory comparison study to assess repeatability and reproducibility. No PAH releases (above the limit of quantification of the method used) were detected in any of the material tested when an aqueous simulant was used as the migration media.

Test results showed that detectable releases of PAHs were only observed in custom-made rubber matrices containing Distillate Aromatic Extract (DAE) as an extender oil when 20 % ethanol solution was used as the migration media. Although, based on information from industry, DAE is no longer used in the EU to produce articles intended for skin contact, custom-made materials containing DAE were used in the project to facilitate the development of testing methods. It was also observed that releases from coated materials (i.e. PU coated rubber granules) were lower than from uncoated ones and that releases of PAHs from the same material containing different type of carbon blacks do not depend on the PAH content of the carbon black, but rather on their PAHs re-absorbing capacity (which itself depends on the surface area of the carbon black).

The 2017 study from Germany, contains the outcome of content and migration tests performed on a number of articles available on the market and a comparison of obtained testing data with data from previous studies (mostly limited to benzo(a)pyrene (BaP)). The study aimed to obtain information on the migration behaviour of different PAHs. The conclusion from Germany was that articles containing BaP close to the limit value of 1 mg/kg would likely lead to an exposure to BaP above the estimated DMEL range for all of the rubber and elastomers analysed. The assessment does not even take into account the additional contribution of other PAHs listed in entry 50. Based on the outcome of their tests, Germany recommended that the current limits in restriction entry 50 should be at least maintained if not replaced by stricter limits. In relation to migration, the study showed large variability in the migration behaviour of different PAHs from different samples of rubber and elastomers and recommended to collect more data to achieve a more systematic knowledge on migration of PAHs from various matrices.

In 2016, the Dutch National Institute for Public Health and the Environment (RIVM), conducted a study[4] to investigate whether the actual content limit for PAHs in rubber tiles (articles) provided adequate protection against the development of cancer. The results of the risk assessment performed by RIVM indicated that the range of extra cancer risk of exposure (for the eight PAHs) lies between 1 per 590 000 and 1 per 7.7 million individuals for a PAH content of 1 mg/kg in tiles. RIVM concluded that "*if the PAH concentration in the rubber tiles is equal to the limit for consumer articles (i.e. 1 mg/kg), the risk range lies around the negligible risk level of 1 per million. At the maximum value of the range, the maximum risk level is slightly exceeded".*

[4] https://www.rivm.nl/bibliotheek/rapporten/2016-0184.pdf

Based on available information when this report was compiled, ECHA has concluded that, although an EU harmonised method for determining the content of PAHs[5] in articles is still under development by CEN, analytical methodologies are available (see Section 2.4.2.2 and Table 5 below in this report for details). They allow the content of PAHs to be determined at a very low level, and are considered sufficiently reliable and easily available in all Member States as well as outside the EU. Costs of such testing seem to be acceptable to industry. Minor shortcomings of these methods could be addressed by the development of a CEN-harmonised method that is being developed by CEN under mandate from the Commission.

The validated method developed by the JRC to measure the migration of PAHs from plastic and rubber matrices showed good performance, although high variability was observed in the inter-laboratory comparison study. The same variability was also observed in the German study from 2017 and it has been attributed to the fact that the determination of PAHs was close to the limit of quantification.

The JRC concluded that the variability could be reduced by making some changes in the standard operating procedure. These proposed changes, however, have not been further implemented in the method. The JRC method can be easily deployed in commercial laboratories and the testing cost can be considered comparable with the costs of the method used for PAHs quantification.

Alternatives

In its Annex XV restriction report (2010), Germany indicated some limitations (technical and due to low availability) in the use of mixtures containing low quantities of PAHs, in the production of articles. However, some of these limitations have been phased out in recent years. Indeed the study conducted by the JRC in the context of the STANPAH project indicates that industry is continually moving towards the use of mixtures with lower PAH content. As an example, Treated Distillate Aromatic Extract (TDAE)-based extender oils with low-PAH content have completely replaced DAE-based oils (with high-PAH content) in the production of articles intended for skin contact. Based on information available and additional discussions with industry, ECHA has concluded that low-PAH carbon blacks and low-PAH extender oils may constitute possible alternatives to medium/high PAH-containing materials that are currently used.

Limit values

New studies on PAHs in articles were made available since the publication of the restriction report from Germany (2010) – i.e. the 2017 PAHs monitoring report from Germany, the 2018 JRC study and the information gathered in the context of the PAHs restriction proposal on infill material (2019).

These studies showed that reducing content of PAHs in articles does not automatically result in a proportional reduction of risks from migration. As explained later in this document, in addition to the PAH content, migration is influenced by a number of parameters. As an

[5] The term PAHs in the sentence refers to the eight PAH substances listed in entry 50 of Annex XVII to REACH.

example, the role of parameters such as thickness[6], ageing, deterioration and coating in reducing the migration rate deserves further investigation. However, the work done by the JRC (and published in 2018) has made more advanced techniques available to detect PAH content at lower levels (i.e. 0.001 to 0.007 mg/kg for 500 mg sample) than reported in the German Annex XV report (2010).

This is a relevant element to take into account if further reduction of the actual PAH content limit is considered by the Commission. Based on available information, ECHA concludes that the actual PAH content limit can be considered protective to avoid risks for consumers. However, a risk assessment is needed to evaluate the effectiveness of a lower content limit in protecting consumers to exposure to PAHs released from plastic and rubber articles. ECHA confirms its availability to perform a risk assessment aimed at establishing a possible lower content limit for PAHs if requested by the Commission.

In relation to migration of PAHs from articles, ECHA concluded that new test methods developed by the JRC to measure PAH migration from articles are sufficiently reliable. However, it is not possible at this stage to confirm that a migration limit for PAHs can be established as a supportive or alternative measure to the current content limit. To assess the possibility of establishing a migration limit, it is necessary to evaluate the release of PAHs from rubber and plastic articles and assess risks to consumers from exposure to these substances. Such an assessment should take into account, among other factors, the migration behaviour of PAHs in different plastic and rubber matrices, use pattern, influence of factors such as time and surface of contact, deterioration etc. Although a migration media such as saliva should be used to evaluate migration in the oral cavity, information from studies conducted with 20 % ethanol as the migration media can be used as a worst case if needed for risk assessment.

Migration of a substance depends on a number of variables such as time, temperature, thickness of the material, amount of the substance in the material and the partition-coefficient/distribution coefficient. Some of these variables were already investigated in the studies considered in this report. Additional information on migration of substances in plastics and rubber is available in literature. The experience gained in past years with food contact materials (for which migration limits already exist in some cases) can be of further help. ECHA confirms its availability to perform a risk assessment aimed at establishing a possible migration limit for PAHs from articles upon request from the Commission.

In relation to the list of PAHs in entry 50, the report from Germany (2017) considered that two newly classified PAHs (dibenzo[b,def]chrysene and benzo[*rst*]pentaphene, RAC opinions adopted on 9 June 2017[7]) could be added to the scope of entry 50. However, based on the opinion of the Scientific Committee on Food (SCF – 2002) and the Annex XV restriction proposal on PAHs in rubber granules (see Section 1.2.1 of this document), the confinement of the proposal to the eight PAHs included in the restriction entry is sufficient to control

[6] Germany (2017) has already examined the effect of thickness of the material on migration (see Section 2.4.4 of this report). However, the tests were conducted on a limited amount of samples and did not include plastic materials.

[7] https://echa.europa.eu/documents/10162/22932537/rac-41_minutes_en.pdf/945ef7eb-1776-85a1-7f1f-43ac5c372f31

risks. For this reason, the impact for industry and the benefits for human health of this proposal have not been assessed.

Report

1. The problem identified

1.1. Introduction

Paragraph 8 of entry 50 of Annex XVII to REACH requires the Commission to review, by 27 December 2017, the limit values in paragraphs 5 and 6 of that entry taking into consideration new scientific information, including migration of the polycyclic aromatic hydrocarbons (PAHs) specified in the entry (see Table 1) from articles and information on alternative raw materials.

Table 1: PAHs included in entry 50

Substance	CAS No	EINECS No
BENZO[A]PYRENE	50-32-8	200-028-5
BENZO[E]PYRENE	192-97-2	205-892-7
BENZO[A]ANTHRACENE	56-55-3	200-280-6
DIBENZO[A,H]ANTHRACENE	53-70-3	200-181-8
BENZO[B]FLUORANTHENE	205-99-2	205-911-9
BENZO[J]FLUORANTHENE	205-82-3	205-910-3
BENZO[K]FLUORANTHENE	207-08-9	205-916-6
CHRYSENE	218-01-9	205-923-4

Restriction entry 50 paragraphs 5 and 6 were the result of a proposal made by Germany in 2010 (hereafter 'the German Annex XV report (2010)'). This proposal was discussed in CARACAL in June and October 2010.

In the October CARACAL, the Commission proposed a regulation to amend Annex XVII using Article 68(2) of REACH. The final restriction was adopted by the Commission in December 2013 (http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013R1272&from=EN).

ECHA made an assessment[8] of the proposal in support of the Commission during the process, which looked at the hazards, the risk and the impacts of such a restriction.

The restriction provides that articles must not be placed on the market for supply to the general public, if any of their rubber or plastic components that come into direct as well as prolonged or short-term repetitive contact with the human skin or the oral cavity, under normal or reasonably foreseeable conditions of use, contain more than 1 mg/kg (0.0001 % by weight of this component) of any of the listed PAHs. Such articles include, among others: sport equipment such as bicycles, golf clubs, racquets, household utensils, trolleys, walking frames, tools for domestic use, clothing, footwear, gloves and sportswear, watch-straps, wristbands, masks, and headbands.

[8] The results of ECHA's assessment (May 2012) have not been published.

In addition, toys[9], including activity toys[10] and childcare articles, must not be placed on the market, if any of their rubber or plastic components that come into direct as well as prolonged or short-term repetitive contact with the human skin or the oral cavity, under normal or reasonably foreseeable conditions of use, contain more than 0.5 mg/kg (0.00005 % by weight of this component) of any of the listed PAHs.[11]

The Commission requested ECHA on 19 December 2016 to prepare an evaluation report to enable them to conduct the required review of entry 50 (5) and (6) of Annex XVII to REACH[12].

In accordance with the request from the Commission, the Agency has investigated:

1. the state of the art of scientific information in terms of available validated analytical methodologies to determine:
    a. the content of the individual PAHs listed in entry 50;
    b. the migration of each of the individual PAHs listed in entry 50 from plastic and rubber materials relevant to the scope of the restriction, paying particular attention to the availability of validated methodologies and to their associated analytical performance parameters, particularly their limit of quantification.
2. the current market situation in terms of the availability of suitable alternative low-PAH raw materials, particularly carbon black and extender oils, used to manufacture rubber and plastic components.

ECHA has also provided additional considerations on the possibility to reduce the actual content limit and/or the possibility to introduce a migration limit.

Related to point 1, ECHA has taken into consideration the report published in 2018 by the JRC[13], carried out at the request of DG GROW, aimed at developing a methodology to measure migration of PAHs from plastic and rubber. During the development of the ECHA report, the JRC was already conducting work aimed at the identification or the development of a methodology for assessing the migration of PAHs from plastic or rubber materials. The availability of such methodologies in commercial national and international laboratories and

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[9] Toys in the scope of this restriction include also electric and electronic toys under the scope of Directive (EU) 2017/2012 (RoHS 2 Directive)

[10] Activity toys are defined in Article 3(21) of Directive 2009/48/EC (Toys Safety Directive). They are toys for domestic use in which the support structure remains stationary when they are used (e.g. swings, slides, trampolines etc).

[11] At the request of the Commission, ECHA prepared a guideline to provide further clarification on the articles within the scope of the entry. The guideline was adopted at the CARACAL in March 2018 and published on ECHA's web pages: https://echa.europa.eu/support/qas-support/browse/-/qa/70Qx/view/ids/1476

[12] https://echa.europa.eu/documents/10162/13641/echa_lead_pah_commission_request_en.pdf/248461e1-cab2-9d23-9d54-42df72d26505

[13] https://ec.europa.eu/jrc/en/publication/migration-polycyclic-aromatic-hydrocarbons-pahs-plastic-and-rubber-articles

their practicality and cost were also investigated and documented by the JRC. The information from the JRC work was taken into account by ECHA for the preparation of this document.

The JRC project, aimed to develop migration testing methodologies (via skin and oral contact), was conducted with collaboration of the industry and research institutes in the framework of the STANPAH project. ECHA participated in the second project meeting in June 2017 to observe the progress being made and discuss the input from the project into this report. The project was finalised in March 2018, and the final report was published in August 2018.

In support of ECHA's investigation, to collect information requested by the Commission, ECHA held a call for evidence from 1 June to 31 July 2017, seeking information on:

1. the analytical methods to establish PAH content; and
2. on alternative substances (carbon black and extender oil) with lower PAH content than those used when the revision to entry 50 was being discussed.

The call for evidence was published on ECHA's website and publicised in the ECHA Weekly news bulletin. In addition, all MSCAs and selected industry organisations (those that have been contacted in relation to the development of the guideline for applicability of this restriction and those that provided comments in the consultation on the guidelines, 33 in total) were approached directly to ensure that all interested parties would be aware of the work being done on reviewing the restriction and be given an opportunity to contribute at this early stage.

In the designated timeline, 11 responses were received: information was submitted by one Member State, one individual, four companies and five industry organisations. Some of the responses came from companies not directly affected by paragraphs 5 and 6 – tyre manufacturers. Two comments were provided by carbon black suppliers.

While most of the comments submitted originated from within the EU, responses were also submitted from Mexico, US and China.

In relation to the questions, all respondents provided information related to the testing methods, but only seven provided information on alternatives.

In addition, after the call for evidence expired, ECHA continued to make attempts to obtain information on alternatives from the organisation representing the manufacturers and supplies of the raw materials used to produce plastics and rubber (CONCAWE). As a result, CONCAWE has submitted information from one of their member companies.

In addition, on 20 December 2017, Germany submitted a report containing additional information to be taken into account in the review. In the context of the German national monitoring programme (2017), they analysed the PAH content of a number of consumer articles taken from the market and the migration rate of PAHs from these articles. These issues will be further discussed in Section 2.4.4.

1.2. Hazard, exposure / emissions and risk

1.2.1. Introduction

The German Annex XV report (2010) stated that 'consumer articles containing one or more polycyclic aromatic hydrocarbons (PAHs) as listed in entry 50 of Annex XVII to the REACH Regulation (Reg. (EC) 1907/2006) are considered severely hazardous based on their carcinogenic and mutagenic properties, as well as their potential for being toxic to reproduction'.

All eight PAHs discussed in the German (2010) report (see Table 1: PAHs included in entry 50) are classified as carcinogens of category 1B (CLP), respectively (see Table 2: Classification of entry 50 PAHs in CLP. Benzo[a]pyrene (CLP Cat. 1b) and chrysene (CLP Cat. 2) also are also classified as mutagens. It was noted that the lack of classification for the other PAH substances does not necessarily indicate absence of genotoxicity, but may rather be attributed to the comparatively limited database available for these compounds.

Table 2: Classification of entry 50 PAHs in CLP

Substance	CAS No	Classification	SVHC identification
benzo(def)pyrene; benzo(a)pyrene	50-32-8	Skin Sens. 1; Carc. 1B; Muta. 1B; Repr. 1B; Aquatic Acute 1; Aquatic Chronic 1	PBT/vPvB
benzo[e]pyrene	192-97-2	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	-
benz[a]anthracene	56-55-3	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	-
dibenz[a,h]anthracene	53-70-3	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	-
benz[e]acephenanthrylene	205-99-2	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	-
benzo[j]fluoranthene	205-82-3	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	-
benzo[k]fluoranthene	207-08-9	Carc. 1B; Aquatic Acute 1; Aquatic Chronic 1	-
chrysene	218-01-9	Carc. 1B; Muta. 2; Aquatic Acute 1; Aquatic Chronic 1	-

In addition to the eight PAHs in entry 50, there are two additional PAHs that have been recently classified by RAC for carcinogenicity (see Table 3: PAHs recently classified in RAC (June 2017)). However, these substances are not yet included in Annex VI to the CLP Regulation ((EC) No 1272/2008).

Table 3: PAHs recently classified in RAC (June 2017)

Substance	EC number	CAS number	Classification
dibenzo[b,def]chrysene; dibenzo[a,h]pyrene	205-878-0	189-64-0	Carc. 1B, Muta. 2
benzo[*rst*]pentaphene	205-877-5	189-55-9	Carc. 1B, Muta. 2

The Scientific Committee on Food (SCF) concluded in 2002 that 15 PAHs, namely benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, cyclopenta[cd]pyrene, dibenz[a,h]anthracene, dibenzo[a,e]pyrene, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, dibenzo[a,l]pyrene, indeno[1,2,3-cd]pyrene and 5-methylchrysene show clear evidence of mutagenicity/genotoxicity in somatic cells in experimental animals *in vivo* and with the exception of benzo[ghi]perylene have also shown clear carcinogenic effects in various types of bioassays in experimental animals.

In 2008, the JECFA concluded that 13 PAHs are clearly genotoxic and carcinogenic. Except for benzo[ghi]perylene and cyclopenta[cd]pyrene, the compounds were the same as those stated by SCF. The JECFA concluded that the concentrations of benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, chrysene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene (EFSA 8) either individually or in combination, are currently the only possible indicators of the carcinogenic potency of PAHs in food.[14]

The confinement of the proposal to the eight PAHs included in restriction entry 50 is further supported by the Annex XV restriction proposal on PAHs in rubber granules[15] as sufficient to control risks. Therefore, it is not proposed to extend the current entry 50 as the eight PAHs can be used as a proxy for all PAHs in the relevant mixtures.

[14] Scientific Opinion of the Panel on Contaminants in the Food Chain on a request from the European Commission on Polycyclic Aromatic Hydrocarbons in Food. The EFSA Journal (2008) 724, 1-114.

[15] See Section 1.2.1 of the Background Document related to the restriction proposal on PAHS in rubber granules: https://echa.europa.eu/documents/10162/ef74f292-0d7e-2462-c062-fdc2146b774c

According to the regulatory management option analysis (RMOA) for coal tar pitch prepared in June 2017 by Germany[16], the following PAHs also meet the PBT/vPvB criteria according to Annex XIII to REACH:

Table 4: Annex XIII properties of certain PAHs

Substance	CAS	Annex XIII properties
fluoranthene	206-44-0	PBT, vPvB,
pyrene	129-00-0	PBT, vPvB
benz(a)anthracene	56-55-3	PBT, vPvB
chrysene	218-01-9	PBT, vPvB
benzo(k)fluoranthene	207-08-9	PBT, vPvB
benzo(ghi)perylene	191-24-2	PBT, vPvB
phenanthrene		vPvB

The focus of the German restriction report from 2010 was on the carcinogenicity of benzo(a)pyrene (BaP) and the other PAHs included in entry 50. The mutagenic properties were considered in a qualitative way, i.e. in establishing the mechanism behind the PAHs' carcinogenicity.

Relating to the additivity of the various PAHs in the risk assessment, this was not reflected in the final proposal. The most recent version of the *Guidance on the Application of the CLP Criteria*[17] (version 5.0, 2017, section 1.6.3.3.3), in relation to CMR properties considers that *"if the mode of action (MoA) of two substances is the same, additivity can reasonably be assumed.(…). When the MoA is different, there may be some cases where it is deemed appropriate to assume additive or synergistic effects".* For the eight PAHs in entry 50, additivity can be assumed in relation to certain CMR properties. However, at the moment as the issue of additivity of PAHs as constituents of UVCB substances and its potential relevance for classification is still under discussion at the Commission, additivity has not been further considered in this report.

In the German Annex XV report (2010), the potential of BaP to cause toxicity to reproduction was noted. However, it was considered unlikely that the DNELs for reproductive toxicity would be stricter than the DMELs calculated in this report on the basis of non-threshold carcinogenicity of BaP. Therefore, reproduction toxicity was not evaluated further in the German Annex XV report (2010).

Related to the absorption of the eight PAHs, the German Annex XV report (2010) evaluated the available animal tests and concluded the following estimates:

- dermal absorption: 50 % from acetone and 20 % from aqueous media (such as sweat); and
- oral route and by inhalation: 50 % absorption.

[16] https://echa.europa.eu/documents/10162/aa0fd19f-a262-db1c-dece-ada1a5361214

[17] Guidance on the Application of the CLP Criteria, v. 5, 2017, at: https://echa.europa.eu/documents/10162/23036412/clp_en.pdf

In its assessment submitted to the Commission in 2012, ECHA evaluated the information provided in the German Annex XV report (2010) and has described any uncertainties related to it. The conclusions of the assessments are presented in the relevant sections below.

1.2.2. Derivation of DMELs for carcinogenicity

In the German Annex XV report (2010), DMELs were calculated from available animal studies following the scheme as provided in the REACH *IR/CSA guidance on dose-response assessment (R.8)*. T25, BMD10, and BMDL10 were all used as dose descriptors. DMELs were calculated applying both the 'Large Assessment Factor' and the 'Linearised' approach' (the latter at both the 10^{-5} and 10^{-6} risk levels and using the 'Probit' as well as the 'Multistage Cancer' algorithms for curve fitting).

The following DMEL results ranges (excluding the Probit calculations) were obtained:

- Large Assessment Factor approach: 0.1 – 30 ng/kg bw/d
- Linearised Approach, 10^{-5} risk level: 0.03 – 10 ng/kg bw/d
- Linearised Approach, 10^{-6} risk level: 0.004 – 1 ng/kg bw/d

In its assessment, ECHA concluded in relation to the derivation of DMEL, that the German Annex XV report (2010) largely follows the methodology recommended in the ECHA guidance. A narrower range of DMELs could have been proposed to facilitate conclusions on risk by adhering to guidance recommendations regarding the dose descriptor and selecting the most appropriate studies for the case at hand.

ECHA recommended a DMEL range of 0.005-0.55 ng/kg bw/day following the 'Linearised approach' (applying a risk estimate of 10^{-6}).

In their recent reports on rubber granules used in infill, both ECHA and RIVM used the BMDL10 for eight PAHs (0.49 mg/kg b.w. per day) derived by EFSA (2008) as the point of departure for the risk assessment of PAHs. In addition, slightly different absorption rates were used based on newer studies.

EFSA's 2008 study has reported that the oral absorption of benzo[a]pyrene varies between 12 and 99 % of ingested dose, depending on the dose and species investigated. It also noted that a higher absorption was observed for lower molecular mass PAHs, whereas higher molecular mass PAHs are poorly absorbed.

The more recent studies (2016/2017) used by RIVM reported an oral absorption rate of 30 % and dermal of 20 %. In its opinion on the Annex XV restriction dossier, RAC[18] observed that "due to the different PAH content and potency in the mixtures, the use of the derived $BMDL_{10}$ value based on a study with coal tar is inherently inaccurate to assess the risk of PAH mixtures in rubber granules for oral and dermal exposure". However, the uncertainties on hazard and exposure, taken together lead to an overestimation of the risk.

[18] https://echa.europa.eu/documents/10162/0a91bee3-3e2d-ea2d-3e33-9c9e7b9e4ec5

Such a conservative approach was nevertheless accepted by RAC with the justification that PAHs are genotoxic and carcinogenic compounds with a non-threshold mode of action. These considerations could be taken into account in any review of the concentration limits.

1.2.3. Exposure

1.2.3.1. Emissions – Content of PAH in articles

The German Annex XV report (2010) evaluated more than 5 300 samples from consumer articles analysed for their PAH content. The analysed samples covered a multitude of different consumer articles: 1. Electrical devices, 2. Grips/handles, 3. Skin contact areas of sports equipment or other consumer articles, 4. Toys and electrical toys, 5. Materials with close contact to the body, 6. Other articles with skin contact, 7. Tyres and rolls, and 8. Other articles.

In all the product groups covered, BaP was not detectable in 91.9 % of the cases and in 95 % of all samples, the concentration was below 1 mg/kg. The corresponding values were 83.9 % not detectable, 90.7 % of the values below 1 mg/kg for the sum of the six out of eight EU-PAHs[19] contained in the EPA-PAH list[20]. However, detected levels vary considerably between different product groups.

In the remaining samples, however, the highest PAH levels found were 1 200 mg/kg for BaP, 25 400 mg/kg for the sum of all EPA-PAHs and 6 930 mg/kg for the sum of all EU-PAHs.

The German Annex XV report (2010) proposed a limit of quantification (LoQ) of 0.2 mg/kg for all articles within the scope of the proposal. The lack of a certified analytical method for establishing PAH content was also identified in the German Annex XV report (2010) as a source of uncertainty.

The assessment performed by ECHA indicated that there were several shortcomings in the description of the PAH content in the articles, including lack of information on the country of origin of the sample (manufacturing and availability of article), inter-batch variability and the link of the PAH content to the 'quality' of the product.

Nevertheless, ECHA concluded that even if the information on PAHs in articles provided in the restriction proposal lacks important details, the information given is considered sufficient to demonstrate that it is not unusual to find PAH levels in the range of 1-100 mg/kg in consumer articles.

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[19] EU-PAHs meaning the eight PAHs restricted with entry 50 of Annex XVII to REACH.

[20] The list of 16 PAHs issued by the U.S. Environmental Protection Agency (EPA) in 1976 aimed originally at protecting human health from exposure to toxic substances in drinking water. (https://archive.epa.gov/epawaste/hazard/wastemin/web/pdf/pahs.pdf). Six of the PAHs included in restriction entry 50 of Annex XVII of REACH are also included in the EPA's list: benzo[a]pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and dibenzo[a,h]anthracene (5)

The Commission took into account ECHA's assessment[21] and a scientific review from the JRC (2012) when establishing the limit values that were adopted for the restriction.

As part of the STANPAH project, the JRC (2018) analysed the methods already available to determine the PAH content in articles and developed an improved method for the determination of the eight PAHs listed in entry 50 of Annex XVII to REACH. A number of consumer commercial articles have been selected by the JRC for its study based on available information on the PAH content. A comparison table of the methods reviewed by the JRC for determining PAH content has been included in a publication from 2018[22] (see Table 5). The method developed by the JRC is based on Randall hot extraction with toluene, extraction cartridges based on molecularly imprinted polymers (MIPs) followed by gas chromatography-mass spectrometry (GC-MS) in selected ion mode. The maximum amount of PAHs (as the sum of all eight PAHs) was 20 mg/kg in rubber, 15 mg/kg in plastics and 5 mg/kg in recycled rubber granules. Rubber materials with the highest amount of PAHs were those prepared with distillate aromatic extract (DAE) as the extender oil.

[21] In its assessment on the German restriction report (2012), ECHA applied a DMEL range of 0.005-0.55 ng/kg bw/day following the 'Linearised approach' (applying a risk estimate of 10-6). In defining the concentration limit for the restriction, the Commission considered the uncertainties identified in ECHA's assessment (see Section 1.2.3.2 of this report), the limited availability of data on migration and the relatively wide range of DMELs.

[22] https://reader.elsevier.com/reader/sd/pii/S0021967318308033?token=B341B125CEDC4CD1F3393112A9E47520BD87D9D30F2DD7BAA5EEAA6A20FB7FEE2129BE20F74ED774949843EC2EBB1958

Table 5: Comparison of methods for determining PAH content in plastics and rubber published (from Journal of Chromatography A, 1566 (2018) 13-22)

Comparison of methods/studies for the extraction and determination of PAHs from rubber and/or plastics with regard to sample extraction and sample purification.

			Sample Extraction				Sample extract purification				Remarks
Method/Study	Year of publication	Extraction Solvent	Technique	Time[d]	Cost[e]	Extraction efficiency	Technique	Time consuming?	Cost[e]	Clean-up efficiency	
Study commissioned by carbon black industry [14]	2009	Toluene	Soxhlet	16 h (320 cycles)	3-5 k€ (6 pos.)	Complete extraction[c]	Silica gel packed column	Yes. Packing and long conditioning procedure.	Variable	Unselective. Only polar compounds are retained.	Extraction of PAHs from cured rubber formulations containing carbon black. Not tested for plastic materials.
ISO/TS 16,190 [11]	2013	n-Hexane	Ultrasounds extractions	1 h	1-2 k€	Incomplete extraction[b]	No clean-up	n/a	n/a	No clean-up	Method for determination of PAHs in footwear materials. Not specific for rubber and plastic materials
CEN EN 16,143 [12]	2013	n-Pentan	n/a[a]	n/a[a]	n/a[a]	n/a[a]	Silica gel packed column	Yes. Packing and long conditioning procedure.	Variable	Unselective. Only polar compounds are retained.	Method for determination of benzo[a]pyrene and other PAHs in petroleum products.
AFPS GS2014:01 PAK [9]	2014	Toluene	Ultrasounds extractions	1 h		Incomplete extraction[b]	Silica gel packed column	Yes. Packing and long conditioning procedure.	Variable	Unselective. Only polar compounds are retained.	Used in the course of German GS mark certification. Method which comes closest to the method described in this study.
Fraunhofer IVV [10]	2017	Cyclo-hexane	Accelerated solvent extraction (ASE)	45 min	45-50 k€	Complete extraction[c]	Normal phase SPE	No. Commercially available.	4 €/cartr.	Unselective. Only polar compounds are retained.	Method for extraction of PAHs from recycled rubber. Not tested for plastic materials.
Method proposed in this study		Toluene	Randall-hot extraction	3 h	10-14 k€ (6 pos.)	Complete extraction[c]	MIP-SPE	No. Commercially available and easy/fast protocol.	5 €/cartr.	Highly selective.	

[a] Petroleum product directly solved in n-pentane. No extraction required.
[b] The current study suggests that ultrasound extraction may be less efficient compared to Randall hot extraction.
[c] Extraction efficiency verified in referenced study.
[d] Total extraction time.
[e] Indicative acquisition cost (Italy).

1.2.3.2. Migration rates

In the Annex XV restriction report from Germany (2010), the migration rates of PAHs under static and dynamic conditions were assessed[23]. Germany concluded that under static conditions, migration rates are strongly influenced by the simulant used. In particular, use of ethanol or iso-octane (highly liphophilic solvents) as the simulant may increase the migration rate of PAHs by several orders of magnitude compared to aqueous simulants.

Germany concluded that, presumably, the use of these highly lipophilic solvents may result in an overestimation of PAH migration rates. Furthermore, studies under static conditions do not take into account the contribution of dynamic processes such as mechanical friction and contact pressure to migration.

To better reflect the dynamic aspects, a more realistic scenario was considered by Germany in the restriction report. This “dynamic scenario” consisted of the use of latex gloves wetted with sweat simulant and simulating the use conditions. The migration rates of BaP under the dynamic scenario had values between 0.02 % and 10 % depending on the material.

Germany concluded that the migration mainly depends on the composition of the material (including the type of added substances used in its production) as already known in the case of food contact materials and on mechanical effects like friction. No correlation between the concentration of BaP and the migration rate could be derived.

Based on these considerations, Germany decided to use migration rates quantified under dynamic conditions for the exposure estimation of consumers. Three different migration rates for BaP were used in the restriction report for the calculations with the intent to cover different materials and the influence of dynamic conditions:

- 10 % migration rate as the worst case of dynamic migration with friction;
- 1.5 % migration rate as the approximate geometric mean of dynamic migration with friction; and
- 0.2 % migration rate as the mean of dynamic migration for materials with low migration, when friction is not considered.

In the German restriction report (2010), it was acknowledged that knowledge about migration of PAHs needs to be improved. The dossier recommended that standardised migration methods that cover the typical uses of the consumer articles investigated should be developed.

ECHA’s evaluation of the restriction proposal noted that the migration of PAHs from consumer articles had not been extensively studied. The available studies indicate that the migration of PAHs is very limited, where migration models with artificial sweat were used.

An analysis of newer (at the time unpublished) information from Hutzler et al[24] described in ECHA’s analysis indicated that the migration of PAHs and their subsequent absorption into

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[23] Paragraphs B.9.3.2.2.3, B.9.3.2.2.4 and B.9.3.2.2.5 of the 2010 restriction report from Germany.

[24] Hutzler C, Heidler J, Tadjine F, Vieth B and Luch A. (2011). Presentation. Polycyclic aromatic hydrocarbons in consumer products: Investigations on the migration and skin penetration of

human skin may be overestimated when migration is derived from models based on migration rates (especially those assuming migration rates of 10 % and 1.5 % per hour used in the restriction report) while it would be underestimated when migration models based on migration to artificial sweat are used. Moreover, ECHA concluded that based on information from Hutzler et al. on absorption in human skin, the lowest value for migration used in the restriction report (0.2 % per hour) could still overestimate the potential migration rate.

The German report from 2017 [25] analysing the migration of PAHs from samples of consumer articles indicates that exposure estimates for BaP based on normalised migration data, essentially confirmed the assumptions made in the restriction report, however data on the migration of PAHs from articles is still limited.

The methodology developed by the JRC in 2017-18[26] fills this gap. In its report, the JRC concluded that migration of each of the eight EU PAHs into aqueous media – artificial sweat and saliva – was under the instrumental limit of detection – from plastic, silicone and rubber matrices. The relative migration rate into 20 % aqueous ethanol for 24 hours, at 40 °C, in dynamic mode is within range between 0 and 0.09 %.

The migration rate is linked to the size and shape of the PAHs' molecules. The highest relative migration value was obtained for chrysene. A type of carbon black used in manufacturing also plays a role: a comparison of the release of PAHs from the same material containing different carbon black lead to the conclusion that, even though materials containing CB N550[27] show lower total content in PAHs than the same material blended with CB N375, migration is lower from matrices containing the latter.

It is explained that carbon blacks have the capacity of re-adsorbing PAHs already released (e.g. from extender oils). This effect would be actually enhanced by the higher surface area of CB 375, resulting in a lower effective release of PAHs.

1.2.3.3. Exposure assessment

Exposure of children to rubber granules

The assessment of dermal exposure of children to rubber granules used as infill in synthetic turf fields described in the German Annex XV report (2010) was performed using a) an approach based on ECETOC TRA; and b) an approach considering migration of PAHs.

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benzo[a]pyrene and detection of highly carcinogenic dibenzopyrenes. https://openagrar.bmel-forschung.de/receive/bimport_mods_00002388

[25] Evaluation of the German National Monitoring Program 2017 on PAH in consumer products and toys, BfR, 18.12.2017, *unpublished*

[26] Migration of Polycyclic Aromatic Hydrocarbons (PAHs) from plastic and rubber articles (JRC 2018)

[27] Nomenclature of carbon blacks is based on ASTM D 24 standard. The prefix (N or S) indicate Normal or Slow curing material. The first of the three digits indicates the measure of the mean particle diameter (expressed in nm) and the other two digit are progressive numbers.

Germany highlighted the uncertainties of the evaluation due to the default assumptions used and an over-conservativeness of the method used. It was also observed that the appropriateness of the approach used in the report can only be evaluated by the use of appropriate migration data that were not available when the dossier was prepared. One additional observation from Germany was that although the knowledge about the release of these compounds needed to be improved, there was already evidence that a considerable amount of PAHs could be released.

In relation to that, ECHA points out that the exposure to PAHs due to the mouthing behaviour of children in relation to rubber granules on playgrounds, which, according to the German Annex XV report (2010) may be a source of the potentially high oral exposure, was subject to the evaluation performed recently at the Commission's request (report published in Feb 2017)[28] and is included in a separate restriction proposal currently in the decision phase by the EU Commission after the adoption of RAC and SEAC opinions[29].

Recently published analysis indicates that in the existing fields, the BaP concentration in the rubber granules made from recycled tyres varies between 0.01 mg/kg and 2.38 mg/kg while the concentration in other recycled material lies in the range 0.02-2.83 mg/kg (BaP).

In new rubber granules manufactured from recycled tyres (i.e. not yet installed as infill), (BaP) concentrations have been found between the detection limit (<0.08) and 1.19 mg/kg. The maximum concentrations found are, therefore, lower than those considered in the analysis presented in the German restriction report (2010).[30]

Furthermore, according to the restriction proposal on PAHs in rubber granules, dermal exposures of workers installing and maintaining artificial turf are in the range of 7.3×10^{-6} – 0.00013 µg/kg bw/d, while for the players the estimated dermal exposure was in the range of 2.1×10^{-6} to 0.00013 µg/kg bw/d (based on REACH-8 PAH content of 17 mg/kg) depending on the exposure scenario.

The life-long exposures for consumers and players are respectively 0.00017 µg/kg bw/d and 0.00018 µg/kg bw/d and exposure for professional goalkeepers is 0.00036 µg/kg bw/d. Based on these data, all estimated exposures are below the predicted level of 1 ng/kg bw/day.

External exposure to other consumer articles

The dermal exposure by consumer articles was estimated in two different ways:

1. The results of the dynamic migration tests described above were used for estimating the external dermal exposure to BaP from those articles included in these tests.
2. The external dermal exposure was estimated based on the estimated migration rates and on the available data on BaP concentrations in consumer articles.

[28] Link to the report: https://echa.europa.eu/documents/10162/13563/annex-xv_report_rubber_granules_en.pdf

[29] https://echa.europa.eu/restrictions-under-consideration/-/substance-rev/20503/term

[30] http://www.bfr.bund.de/cm/349/pak_annex_XV_restriction_report_proposal_for_a_restriction.pdf

The dynamic test approach (Approach 1) consisted in the quantification of the amount of BaP migrated into gloves after contact with a number of consumer articles under typical conditions of use. Based on these values, the external dermal doses were estimated by the formula described in Section B.9.3.2.3.3 of the German Annex XV report (2010), which allows the calculation of the dermal dose (ng/kg bw/d) by taking into account the amount of BaP migrated from the glove (per hour), the mean number of exposure events per day, the contact duration between the article and the skin and body weight (BW). While for BW the value of 60 kg has been used as a default value for adults, for the other parameters (such as contact duration and number of events per day) the ordinary behaviour of consumers has been assumed as no default value was available.

The results obtained by Approach 1 varied between ca. 2 ng/kg bw/d up to 6.7 µg/kg bw/d for different types of articles. The highest doses were estimated for skin contact with a tool grip and a cover of a steering wheel both made of rubber.

For the estimation of the external dermal dose, a number of consumer articles – likely to be in contact with the skin – were selected and separate exposure estimations were performed for adults and for children. Articles for use by adults included grips of different handheld tools or bicycles, skin contact area of sport tools and other consumer articles, footwear, gloves, covers of steering wheels, watch straps. Children' articles included grips of bicycles, skin contact areas of sport tools and other consumer articles, footwear (sandals), rubber boots, watch straps and toys.

The exposure estimation based on the estimated migration rate (Approach 2) has been based on the method described in *ECHA guidance R 15* which takes into account the migration fraction, contact area for skin, fraction of PAHs in the articles, contact time duration, number of exposure events and the weight of the article used.

For determining the dermal dose (expressed in ng of PAH per kg BW per day) three values for the migration fraction (10 %, 1.5 % and 0.2 %) were used. These values were meant to reflect the large variability of migrating fractions that depend on the materials and the influence of the dynamic conditions.

Separate exposure estimations were performed for adults and children for a number of articles assumed to be used by adults and by children. For a given set of default parameters, the calculation of the dermal dose was performed for each article considering the measured fractions of PAHs in the article.

Using the highest (most conservative) assumption of 10 % migration/h, obtained exposure estimates ranged between 0.3 and 68 613 ng/kg bw/d for adults and between 3 and 66 780 ng/kg bw/d for children. Estimates using 1.5 or 0.2 % migration/h ranged lower by a factor of 6.67 or 50, respectively. Summarising the results, there is clear evidence that under normal use conditions considerable amounts of BaP can be released even when a comparatively low migration rate is assumed.

To simulate the effect of the proposed restriction, another set of calculations was described in the German Annex XV restriction report (2010), this time assuming that the same articles, used with Approach 2 before, would have contained 1 or only 0.2 mg BaP/kg product (but otherwise making the same assumptions regarding exposure scenarios and migration rates):

- For the 1 mg BaP/kg article simulation, this resulted in a dermal exposure range for adults between 133.3 ng/kg bw/d (for a grip of a tool) and 750 ng/kg bw/d (watch strap) for adults assuming 10 % migration/h and between 8.5 ng/kg bw/d (training bike) to 1 600 ng/kg bw/d (rubber boots) for children. For 1.5 or 0.2 % migration/h the exposure range is respectively 20-112.5 ng/kg bw/d and 2.67-15 ng/kg bw/d again depending on the type of article.
- For the 0.2 mg BaP/kg article simulation, corresponding dermal exposure values could be obtained by dividing the results from the 1 mg/kg simulation by a further factor of 5, i. e. a range of 26.67 – 150 ng/kg bw/d for adults assuming 10 % migration/h was calculated (children: 1.7 – 320 ng/kg bw/d). Estimates using 1.5 or 0.2 % migration/h again would be lower by factors of 6.67 or 50, respectively.

Exposure at the workplace, indirect exposure through the environment via food or smoking, oral combined/aggregate human exposure assessment was not considered in the German Annex XV report (2010). However, on the latter point the German proposal states that, from the analytical data presented in the dossier as well as from everyday experience, it is clear that consumers are exposed to a multitude of potentially PAH-containing articles via several routes and will most likely come in contact with more than just one of these articles on a daily basis.

ECHA's assessment conducted in 2012[31] points out that *"for neither of the groups of articles for which exposure assessment was performed, the calculated exposure was specifically addressing the eight PAH substances for which a restriction is proposed".* Furthermore, information on exposure (or content in articles) was not available for all substances, and justifications for assuming that exposures to all substances would be a reason for concern were not provided.

As only dermal exposure to a single source of PAHs was assessed, it can be concluded that the total exposure level, including exposures via the oral route and inhalation, from a variety of sources, could be higher than the exposures (from individual articles) reported in the German Annex XV report (2010).

In general, ECHA's assessment concluded that *"while not all routes of exposure were taken into consideration, the scenarios for dermal exposure described in the report may be accepted for that route".* However, some uncertainties have been identified in the exposure assessment (e.g. use of 'expert judgement' in establishing parameters of exposure). One of the main uncertainties relates to the migration rate of PAHs from articles. ECHA considered that even the lowest value for relative migration used in the restriction report (0.2% per hour) can lead to an overestimation of the potential migration rate. This is confirmed by new information on absorption in human skin[32] which was not available during the preparation of the German restriction proposal.

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[31] Review of the Annex XV report (PAHs), ECHA, 15 May 2012, not published.

[32] Hutzler C, Heidler J, Tadjine F, Vieth B and Luch A. (2011). Presentation. Polycyclic aromatic hydrocarbons in consumer products: Investigations on the migration and skin penetration of benzo[a]pyrene and detection of highly carcinogenic dibenzopyrenes. https://openagrar.bmel-forschung.de/receive/bimport_mods_00002388

The study performed by the JRC in the context of the STANPAH project further contributes to reducing the uncertainty linked to the migration of PAHs from the articles mentioned above. In their report, the JRC indicates that the migration rate of PAHs in 20 % ethanol is between 0 and 0.09 %. These results were established examining the migration rates in dynamic conditions, designed to imitate real use parameters.

Migration of PAHs from rubber granules was also investigated by the JRC. The JRC analysed recycled granules (coated and uncoated) originated from end-of-life tyres produced before and after 2010 and recycled granules from polyurethane-coated rubber tiles. The results of dynamic migration tests performed with 20 % ethanol as the migration media, returned relative migration rates (expressed in % wt/total wt) from 0 to 8.6 for uncoated granules and from 0 to 2.7 for PU coated granules. The results showed that, despite the total content of PAHs being similar in coated and uncoated granules, coating reduces the migration by a factor of ~3. It was also noted that PAHs were not detected in parallel tests performed using aqueous media (artificial sweat or saliva) above the detection limit (LoD) of the method used by the JRC.

LoDs, calculated for each PAH separately, range from 0.1 to 0.2 ng/ml; the limits of quantifications (LoQs) range between 0.1 and 0.6 ng/ml (expressed as a concentration of substance in the media) while the relative LoQs range between 0.03 and 0.18 mg/kg for a 20 g sample and between 0.001 and 0.007 mg/kg for the sample of 500 mg. The lowest values were noted for dibenzo[a,h]anthracene, and the highest for benzo[b]fluoranthene.

In relation to migration, the JRC considered that migration is a diffusion process and it can be described by mathematical formulas derived from Fick's Law. The diffusion process depends on time, temperature, thickness of the material, amount of chemical in the material and the partition-coefficient/distribution-coefficient. The mobility of the chemical in the specific matrix also plays an important role in the diffusion process.

In the tests performed by the JRC, most of the parameters influencing diffusion, such as temperature, and material thickness, were kept constant. Therefore, the amount of migrated PAHs depends mostly on the content of PAHs in the matrices and their molecular structure. It was also noted that although the relative amount of PAHs that is released increases over time, there is a decrease in the release of PAHs after a certain time as materials have the tendency to re-uptake released PAHs. The release-re-uptake process depends on a number of factors including the mobility of the individual PAH molecule, its total content and the type of matrix.

It has been observed that re-uptake is much higher in rubber granules compared to other rubber materials analysed by the JRC. This fact has been explained with the larger surface of rubber granules in contact with the simulant.

1.2.4. Risk

In the German Annex XV report (2010), the risk characterisation (RC) was only performed for the scenarios directly relevant for this restriction proposal, i.e. use of PAH-contaminated consumer articles. Furthermore, only the dermal route was taken forward to quantitative risk characterisation (cf. Section B.9.3).

1.2.4.1. Risk characterisation for articles

In the German Annex XV report (2010), DMELs (or rather, DMEL ranges) were compared with the exposure estimates for adults and children, respectively, for those consumer articles which had been tested positive for PAHs. For these articles, the following conclusions with respect to the situation without the restriction were drawn when comparing DMELs and exposure estimates:

- When using the most conservative estimate of a migration rate of 10 %/h, estimated external dermal exposure of adults may amount to as much as 70 µg/kg bw/d and would thus range as high as >2 000-fold above the highest (i.e. least conservative) DMEL values given in Table 32.
- When using the least conservative migration assumption of only 0.2 %/h, adult exposure could be assumed to be up to 1.5 µg/kg bw/d (approximately) from the most highly contaminated articles.
- or children, comparably high exposure estimates of up to ca. 70 µg/kg bw/d (assuming 10 % migration/h) and 1.3 µg/kg bw/d (0.2 %/h) were obtained.

1.2.4.2. Risk reduction achieved by the proposed restriction options

Case 1: BaP restricted to a limit of 1 mg/kg article. The German Annex XV report (2010) assessed that:

- In the case of adults, a limit of 1 mg BaP/kg product (component) would – depending on the exposure scenario – reduce the exposure to levels of up to 750 ng/kg bw/d (assuming 10 % migration/h), or 15 ng/kg bw/d (assuming 0.2 % migration/h).
- For children, nevertheless, on top of their postulated higher vulnerability, a clearly higher exposure of up to 1 600 ng/kg bw/d would be expected at a BaP level of 1 mg/kg product (assuming 10 % migration/h). If a low migration rate of 0.2 %/h is assumed, exposure would be clearly reduced. However, the highest estimate still amounts to as much as 32 ng/kg bw/d, which is in the order of the least conservative DMELs derived, but clearly above those DMEL ranges obtained by the calculation methods recommended in the REACH guidance.

Case 2: a hypothetical limit set at 0.2 mg/kg article (LoQ of the analytical method). This limit can be shown to bring exposure down to a level that could be considered tolerable (increased cancer risk of not more than 10^{-6}) for the bulk of articles/uses examined. However, for some extremely contaminated articles an exposure up to one order of magnitude above the least conservative DMELs is still found when assuming the most conservative migration rate:

- According to the calculations performed, adults would be at most exposed to levels of 150 ng/kg bw/d when assuming 10 % migration/h, or 3 ng/kg bw/d, when using 0.2 % migration/h.
- For children, maximum exposure levels account for 320 ng/kg bw/d with 10 % migration/h or 6.4 ng/kg bw/d with 0.2 % migration/h.

At the time of development of the German Annex XV report (2010), 0.2 mg BaP/kg article (component) constituted the LoQ of the analytical method. Therefore, it was considered prudent not to propose a restriction limit value below this level. Thus, the proposal from

Germany was to use the LoQ value of 0.2 mg/kg for any of the listed PAHs in all articles within the scope of the restriction proposal. However, the methodology developed by the JRC (2018) allows significantly lower concentrations of PAHs in rubber and plastic materials to be measured and it is 50-100 times more sensitive than the methodology available at the time of the German Annex XV restriction report (2010).

In its assessment of the German Annex XV report (2010), ECHA noted that the risk characterisation presented is rather open to interpretation, as it is based on a wide range of DMELs. ECHA considered that "*a narrower range of DMELs could have been proposed to facilitate conclusions on risk by adhering to guidance recommendations regarding the dose descriptor and selecting the most appropriate studies for the case at hand*". Furthermore, ECHA concluded that "*for the sake of confirmation of the risk characterisation ratios for PAHs in consumer articles, ECHA has applied a DMEL range of 0.005-0.55 ng/kg bw/day following the 'Linearised approach' (applying a risk estimate of 10^{-6})*."

In addition, ECHA reported that the exposure estimates (applying a migration factor of 0.2 %/h) are uncertain, in particular, due to limited availability of migration data and limitations of analytical methods. Taking into account new information on migration (Hutzler et al. 2011) that became available during ECHA's assessment it appeared possible that the exposure estimates used for the risk characterisation in the German Annex XV report (2010) may have been overestimated.

However, as most RCRs calculated in the German Annex XV report (2010) were well above 1 – some of them by several orders of magnitude – ECHA agreed that exposure to PAHs in articles could constitute a risk for consumers even for the DMEL range of 0.005-0.55 ng/kg bw/day (based on the 'Linearised approach') and assuming that an exposure above 1 ng/kg bw/day may be realistic. The uncertainty in the estimates was however acknowledged.

The 2017 German study on migration of PAHs from consumer articles indicates that for all scenarios analysed, the possible additional BaP exposure doses were in the range of 0.0127-1.96 ng/kg bw/d and 0.15-23 ng/kg bw/d for worst case, exceeding clearly, in some cases, the upper limit of the DMEL level derived for a tolerable risk of 10^{-6} (DMEL range 0.005 – 0.992 ng/kg bw/d) as proposed in the restriction. Based on the outcome of the German study, articles containing BaP at the limit value of 1 mg/kg will mostly lead to an additional exposure to BaP above the estimated DMEL range for all rubber and elastomers even without taking into account the additional contribution of other PAHs listed in entry 50. Germany concluded that the current limits should be at least maintained if not replaced by stricter limits. The study also shows that there is a large variability in migration behaviour of different PAHs from different samples of rubber and elastomers into 20 % ethanol and, therefore, more data and systematic knowledge about migration of PAHs from various matrices was needed.

The JRC study also notes the effect of the matrix on the migration of PAHs. While migration to the aqueous medium is not observed from either plastic or rubber matrices, the migration into 20 % aqueous ethanol (simulating sweat) occurs from some rubber matrices, but not from plastic. Specifically, migration from rubber seems to be related to the type of extender oil used in their formulation: release was observed from rubber matrices containing distilled aromatic extract (DAE) while no release was observed from rubber matrices containing treated distilled aromatic extract (TDAE). No release was detected from silicones, which suggests that extender oil, which is not contained in silicone matrices, has a major impact on PAH release. Highest migration rates were observed for chrysene and BaP (structures with lower MW and higher total content).

The JRC concluded that although migration is a function of time, temperature, thickness of the material, the amount of chemical in the material and the partition/distribution coefficient, it also depends on mobility of the chemical in the matrix (rubber), the size and the shape of the migrant's molecule. Relative migration of BaA (lower MW and higher mobility) is higher than BeP which is contained in higher quantities but has lower mobility.

The JRC has also observed that migration depends on the type of carbon black used in the production process of the rubber material. For example, migration of PAHs was lower from matrices produced with carbon black CB375 than from those produced with carbon black CB550 even if the total PAH quantity in CB375 was higher than in CB550. This fact has been explained by the tendency of certain carbon blacks to reabsorb PAHs. In particular, CB375 has a higher surface area and as such higher reabsorbing capacity resulting in a lower effective release of PAHs.

The relative migration range from 0 to 0.09 % (for CB 375) was observed in the JRC study, confirming the variability scale (two orders of magnitude), and approximately two times lower for CB 550. The work done on developing the migration assessment may be used to evaluate the scope of applicability of paragraphs 5 and 6 from the perspective of materials to be included and routes of exposure considered. However, the decision on the review of the concentration limit should not be based solely on the technical parameters of the analytical methods, but on the potential exposure (migration from the articles) and resulting risk level. The BMDL10 value proposed and used in the restriction report relating to the exposure to PAHs from rubber granules could be used as a benchmark in the risk assessment.

1.3. Justification for an EU-wide restriction measure

Union-wide measures to restrict PAHs in consumer articles were considered necessary based on considerations of human health risk, the marketing profile of the articles under question, and technical feasibility in the discussions of the German Annex XV report (2010).

Since the risks related to consumer exposure to PAHs resulting from use of articles extend across all EU boundaries, a harmonised risk management measure within the EU was also appropriate to avoid trade distortions between and within actors of the supply chain that might inhibit the functioning of the internal market for consumer articles containing plastic or rubber with PAH content.

The justifications provided in the German Annex XV restriction report (2010) are considered to still be appropriate. Additional considerations on the possible revision of content limits, possible introduction of migration limits and availability of alternatives are discussed further in this report.

1.4. Baseline

Not relevant for this report.

2. Impact assessment

2.1. Introduction

The Commission has requested ECHA to review the available information on alternative materials used to produce rubber and plastic articles, in particular, carbon black and extender oils. Part C (available information on alternatives) of the German Annex XV report (2010) presented the following information related to alternatives.

2.1.1. Alternative substances (raw material) and techniques

2.1.1.1. Introduction

The German Annex XV report (2010) reported that in the product tests that had been evaluated, the PAH levels found in most articles demonstrate that it is technically possible to produce consumer articles with PAH levels below the LoQ of 0.2 mg/kg. The analytical data of various tested product groups show that while most articles do not contain PAHs, some articles of the same group contain PAHs.

One contributing factor related to a high PAH content in articles was identified in the cost (higher PAH content in the low-price sector articles). This indicates that the use of PAH–containing ingredients is mostly due to economic reasons and not to technical reasons. Nonetheless, it should be noted that high PAH concentrations were also found in more expensive articles.

Information from several industrial organisations reported in the German Annex XV report (2010) also indicates that PAHs in consumer articles are not necessary. For example: "*The member companies of Plastics Europe do not use PAHs intentionally in their articles. Only for plastics which use carbon black as filling material can technical contaminations with PAHs not be excluded. For critical applications like food packaging materials or toys, carbon black is used which complies with the purity requirements of the 'plastics recommendation IX on colorants for food packaging and commodities*' of the German Federal Institute for Risk Assessment (BfR)" (statement translated from German to English). It, therefore, seems that the problem of PAHs in consumer articles might be mainly a problem of imported goods.

In addition, it was explained in the German Annex XV report (2010) that as extender oils used for tyres placed on the European market have restricted PAH content (since 1 January 2010), there is already experience in replacing PAH-containing extender oils for a high volume product which has to comply with high technical requirements. The examples include extender oils with reduced PAH content (e.g. MES – mild extract solvates, TDAE – treated distilled aromatic extracts, TRAE – treated residual aromatic extracts or naphthenic oils). This example of successful substitution shows that alternatives exist and can be used.

The German Annex XV report (2010) argues that consumer articles should not be a subject to a lower protection level than tyres regarding the content of hazardous PAHs.

2.1.1.2. Potential alternative substances or technologies

<u>Extender oils with reduced PAH content</u>

Extender oils are predominantly used in rubber articles, however, there is a limited use in plastics (e.g. as plasticisers in soft PVC).

The German Annex XV report states the first alternative is to use extender oils which have a reduced PAH content or which are free of PAHs. These alternatives have been tested for use in tyre rubber, but are also suitable for other rubber applications. They are also suitable to replace extender oils in plastics like soft PVC.

The original extender oils for tyres were DAE (distilled aromatic extracts) with a high content of PAHs, therefore, commonly named "labelled oils" since they had to be classified and labelled according to the Dangerous Substances Directive (67/548/EC), replaced by the CLP Regulation ((EC) No 1272/2008).

Different alternative oils could be used for their replacement, commonly named "unlabelled oils" with no labelling required. Restriction entry 50 has been amended in March 2015 to require the use of the standard EN 16143[33] to demonstrate conformity with the PAH limits established for extender oils used for the production of tyres or parts of tyres: "(..)the limits are regarded as kept if the vulcanised rubber compounds do not exceed the limit of 0.35 % Bay protons as measured and calculated by ISO 21461 (Rubber vulcanised-Determination of aromaticity of oil in vulcanised rubber compounds)" (REACH, Annex XVII, No. 50)[34].

Beyond this there is a wide variety in the exact chemical composition of the different oils.

The following types of unlabelled oils can be distinguished (Shaw, 2008; Shaw, 2009; Neau and Rangstedt, 2009; Joona, 2003; Null, 1999). A process scheme is given in Neau and Rangsted (2009):

- MES (mild extract solvates) consist mainly of paraffinic oils, i.e. linear alkanes, which result from the lube base oil production and where aromatic components with two or more rings have been removed by extraction. Further refining can lead to so-called "white oils".
- Treated distilled aromatic extracts (TDAE) are produced from distilled aromatic extracts (DAE) which are further treated by a solvent extraction to remove the aromatic components with three rings and upwards.
- Treated residual aromatic extracts (TRAE) are produced from residual aromatic extracts (RAE), a heavy oil fraction produced from the de-asphalting of heavy petroleum residues, by solvent extraction of aromatic components.
- Naphthenic oils consist mainly of cyclic alkanes. They are produced by hydro-treatment of heavy vacuum petroleum distillates.

Nevertheless, the aromatic extracts may contain alkylated poly-aromatic constituents other than PAHs, which has been demonstrated by chemical analysis of these multi-component mixtures.

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[33] EN 16143:2013 (Petroleum products — Determination of content of benzo(a)pyrene (BaP) and selected polycyclic aromatic hydrocarbons (PAHs) in extender oils — Procedure using double LC cleaning and GC-MS analysis) as the test method for demonstrating conformity with the limits referred to in the first paragraph of the entry.

[34] Since the introduction of the restriction, entry 50 has been amended (March 2015), to require the use of the standard EN 16143:2013 (Petroleum products — Determination of content of benzo(a)pyrene (BaP) and selected polycyclic aromatic hydrocarbons (PAHs) in extender oils — Procedure using double LC cleaning and GC-MS analysis) as the test method for demonstrating conformity with the limits referred to in the first paragraph of the entry.

There is also scientific concern that several alkylated poly-aromatic compounds possess carcinogenic potency. As a consequence, the use of extender oils that are free of aromatic compounds (e.g. "white oils") is recommended for consumer articles.

Much attention has been paid by the manufacturers of tyres to the question of the availability of alternative extender oils, because they need a huge quantity of extender oils of around one million tonnes per year.

At the time the restriction proposal for PAHs in extender oils was developed, it was noted that the conversion to unlabelled oils has started not only in Europe but worldwide, with varying preferences for the different alternative extender oils between the different companies (Shaw, 2008; Shaw, 2009; Anonymous, 2009).

Carbon black with reduced PAH content

Carbon black is used both in rubber and plastic articles. Carbon black with a reduced content of PAHs is available on the market. To produce carbon black with a low PAH content, several methods of removing the PAHs after the initial production of carbon black are possible.

The most common methods seem to be thermal treatment under vacuum or inert gas atmosphere at temperatures >300°C and solvent extraction of the carbon black. This is mainly done using a Soxhlet Extractor and common organic solvents like hexane or toluene.

The alternative is available because it is already required for special applications, such as in food contact materials[35]. No market shares are known, but they are probably still as low as could be expected when there is no regulatory driver for its use.

In the restriction proposed by the Netherlands for rubber granules, a restriction option on limiting the PAH concentration in carbon black was considered as this would have a knock-on effect to the PAH concentration of rubber granules produced from tyres (Risk Management Option (RMO) 6). However, this restriction option has been disregarded by the Netherlands due to a lack of information on technical and economic feasibility. Based on available information, the use of carbon black in plastic articles is very limited. The JRC study has also evidenced that the contribution of carbon black on PAH releases from rubber articles seems to be limited (if compared to the contribution from extender oils).

[35] Regulation (EU) No. 10/2011 on food contact materials (FCM) sets limits for carbon black used in FCM: BaP ≤0.25 mg/kg of carbon black, maximum level of carbon black in polymer: 2.5 % w/w https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02011R0010-20160914&from=EN

RMO6: Limiting the PAH concentration in carbon black	In analogy with the existing extender oil restriction limiting PAHs in tyres in the oils used in tyre production, also the PAH concentration in the carbon black feedstock of tyres can be reduced with a legal limit.	Effectiveness of this RMO in terms of risk reduction of the use of granules and mulches in sport and play applications is expected to take years or decades as tyre manufacturers would need time to adapt and it takes a tyre lifetime before any effect would be seen in ELT granules and mulches. Furthermore, the dossier submitter has no information on the technical and economic feasibility of this RMO. This RMO is disregarded by the dossier submitter.

Thermoplastic elastomers (TPE)

According to the German Annex XV report (2010), thermoplastic elastomers, which do not need extender oils or plasticisers at all, can be an alternative for the manufacture of plastic articles. Thermoplastic elastomers contain a hard, thermoplastic compound and a soft, elastomeric compound which are physically bound to each other to form the final elastic polymer.

Different types of thermoplastic elastomers are TPE-O or TPO (thermoplastic olefins), TPE-S or TPS (styrenic block copolymer), TPE-U or TPU (thermoplastic polyurethanes), TPE-A or TPA (thermoplastic polyamides), TPE-E or TPC (thermoplastic copolyester) and TPE-v or TPV (thermoplastic vulcanisates). In this field of different types of thermoplastic elastomers, a big variety of specific thermoplastic elastomers is available.

Thermoplastic elastomers are well established materials on the plastics market. There is no reason known for a lack of availability. ECHA did not receive any further information through the call for evidence on the use of thermoplastic elastomers in articles falling within the scope of the restriction.

Surrender/discontinuation of use of extender oils and carbon black

In some cases, the best alternative might be not to use any extender oils or carbon black at all. Carbon black (soot) is added to elastomers to achieve specific properties (e.g. flexibility, damping, solubility in the polymer matrix). In plastics, it is used as a pigment, conductive filling material, UV absorber and particulate reinforcer.

Extender oils are used in rubbers (in particular in the production of tyres) as processing aids (to facilitate mixing of different substances used, soften the rubber mass and improve workability). They are also used in plastics as a cheap additive to soften the plastic (e.g. in the production of soft PVC). In many cases, extender oils are necessary because of the high demand of economically cheap filling materials. A reduction of the demand of filling material could make it unnecessary to use extender oils in some cases.

2.1.1.3. Human health and environmental risks related to alternatives

The German Annex XV report (2010) reported that no specific data on human health or environmental risks potentially arising from the use of the above alternatives as compared to using PAH-rich articles was available to the authors of the report.

2.1.1.4. Technical and economic feasibility of alternatives

Table 6: Technical and economic feasibility of alternatives, presented by Germany in the restriction proposal in 2010

Alternative	Technical feasibility	Economic feasibility
Extender oils with reduced or no PAH content	• Extensively studied in tyre industry: available alternatives show good technical characteristics. • Some reformulation of the rubber had to be made to obtain the same wet grip. • As technical requirements for consumer articles are, in most cases, considerably lower than for tyres, there is no doubt about the technical feasibility of the alternative extender oils. • Some manufacturers raised concerns related to product parts which have to endure high mechanic stress at high temperatures. • Alternative oils might also technically serve as a secondary plasticiser for soft-PVC as shown in the product information at the homepage of Nynas[36].	Unlabelled oils are more expensive than labelled ones, but the burden is the same for all producers for the European market. Since a restriction also addresses imports, the same rules and burdens also exist for all actors on the market.
Carbon black with reduced PAH content	• The technical feasibility is assumed, as there are already some applications which require carbon black with reduced PAH content	The product price might increase slightly, because an additional processing step for the reduction of the PAH content would be necessary.
Thermoplastic elastomers	• Thermoplastic elastomers - behave in a wide temperature range like rubbers and show elastic properties. Above this temperature	Thermoplastic elastomers are engineering plastics with a higher price than the usual commodity plastics (like soft-PVC). It is not

[36] https://www.nynas.com/en/product-areas/process-oils/news/nynas-process-oils-provide-flexible-solutions-for-pvc/

	range, they lose their elasticity, start to melt and can be moulded. After cooling down they become elastic again. • Thermoplastic elastomers show some advantages during the manufacture compared with rubber: they consist of few compounds which are easy to control and to mix, energy consumption during the manufacture is relatively low and they are easy to mould by extrusion or injection moulding. • Thermoplastic elastomers can be produced in different hardness grades, are easy to dye and recyclable. • The disadvantages of thermoplastic elastomers lay in their poor chemical and heat resistance and their lower compression and thermal stability. • Thermoplastic elastomers already replace rubber or soft-PVC in applications like coatings for wires and cables, tubes, pipes, spring elements, joints and gaskets, tool handles, shoe soles, conveyor belts, kitchenware and consumer electronics.	possible to load them with cheap filling materials like it is possible with rubber. It depends on the required characteristics and the special purpose of the end articles, if an elastomeric plastic might be an economically feasible alternative.

The evaluation of the 2010 restriction proposal from Germany conducted by ECHA in 2012 does not include the review or assessment of the information related to the analysis of alternatives presented in the dossier. However, the recent (2017) call for evidence resulted in some additional information, presented below (Section 2.2).

2.2. Information related to the substitution potential received in the call for evidence[37]

2.2.1. Introduction

The call for evidence undertaken by ECHA from 1 June to 31 July 2017 aimed at gathering, among others, additional information on low PAH raw materials used in the production process of rubber and plastic articles, in particular, carbon black and extender oils with lower PAH content than the ones typically used. Seven out of 11 total responders provided some information on alternatives. However, most of the information provided was already included in the restriction report from Germany (2010).

2.2.2. Low PAH carbon black

Carbon black is a material produced by the incomplete combustion of heavy petroleum articles such as FCC tar, coal tar, or ethylene cracking tar. The manufacturing process results in the formation of unavoidable impurities, among them – PAHs.

The most common use (around 70 % of total global production) is as a pigment and reinforcing phase in automobile tyres. It is also used in the production of belts, hoses and other rubber goods as a reinforcing filler to reduce abrasion and improve tension strength. Other uses are as pigment in inks, coating plastics and in electronic applications as it has good conductive capacity.

There are several grades of carbon black, with varying content of PAHs, starting from N 110, (used in the tread compound of truck and passenger tyres). It is also used in rubber articles with high strength and high abrasion resistance such as high strength conveyor belt and industrial rubber articles).

Carbon black N 220 is used in tread compounds of truck tyres, passenger car tyres and high strength high abrasion rubber articles, such as high strength conveyor belts and industrial rubber articles etc.

Carbon black N 375, tested by the JRC, is mainly used in the tread compounds of passenger car tyres, truck tyres and cross-country car tyres and also used in coating compounds of conveyor belts.

Carbon black N 550, also present in the tested samples is mainly used in fabric cords of tyres, tyre sides, extrusion and rolling compounds.

Carbon black N 660 is used in fabric cords of tyres, inner tyres, bicycle tyres, hoses, bels, cables, shoes, extrusion compounds and rolling compounds.

[37] Not all responses received in the recent call for evidence contained information on the alternatives and substitution options

The content of PAHs varies with grade. According to literature, the content of benzo(a)pyrene in N 330 is 0.1-0.16 mg/kg, while for N 550 it is 0.03-0.3 mg/kg.[38]

According to the comments from the call for evidence, the amount of PAHs from carbon black in rubber parts of articles does not exceed 1/3 (in weight) of the amount of PAHs in the carbon black as a reinforcing substance, when mechanical robustness and durability of the final article are required.

Reduction of PAH content is linked to reduction of abrasion resistance, inadequate integrity of the compound and faster degradation during use, defeating the initial purpose of adding carbon black to make the article mechanically stronger, safer and more durable.

It was pointed out that in many rubber moving parts, carbon black also has an important role as an electro-dissipative agent, the use of any other substitute would imply a need to use antistatic agents to avoid dangerous electrostatic discharges. However, it has to be noted that most of the applications where mechanical strength is required are not supposed to come into frequent contact with skin and, therefore, are likely to be outside of the scope of the restriction.

Other applications include use as fillers and as pigments, providing specific tones of the colour. Some carbon black grades that can be used for colouration – in particular in plastics – do contain lower levels of PAHs, however they are not at all suitable for rubber article production, where high mechanical, thermal or elastic performances are required.

Aesthetic properties of the goods manufactured using carbon black was also raised as an issue. Carbon black enables colour matchers to prepare darker shades of a colour produced by a pigment/combination of pigments and adds the undertone – a slight hue that carbon black can impart on articles are also relevant. This undertone can be blue or brown, with the blue undertone being strongly preferred by the colour matcher, customers, and unknowingly the entirety of society as it makes a product feel more luxurious than when a brown undertone is used. Unfortunately, the colour most appreciated by consumers and colour matchers is based on the use of carbon black with slightly higher PAH content.

In addition, the less-preferred brown tone carbon blacks are more difficult to produce, requiring more energy use. Furthermore, the dispersion of these brown undertone carbon blacks into a polymer matrix is more difficult to achieve, again requiring more energy.

So, while there are alternative carbon black grades with lower PAH content available on the market, switching to these has an economic, environmental, and aesthetic implication for society.

One of the respondents – manufacturing rubber articles mainly for the automobile industry – has stated that carbon black is used as a filler in production of technical automotive rubber parts. These parts, however, are not meant to be in repetitive contact with the skin and are therefore not in the scope of the restriction. However, they do acknowledge the need to use special rubber types (with low levels of PAHs) for parts in skin contact, but such rubber parts are just a small group compared to all rubber parts. Non-consumer uses were addressed too: for the intended function of carbon black as a reinforcing agent in rubber,

[38] Stępkowska Aneta: Polycyclic aromatic hydrocarbons (PAHs) in carbon black, in Elastomery, tom 20, January. March 2016, available at: http://www.elastomery.pl/streszczenia/E2016_1_Stepkowska.pdf

the compliance of rubber articles with low content limits mentioned in Regulation EU 1272/2013 (entry 50 of Annex XVII to REACH) is challenging[39].

While the methodologies of reducing PAH content using solvents or thermal treatment are well known, this would significantly alter the surface properties of the carbon black, making such post-production processing unfeasible. This would also result in greater CO_2 emissions, higher costs for consumers, and more waste generated due to the shorter life cycle of the rubber articles. In addition, such purification processes would require the use of millions of tonnes of hazardous organic solvents resulting in potentially significant environmental impacts.

At the same time, it is acknowledged that carbon black grades used for colouration – in particular in plastics – already contain lower levels of PAHs, while due to technical reasons these are not suitable for use in rubber article production, where high mechanical thermal or elastic performances are required. However, high technical performance could not be an issue in consumer articles. Cost is another factor limiting the use of carbon black with lower PAH content. Environmental and aesthetic implications for society are also listed as reasons for not using alternative materials.

Three responders also presented their view on the impact of the restriction requiring lowering the PAH content. These views range from the necessity to identify the articles that comply with new conditions to the need for modification of production processes and assessment of their economic viability. It is also considered that the content limit as such penalises the use of certain grades of carbon black in polymers which have a strong matrix encapsulation effect versus those that have a weaker matrix encapsulation effect, as content limits need to be set to ensure that consumers' exposure to the worst case material does not lead to a risk. This consideration is also linked with the concept of risk resulting from actual exposure, which may be assessed better with migration rate than with content limit value.

2.2.3. Low PAH extender oils

No information was received on low PAH extender oils in the call for evidence. However, at a later stage, CONCAWE has provided information on the content of PAHs in extender oils from one of their member companies.

The measurement data indicates, that the concentration of individual PAHs in analysed oil samples is generally below the limit for consumer articles. The content limit established for toys and general articles is slightly exceeded only in a limited number of cases. However, the limits set in paragraph 1 of restriction entry 50 for extender oils are related to their placing on the market or use in the production of tyres and parts of tyres. In relation to use in other articles the data reflects the concentrations of PAHs in raw materials so the final article may still have lower PAH concentrations, falling within the limits set by the restriction.

The information on the type of articles manufactured with the extender oils analysed is limited to 'polar rubbers, E/S-SBR natural rubber types'. Therefore, it is not possible to

[39] Some examples of articles which are affected include: tyres (automotive, trucks, industrial, construction and agricultural engines), industrial hoses (pressure hoses, hydraulic hoses, sand-blasting hoses), anti-vibration parts (in building, automotive sectors), conveyor belts, shock absorbing parts or objects (shoe soles, military tank track pads).

identify in which (if any) consumer articles these oils are used in manufacturing. It is to be noted that extender oils are normally not used in plastics.

2.3. Economic impacts

2.3.1. Background information

In ECHA's assessment of the German Annex XV restriction proposal (2010), the Agency evaluated the proportionality of the proposed measure and concluded that it was not possible to assess the proportionality of the proposed restriction. This was the result of the fact that the German Annex XV report (2010) contained limited information on the potential costs and benefits of introducing the restriction. A number of issues were identified:

- *While ECHA believed it possible to carry out a meaningful quantification of costs and benefits when regulating carcinogens in articles, the information presented in the dossier did not allow such an analysis to be performed.*
- *The proposal included anecdotal and apparently contradictory evidence in relation to the costs of compliance with the restriction and administrative costs.*
- *The information provided did not substantiate the claim that 'the proposed restriction's human health benefits in combination with its economic benefits are found to clearly outweigh its economic costs'. The information provided indicated that both the benefits and costs of the proposed restriction could be either very high or quite low. It is not possible to say in which direction the scale of benefits or costs might move.*

Should a revision of entry 50 be proposed – such an assessment of economic impacts of any further changes would be performed as part of the dossier.

2.4. Practicability and monitorability

2.4.1. Background information

According to the German Annex XV report (2010), PAHs occur in oil, coal, and tar deposits, are produced as by-products of fuel burning (whether fossil fuel or biomass), and are not intentionally produced substances, but impurities. In the report, it was claimed that as PAH-free alternatives are available, consumer articles can be produced from materials without PAHs. However, the report focuses on consumer articles for which direct contact with skin or mucous membranes is foreseeable. In addition, the dossier points out that analytical methods exist to monitor PAH-free production or the import of articles by producers/importers and that these methods can be used by national enforcement authorities.

The report from Germany anticipated that targeting PAHs through Article 68(2) of REACH would assure a rapid implementation and enforcement of a possible restriction. They also assumed that most Member States have regulatory agencies to monitor the market for consumer articles. The roles of non-governmental organisations (NGOs), that are also active in this field in some Member States, and of the EU-wide alert system for dangerous consumer articles – the Rapid Exchange of Information System (RAPEX), administrated by

the authority of the Directorate-General for Health and Consumers of the European Commission, were also acknowledged.

It allows the rapid exchange of information between Member States (via central contact points) and the Commission about measures taken to prevent or restrict the marketing or use of articles posing a serious risk to the health and safety of consumers.

Both measures ordered by national authorities and measures taken voluntarily by producers and distributors are covered by RAPEX. Every Friday, the Commission publishes a weekly overview of the dangerous articles reported by the national authorities (the RAPEX notifications).

Practicability and monitorability were not evaluated by ECHA in its assessment of the restriction proposal by Germany.

2.4.2. Information from the call for evidence

2.4.2.1. General comments

In addition to responding to specific questions, some respondents to the 2017 call for evidence also provided general comments related to paragraphs 5 and 6 of entry 50. These can be summarised as:

- Support of industry for use of the migration rate as the basis for restriction rather than PAH content. It was stressed that migration assessment is crucial for the assessment of risks arising from the presence of PAHs in articles: PAH content is not a measure of risk, as, for example, encapsulation affects the actual exposure to PAHs. Therefore, the evaluation of the content of PAHs that can be absorbed by the skin of the user in cases of use in accordance with the intended purpose or foreseeable use is essential.
- Somewhat linked to the support of the risk–based approach is the request to take into consideration 'the problems that the manufacturers have in meeting such low standards (meaning the low PAH content expectation) and in some cases without a clear justification'. Migration-based restriction would validate the content-related parameters, if those would be left in.
- Importance of the availability of guidance, providing clear and consistent interpretation of the provisions of the restriction, but also the importance of strong market surveillance, which is critical for guaranteeing protection to consumers and a level playing field for industry.
- While there are already provisions in place limiting the content of PAHs in toys and parts that are in repeated skin contact – there is no need for the use of low-PAH carbon black alternatives for technical rubber parts.

2.4.2.2. Specific responses related to the content analysis methodology

The analytical methods identified as being used for the PAH content assessment are:

- The majority of the respondents mention ZEK 01.4-08 - *Harmonised Method for Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Polymers* described in the German AfPS GS 2014:01 PAK.

- The method CEN ISO/TS 16190: '*Footwear — Critical substances potentially present in footwear and footwear components — Test method to quantitatively determine polycyclic aromatic hydrocarbons (PAH) in footwear* materials' is mentioned by one respondent.
- ISO 18287 'Soil quality -- Determination of polycyclic aromatic hydrocarbons (PAH) -- Gas chromatographic method with mass spectrometric detection (GC-MS)' was mentioned in single response.
- Cabot method, a well-recognised method used for the determination of PAHs for the Food and Drug Administration (FDA) agency) – one response.

In addition, ASTM D7771 is used to measure the benzo(a)pyrene content and referenced as a means of checking compliance with the requirements of the Plastics Food Contact Regulation (EU 10/2011).

Furthermore, a new ASTM standard dedicated to the individual eight EU-PAHs in carbon black was published in 2017[40]. However, while these were listed, the respondent did not indicate clearly, that these methods are used by them.

Some respondents pointed out that there is no harmonised method for PAH content assessment in plastic and rubber consumer articles. Some respondents also identified shortcomings of the methods used: ZEK – not peer-reviewed, use of toluene may affect the analysis due to the rubber components, GS Mark method – not suitable for quantifying PAHs in carbon black.

None of the respondents identify problems with access to the testing facility. In fact, at least two of the laboratories mentioned have facilities worldwide, including in multiple EU Member States.

However – the *cost of testing* may be a limiting factor at least for some: 'high cost', even €600 per sample is mentioned (response 450). While cost of testing was not provided in all responses, the majority of respondents informed, that the cost of the analysis ranges between €50 and €200 per tested material, depending also on the laboratory.

The *analytical parameters* of the methodologies were not provided in all responses. Limit of quantification (LoQ) is generally being reported at 0.2 mg/kg for each PAH. However LoQ has been significantly reduced by the method developed by the JRC (see Section 2.4.3 for details). One of the respondents added that this LoQ is achievable for "clean" polymers without significant amounts of additives, stabilisers, plasticisers, extenders or even residues from the manufacturing of the polymer (e.g. monomers, oligomers). For less "clean" polymers, an LoQ lower than 0.5 to 0.6 mg/kg is extremely difficult to achieve (with a loss of analytes as a side-effect).

Two of the responses also mention a lower limit of detection – 0.001 ppm and 0.1 mg/kg. Although these lower values are not consistent with the LoQ listed in the identified method's manual (0.2 mg/kg), they support the LoQ established by the JRC. It was also noted that the LoQ may be quite higher (value not identified) if soft plastics are tested.

In response to the question related to the actual PAH content of articles manufactured or imported – the information is not very detailed. Four respondents gave limited information

[40] The ASTM standard D8143-17 - Standard Test Method for Determination of the EU-8 List of PAH Compounds in Carbon Black - has been published in 2017.

to the statement, that their or their members' articles comply with the requirements presented in paragraphs 5 and 6 of the entry 50 (<1 mg/kg of each PAH for consumer articles and <0.5 mg/kg of each PAH in toys).

Other responses, including also laboratory reports, led to a conclusion that the limit values provided in the paragraphs 5 and 6 of the entry 50 are not strictly complied with.

2.4.3. JRC report on Migration of Polycyclic Aromatic Hydrocarbons (PAHs) from plastic and rubber articles

As reported in the introduction and referred in several parts of this report, the JRC published their report on *Migration of Polycyclic Aromatic Hydrocarbons (PAHs) from plastic and rubber articles* in 2018. The report has been issued as part of the STANPAH project the scope of which was for the JRC to provide scientific support to the Commission in the implementation and potential amendment of the restriction of PAHs, in particular, paragraphs 5 and 6 of entry 50 to Annex XVII to REACH.

The project aimed to gain a better understanding of the migration behaviour of the eight PAHs listed in restriction entry 50 in plastic and rubber components of the articles and to develop a reliable methodology to determine PAH migration from plastic and rubber matrices under condition simulating, to the best possible extent, dermal contact (including oral cavity).

These activities leading to this report included:

Literature search

In the context of the project, the JRC has performed a literature search aiming at identifying methodologies available for the evaluation of the PAH content in the articles, and then methods used to establish the migration rate (see Table 5 in this report).

The conclusions of the literature search related to the PAH estimation methodologies seem to support the conclusions of the outcomes of ECHA's call for evidence: while there are methodologies available, there is no standardised method to establish PAH content in the rubber or plastic materials.

The literature search also established a lack of standardised methodologies for evaluating the migration of PAHs from plastic and rubber materials. This conclusion is followed up with the project aiming at the development of the migration methodology and suitable media that can be used in the assessment.

STANPAH project

The project technical committee included representatives of DG GROW, the JRC, European standardisation organisations, industry stakeholders, experts from Member States, governmental laboratories, academia and ECHA.

At consecutive meetings, the scope of work, source materials and parameters of testing were presented and discussed. Following the development of accepted methodology, the inter-laboratory comparison (quality control) was conducted; the method was validated by independent laboratories. The STANPAH project was finalised in March 2018 and the final report was published in August 2018[41].

[41] https://publications.jrc.ec.europa.eu/repository/handle/JRC111476

The studies on content and migration of the eight PAHs listed in entry 50 of Annex XVII to REACH have been performed on 20 polymeric plastic and rubber materials, manufactured ad-hoc, with known origin and content of PAHs. Various quality grades and types of ingredients known to be PAH sources were used in the formulation of the manufactured materials. The matrices were chosen on the basis of the known frequency of their use in articles in the scope of the restriction and the likelihood of the presence of high PAH content.

Recycled rubber granules (coated with polyurethane and uncoated) originating from end-of-life tyres produced before and after 2010 were also made available for this study. In addition, eight commercially available brand new and one used items were also included in the tests.

For ad-hoc manufactured plastics, the matrices (i.e. low density polyethylene -LPDE-DPE, polyvinyl chloride -PVC- and polystyrene -PS) were selected to cover a multitude of consumer applications and to represent a wide range of diffusivity characteristics. Two types of carbon black (with low and high PAH content) were selected as ingredients to the plastic formulation to function as a source of PAHs (extender oils are not used in plastics). The concentration of carbon black in the manufactured plastic materials was set as 2.5 % and 40 %, to represent typical loading used for colouration and conductive properties respectively.

Ad hoc manufactured rubber materials contained both carbon black and extender oils. According to industry, distillate aromatic extract (DAE) with high PAH content is no longer used as an extender oil in commercial articles intended for skin contact and it has been replaced by treated distillate aromatic extract (TDAE) with low PAH content. However, in the preparation of the rubber test material, both DAE and TDAE were used as extender oils in addition to different types of carbon black.

Recycled rubber granules (coated with polyurethane and uncoated) originated from end-of life tyres as well as a number of samples from commercial articles were also investigated to measure the content and the migration of PAHs. However, it is to be noted that rubber granules are mixtures and thus not within the scope of the restriction entry 50.

A number of experimental studies were carried out to generate data and information to improve the knowledge on migration of the target PAHs.

As a preliminary step to the development of an analytical method for the assessment of migration of PAHs, the JRC has developed a method for determining the content of PAHs in the plastic and rubber matrices. Existing methodologies were taken as a starting point, improving in particular the extraction and the clean-up procedures.

Randall hot extraction of the rubber or plastic material with toluene, followed by sample extract clean-up with PAH selective solid phase extraction cartridges, based on molecularly imprinted polymers (MIPs), in combination with gas chromatography-mass spectrometry (GC-MS) analyses in selected ion mode was found to be the optimal method in terms of extraction efficiency, extract purity, and time demands.

A detailed standard operating procedure (SOP) of the proposed method was presented in the published report. This method has been used in further work on the quantification of the amount of the eight REACH PAHs in the reference test materials, to estimate the migration relative to the content. The absolute limit of quantification of the method is in a range between 0.6 and 3.6 ng/ml, with a sample-specific limit of 0.001 to 0.007 mg/kg for 500 mg sample.

This methodology allows then to test for concentrations of PAHs significantly lower (up to two orders of magnitude) than any of the other methods currently used. The JRC has also performed a number of tests using ultrasonic extraction for comparative purposes. The performance achieved with Randall hot extraction was always higher when compared with ultrasonic extraction. In addition, the Randall hot extraction process requires a considerably shorter extraction time (reduced by a factor 4 to 5) if compared with classical Soxhlet method (normally used to determine PAH content in plastic and rubber materials) and requires a lower amount of solvent.

The migration into aqueous solutions – artificial sweat and saliva simulants as well as 20 % ethanol (selected later as the test medium of choice) and skin surface film (containing artificial sweat and sebum) are described in literature as good models for human skin absorption simulation and with good correlation to *in vitro* measurements using human skin (Franz-cell tests).

The migration tests were carried out by total immersion – 0.2 dm^2 surface area of test sample in 20 mL of medium – in a dynamic mode at 40ºC, which were considered to be representative of potential exposure situations. The amount of PAHs released after 24 hours was measured. The absolute quantification limit was in the range 0.2-0.6 ng mL^{-1} depending on the specific PAH detected with an LoQ of 0.1-0.5 µg/kg for samples of 2g.

Overall, no migration into aqueous solutions (artificial sweat and saliva) from all material tested and no migration from plastic matrix (irrespectively of the migration medium) for none of the target PAHs was detected. For rubber materials, it was noted that no release was observed from the matrices containing TDAE and from silicone matrices containing two types of carbon black. Detectable migration of PAHs was observed only for rubber matrices containing DAE as an extender oil when using 20 % ethanol as the migration solution. Therefore, it was concluded that the migration of PAHs is linked to the type of the extender oil used as their source.

According to the report, the type of carbon black used is also relevant: it was noted that while CB550 has a lower PAH content than CB375, the migration rate for the latter is lower. It is considered that forms of carbon black have a capacity to re-absorb PAHs already released (e.g. from extender oils). CB375, having a larger surface area, has a higher absorption capacity, therefore, reducing the migration rate. The migration rate is also affected by the concentration of an individual PAH in the matrix and the size of the particle: the highest migration rates are recorded for chrysene, with the lowest molecular weight, followed by benzo[e]pyrene, which had the highest total content in the four types of rubber materials tested.

Artificial skin surface film liquid (SSFL) has been used as a media for release measurement to make a comparison with 20 % ethanol. Plastic and rubber matrices (with high PAH content) which have shown PAH migration with ethanol, were exposed to different SSFL formulations (sebum content varied from 0.1 % to 2 %). No release was detected from plastic or silicone. Release was detected in Neoprene rubber-Butadiene rubber (NR-BR) and ethylene-propylene-diene-monomer rubber (EPDM). Releases increased with increasing sebum concentration and migration time. SSFL with 0.1-0.2 % sebum in EN 1811 sweat showed good agreement with data obtained with 20 % ethanol. 0.2 % sebum reproduces well real skin from the female abdomen.

Although there are no sebaceous glands in the skin of the palms of the hands it has been assumed that sebum is transferred from the dorsal parts of the hands or from other parts of the body and, therefore, the palmar parts are treated as any other body part. The data with

sebum represent well the conditions of human skin and, differently from the ethanol, it does not interfere with the matrix (this interaction may generate a potential higher release).

However the preparation of the SSFL is very laborious and could potentially lead to errors when measuring PAH releases. That is why the 20 % ethanol solution is preferred. Additional tests have been performed with sebum imbued filter (SIF) paper strips. These tests showed that the migration rate increases with time. The highest migration rate was obtained for BeP followed by chrysene, while with SSFL the order of the two components was reversed. This indicates that molecule mobility has a lower impact in SIF than when SSFL is used. The migration rate with SIF matches best with SSFL containing 1 % sebum. However, this method was not further developed as the preparation of the media is very complex and the homogeneously sebum-imbued strips could be difficult to standardise.

The type of matrix plays a role in the rate of migration: it was noted that for the rubber samples containing DAE, the migration rate was higher from ethylene-propylene diene monomer (EPDM) than from natural rubber (butadiene rubber), irrespective of the type of carbon black present. The main findings can be summarised as follows:

- Migration of PAHs into aqueous solution (artificial sweat and saliva) was not observed from any of the matrices.
- Migration into a sweat simulant (containing sebum) was noted to be comparable to migration into 20 % ethanol and human cells *in vivo* (Franz Cell chamber assay). Migration to these simulants was noted only from the rubber matrices containing DAE as extender oil.
- Tests performed with SSFL as the media (to make a comparison with 20 % ethanol) showed that release increases with increasing sebum concentration in the media and with migration time. SSFL with 0.1-0.2 % sebum (reproducing human skin conditions well) showed good agreement with data obtained with 20 % ethanol. However, the preparation of SSFL is very laborious and could potentially lead to errors when measuring PAH releases. For this reason, the 20 % ethanol solution has been preferred.
- None of the plastic polymeric materials (PAHs originating from carbon black and extender oil) led to detectable releases of the target PAHs in any of the migration media used in this study.
- The tests with silicone rubber materials (PAHs originating from carbon black) did not result in detectable migration in any of the biosimulants.
- Migration of PAHs from rubbers seems to be related to the type of extender oil used in their manufacturing process: no release was observed from rubber matrices containing treated distilled aromatic extract (TDAE).
- Natural rubber is linked with lower PAH migration than EPDM.
- Qualitatively, it appears that PAHs contained in the extender oils migrate more easily than those in the carbon black component of the rubbers.
- For similar conditions, the relative migration of PAHs depends on the molecular weight of each substance, as well as the content and the matrix.
- Coating (polyurethane coating) acts as a barrier to migration and reduces the migration rate by 2-3 times (new articles).
- There are indications that the contact surface is a factor affecting migration: the relative migration expressed in mass percentage was higher for rubber granules, characterised by the high surface contact area with the medium.

The migration test method using 20 % ethanol has been validated in-house by the JRC and showed good method performance allowing PAHs to be determined at trace level.

Furthermore, the JRC has performed an initial inter-laboratory comparison study (ILC) aiming to investigate method applicability and transferability in a variety of laboratories.

Tests were done in 21 external laboratories to assess the method applicability and transferability. The aim was not to assess individual performance of the laboratories but to evaluate the analytical method proposed. Test specimens of different plastics and rubbers were prepared. Some of them were randomly selected for a homogeneity study and the rest were coded and sent to test participants. Homogeneity tests, performed in accordance to ISO 13528:2015 standard, showed no significant heterogeneity in the specimen, therefore the pieces could be considered homogeneous for the target PAHs and then suitable for inter-comparison study.

The within-laboratory precision, expressed as the ***relative standard deviation for repeatability (RSDr)***, and the between-laboratory precision, expressed as the ***relative standard deviation for reproducibility (RSDR)*** were assessed. In general, the between lab variability (RSDR %) ranged from 28-113 % and the within lab variability (RSDr %) from 7-23 %. Similar values have been reported in a recent German study (2017) with the participation of nine laboratories on the migration of PAHs from rubber materials in contact with aqueous ethanol.

Better values of RSDr and RSDR were obtained for chrysene and benzo(e)pyrene that had the highest concentrations in the final migration solutions and for which the analysis of the control solution used in this exercise showed a good reproducibility (RSDR % <10 %). This fact confirms the possibility to reduce the variability between laboratories with a revised operating procedure in terms of injection volume and/or elution volume.

In conclusion, the JRC report makes new data and scientific information available on the migration behaviour of certain PAHs from selected plastic and rubber polymeric matrices, in support of the European Commission's legal obligation to review the restriction of PAHs under REACH.

Standard operating procedures for quantification of the content of each of the eight restricted PAHs as well as their migration into 20 % ethanol have been developed.

Moreover, the information gathered in STANPAH (e.g. literature search), the ad-hoc manufactured materials still available, as well as the JRC in-house analysis method for PAH content could be of great benefit to accelerate the work towards standardisation of PAH content analysis in consumer articles that has been recently undertaken by the European Standardisation Committee following a request by DG GROW.

2.4.4. Additional information

Forum project

Independently from the Commission’s request related to the implementation of the restriction in entry 50, ECHA’s Forum for Exchange of Information on Enforcement (Forum) conducted a harmonised enforcement project on restrictions (REF 4) in 2016, aiming to raise awareness about restrictions, to evaluate compliance on the EU-market, to follow up non-compliances with enforcement action and to achieve a greater degree of protection for

health and environment. Entry 50 was included among the restrictions for which implementation was evaluated.

For this project, a manual was prepared during 2015, to ensure greater consistency of inspections. Among other elements, it includes information on the analytical methods that may be used in the evaluation of compliance with relevant restrictions. As entry 50 was included in the scope of the project, the manual includes the information on the analytical method that can be used to assess the compliance. The committee developing the manual, including Forum Members, invited experts from EEA national enforcement authorities and the Commission, has identified the German GS quality mark analytical method as the monitoring method, which can be used to determine the compliance parameters (i.e. the concentration of the regulated PAHs, see the Annex of the updated GS specification document, Version August 2014[42]).

This was the only method identified and recommended for assessing the content of PAHs in the articles.

The REF 4 project was conducted in 2016. The final report was adopted by Forum in November 2017 and was published in February 2018[43]. The report indicates that while the significant majority of articles (82 % of 5 625 articles inspected) fulfilled the legal requirements, some non-conformities with the provisions related to the restrictions being examined, including those for entry 50, were also identified. The main conclusions on inspections related to paragraphs 5 and 6 of entry 50 and non-conformities identified include the following:

- 7.8 % of the project sample (30 out of 385 items) were non-compliant for PAHs[44].
- Sampling importers and distributors is effective for identifying non-compliant articles.
- The overall proportion of non-compliant tested articles relevant for entry 50 coming from the EEA/EU was 30 %.
- In relation to all articles, 27 % of the all examined non-compliant articles were placed on the market via internet. 75 % of these articles find their origin in China.

It seems, therefore, that the assumptions made in the restriction proposal related to its monitorability based on the content limit are justified. It needs to be noted that the prevalence on the market of the articles covered by derogation (paragraph 7 of entry 50) is not considered in the REF 4 report.

German National Monitoring Programme 2017 on PAH in consumer articles and toys

In the context of the national monitoring programme, in 2017 in Germany the content of PAHs subject to restriction entry 50 and their migration from consumer articles with potential for skin contact and toys was examined.

145 sample articles were tested including 35 toys. The testing methods used had an LoQ that allowed to quantify the eight individual PAHs regulated by entry 50 in REACH Annex

[42] https://www.baua.de/DE/Aufgaben/Geschaeftsfuehrung-von-Ausschuessen/AfPS/pdf/AfPS-GS-2019-01-PAK-EN.pdf?__blob=publicationFile&v=5

[43] https://echa.europa.eu/documents/10162/13577/ref_4_report_en.pdf

[44] The testing of content of PAHs in the nine commercially available items described in the JRC report indicates non-compliance PAH levels in four cases and not-detectable PAH levels in two articles.

XVII in the content range of the limit values of 0.5 mg/kg for toys and 1.0 mg/kg for other consumer articles with prolonged or repeated skin contact.

The methodology used for evaluation of migration is based on the use of 20 % EtOH as a simulant – which (according to the JRC report) produces results similar to the migration to artificial sweat with sebum – imitating the skin. This method (use of 20 % EtOH) was also validated by the JRC and is proposed to be used for testing the migration of PAHs through the skin.

The results of the study indicate that in some articles (including toys) the content of individual PAHs exceeds the limits adopted in the restriction (non-compliance rate of 4.14 % lower than over 7 % in the pan-EU REF-4 project).

In most of the samples which were found to contain at least one of the restricted individual PAHs in amounts of 0.5 mg/kg or higher, PAHs were also detected in the migration solution. In two additional samples, which did not contain individual PAHs above 0.5 mg/kg, migrated PAHs could also be quantified.

The migration rates derived (through the skin only) were used in the exposure scenarios for adults and children. The estimated exposures seem to confirm the assumptions made in the preparation of the original restriction dossier. Should the BaP content be 1 mg/kg, the potential exposures resulting from handling objects may exceed the level of risk considered to be tolerable for consumers of 10^{-6}. However, the report also acknowledged that the migration rates differ between different materials by more than two orders of magnitude, so the risk conclusion may not be valid for all articles. For that reason, the report concludes that there is a 'need for more data and systematic knowledge about migration of PAHs from various relevant matrices' pointing out, at the same time, that more specific information on the migration over time is needed.

It needs to be noted, that the German monitoring programme (2017) did not consider migration through the oral cavity for which artificial saliva is used as the migration medium. However, migration to saliva simulant was tested in the JRC study and test results were below the LoQs. As a worst case scenario, test results obtained with 20 % ethanol (sweat simulant) could be considered representative also for the migration through the oral cavity.

The conclusions from Germany were that the PAHs' limit values established in paragraphs 5 and 6 for the analysed consumer articles were documented to be exceeded in 7 out of 146 samples and found that the PAH content exceeded 200 mg/kg in two cases.

Germany also considered that the current limit values may not be sufficiently strict to completely exclude risks for human health and that further studies to investigate the migration behaviour of PAHs in different matrices are needed to assess risks for human health.

<u>Fraunhofer Institute project: Investigations on the migration of Polycyclic Aromatic Hydrocarbons (PAHs) from rubber articles containing recycled tyres, December 2017</u>

Based on current literature and standards, two methods of migration from rubber matrix were developed and evaluated: migration onto Tenax® (porous polymer resin, considered to be a good simulant for skin contact) and into 20 % ethanol.

The factors affecting the total migration were examined. The findings include a conclusion that the contact area is the main influencing factor determining the extent of migration, and not the total amount of PAHs.

This is clearly evident especially at stronger migration–promoting conditions like 10 d / 60°C. Experiments using 20 % ethanol noted that this is a good medium for the evaluation of the actual exposure of human skin against B[a]P. This conclusion was also reached by the JRC.

The results of migration using 20 % ethanol/water and Tenax® as a medium are consistent. Both methods are considered to be adequate in support of the assessment of risks from rubber materials in contact with skin. Results from both studies show that the theoretical maximum migration (based on the total mass transfer assumption) is by far not reached.

Therefore 'worst case' exposure scenarios based on the assumption of total mass transfer would highly overestimate exposure and risk. The effect of the thickness of the material on the migration (samples of 3 and 10 mm) was examined, and it was concluded, that the area of contact is the migration determining factor, not the thickness of the material: the migration rates for both samples were almost identical. The project did not include evaluation of migration from plastic matrices and into aqueous media through oral contact.

Assessment of product limits for PAHs in shock absorbing tiles (RIVM, 2016)

The Dutch National Institute for Public Health and the Environment (RIVM) has investigated whether the current limits for PAHs in rubber tiles provide an adequate level of protection against the development of cancer. In their work, RIVM concluded that if the concentration of PAHs in rubber tiles is equal to the limit, the risk level lies around one in a million exposed people (regarded as negligible).

Opinion of professor Hoffman (university of Mainz) on toxicological risk assessment of PAHs in rubber articles and safety slabs made of granulate from recycled used tires (June 2020).

Upon mandate from industry, Professor Hoffman (university of Mainz) assessed the toxicological risk of the eight EU-PAHs contained in safety slabs on the basis of their bioavailability and their migration behaviour as assessed by the Fraunhofer Institute in 2017 and compared the levels of PAHs absorbed from rubber tiles with the levels absorbed from human food.

Hoffman concluded that the migrating quantities of PAHs after a 24-hour exposure period at 40ºC correspond to the quantities of PAHs that can be absorbed by children through one time consumption of a food combination containing PAHs in accordance with the maximum total limits in Regulation EU 1881/2006.

Additional / other relevant on-going activities relevant to PAHs:

1. Guidance on the applicability of the entry 50, paragraphs 5 and 6 – published in April 2018[45].
2. The restriction proposal for PAHs in infill material used in playing fields (the Netherlands with ECHA's support) – submitted to ECHA in July 2018.
3. Validation/inter-laboratory comparison of the method for assessment of migration of PAHs from rubber and plastic articles to skin developed by the JRC – outcomes published with the report on the migration methodology, confirming the validity of the method.
4. Development of the standardised method for assessing PAH content in articles (Commission's request to CEN). The method developed by the JRC for determining PAH content has not been validated and is currently under consideration by CEN in developing a proposal for a harmonised method that would be subject to inter-laboratory testing. Its description is published in the JRC report on migration of PAHs (Annex 2) with detailed information on the method's performance.

   Regardless of/in parallel to the work being done on the development of the methodology for assessment of the migration rate of PAHs from plastic and rubber articles, the Commission has approached CEN to develop a standardised methodology for assessing the content of PAHs in plastic and rubber. The JRC method is one of the methods being considered by CEN.

   CEN, in response to the Commission's request, is developing a standardised method for assessing PAH content in plastic and rubber articles. Once the CEN standardised method is released, the framework of the restriction in its current form will be more consistently applied across the EU.
5. Development of the dose-response relationship for Anthracene oil (EC 292-602-7) and Pitch, coal tar, high temp (EC 266-028-2) in the context of authorisation. The relationships are going to be based on the PAH constituent benzo(a)pyrene. The target populations will be workers and the general public. Development of the dose-response relationship for the general population related to oral and dermal exposure are expected to be included. RAC-45 has adopted the Note on reference dose-response relationship for the carcinogenicity of pitch, coal tar, high temperature and on PBT and vPvB properties in its June 2018 session[46].

2.4.5. Discussion on possible implementation of a migration limit

The Commission has requested the JRC to develop a migration methodology for PAHs, taking into account dermal and oral routes of exposure. The methodology has been developed and validated. The work undertaken by the JRC to develop a standardised method of assessing the migration rate of PAHs from plastic and rubber helps to better

[45] https://echa.europa.eu/documents/10162/106086/guideline_entry_50_pahs_en.docx

[46] https://echa.europa.eu/applying-for-authorisation/evaluating-applicationsapplicationsd

understand one of the current uncertainties, related to the actual level of exposure to PAHs resulting from use of relevant articles.

There are several comments in the call for evidence justifying why a migration limit might be implemented in practice as it is considered that the concentration limit, being the basis of the current restriction, does not appropriately reflect the actual exposure and risk. It is argued, that for a consumer to experience adverse health effects related to a substance, exposure must occur.

It is further argued that a presence of a substance in the matrix by itself does not allow for exposure to occur: migration of the substance is needed for exposure giving raise to risk. Moreover, lower content of a substance in the matrix does not automatically translate into lower exposure risk as migration depends on several factors.

Therefore, the comments strongly advocate to replace (or complement) the currently used content limit by a migration limit. The implementation of such a proposal would bring this restriction in line with other restrictions, where the migration limit is used to establish the applicability of restriction. If the concentration limit still had to be respected, this would mean that complying with a migration limit would not overrule it but the possibility could be considered to introduce a derogation from the content limit if a given risk-based maximum migration limit is not exceeded (similarly to the lead migration-based derogation for consumer articles in entry 63 of Annex XVII to REACH).

The option of introducing a migration test for PAHs would need to be assessed against the specific exposure scenarios that were targeted by the restriction proposal. While the content and source of PAHs in articles vary across articles, depending on their type, origin and brand, there are many parameters that are likely to affect the migration rate of PAHs. These would include, but are likely not to be limited to: the source of PAHs, the matrix in which PAHs are present, the thickness, the deterioration level, the surface coating and its condition. The concentration level of PAHs in the article is also a factor.

Some of these factors are discussed in the JRC report on migration and already mentioned in this report: the migration from the plastic matrix into saliva or sweat simulants at a rate below the LoQ of the method used, as well as equally low migration from all tested matrices into aqueous media. The migration-reducing effect of coating of new articles was also noted in the JRC report. However, neither the JRC nor the Fraunhofer Institute have examined in their work the effect of thickness of the PAHs-containing layer, or the use pattern and deterioration on the migration rate.

The assessment of PAH content and migration conducted by the German authority in 2017, limited to the migration through the skin, also indicates that there is a wide range of migration rates of PAHs from various materials and has suggested that the content limit values of the restriction should be kept if not reduced. The large variability in migration, may lead to a wide spread of risk characterisation conclusions – from a ‘tolerable’ to ‘non-tolerable’ risk level.

The information presented in the JRC report may be used to evaluate the scope of applicability of paragraphs 5 and 6 of entry 50. The JRC assessed PAH migration in different types of plastics and rubbers that are considered representative of the materials commonly used to produce consumer articles. However, to conclude whether a migration limit may be established in replacement (or in addition) to the content limit, it is necessary to perform an

assessment of the risk of exposure of consumers to PAHs released from plastic and rubber articles.

The assessment should take the analytical data provided in the JRC report and in other literature studies into account and use a modelling approach to evaluate exposure to consumers. It is also important to consider the uncertainties related to the interpretation and applicability of the migration limit.

2.5. Assumptions, uncertainties and sensitivities

The assumptions made and uncertainties identified in the analysis are summarised in this section. Sensitivity analysis is not relevant for this report.

2.5.1. Assumptions

Not relevant for this report.

2.5.2. Uncertainties

Assessment of PAHs content

While the methodologies currently used for the estimation of the PAH content in the articles are available, they also have some uncertainties linked to them: the methods are not standardised. The method developed by the JRC was validated internally and it was subject to an inter lab comparison study with external laboratories. The results from the study have been analysed by the JRC which has identified the main reasons for the variability and identified some actions to reduce the uncertainty.

It is expected that the development of the CEN methodology, contracted out by the Commission, would address this source of uncertainty in full.

Migration methodology

The recently published report by the JRC describes the methodology for the assessment of migration PAHs from rubber and plastic materials. The methodology was tested by other laboratories. However, some uncertainties remain in relation to the effect of factors such as, for example, the deterioration of the contact surface of the article, thickness of material, use pattern on the behaviour of PAHs in plastic and rubber matrices.

Some of these elements were identified in the report as factors affecting migration, however their impact was not in the scope of the mandate to the JRC and, therefore, it was not analysed. The report on the study of content of PAHs in consumer articles and toys and their migration presented by Germany (2017) stresses the impact of the matrix type which may result in a migration rate difference of more than two orders of magnitude. This is in line with the conclusions of the JRC related to the migration from the plastic matrix to any medium and from all matrices into aqueous medium.

It is not certain how the thickness of the material would affect the migration, especially in combination with deterioration of the article. While it may be reasonable to assume, that the migration occurs at a higher rate from the superficial layer of the PAH-containing material, the deeper layers may still be a source of ‘fresh’ PAHs, especially if the contact surface is damaged, which would make the deeper layers more accessible. The JRC report identified polyurethane coating on rubber granules as a migration-reducing factor. However, the effect of other potential types of coating, and the longevity of the reduction effect

should be further investigated. Such effects would most likely depend on the use pattern, type of coating material and its thickness.

The results from the JRC study could be used as a reliable basis for a risk assessment which should take into account the impact on migration of factors such as thickness of the material, coating, environmental conditions (e.g. UV radiation) and the use pattern.

ECHA confirms its availability to perform a risk assessment if the Commission requests.

Availability of alternatives

The information provided in response to the call for evidence is not sufficient to identify any alternatives to currently used PAH-containing substances.

One of the conclusion of the JRC report relates to the relevance of the type of carbon black used (the lower migration rate CB375, with the higher PAH content is linked to its capacity to re-absorb PAHs already released due to its larger surface area resulting in a higher absorption capacity). However, it needs to be noted that most of the rubber samples had a dual source of PAHs: in all of them there was one of the forms of CB and one of the extender oils. Only in the silicon rubber sample was there solely CB, and in none of the sample articles tested were extender oils the only source of PAHs. The effect of a second source of PAHs is not considered.

Additional elements for consideration

The inclusion of additional PAHs in entry 50

Since entry 50 and its consecutive elements were added to Annex XVII, the state of knowledge about the hazards related to individual PAHs has increased considerably. It resulted in changes of classification for a number of other PAHs, as discussed in Section 1.2. As the relevant sources of PAHs (carbon black and extender oil) contain multiple PAHs, it seems that those that are not included in the scope of the restriction should be added.

2.6. Conclusions

2.6.1. Availability of methodology for assessing PAH content and considerations on reducing content limit.

The information collected in the call for evidence clearly indicates that while there are not yet CEN-harmonised test methods (they are under development by CEN), there are still methodologies developed for assessing PAH content.

These methods are considered to be easily available in all Member States and across the world. Costs of such testing – in the range of hundreds of euros for each article – seems to be acceptable to the industry.

This conclusion, drawn on the basis of the statements of industry, seems to be corroborated by the results of the REF 4 project, in the scope of which sample articles were tested in various Member States. Nevertheless – some limitations of the methods currently used were also identified in the information submitted for the call for evidence – for example, the lack of peer review or limited applicability/reliability of testing methods for quantifying PAHs in carbon black.

However, the recent work of the JRC on assessing PAH content in plastic and rubber materials introduced relevant changes in terms of test methods to measure PAH content.

The JRC has developed its own method for quantification of PAHs from rubbers and plastics. This method has been optimised and tested in a multitude of sample types and at the relevant concentrations. The use of an MIP-based column has increased specificity and decreased LoQ significantly compared to other methods normally used for PAH quantification (e.g. the ZEK method in use in Germany for many years).

The JRC method has only been validated in-house, however the JRC has developed a functioning SOP which is included in Annex II of the report on migration of PAHs. The development of the CEN-harmonised method may address the shortcomings of the currently used methods: provide a peer review and ensure applicability to all sources of PAHs – including carbon black.

In relation to the content limit, new information available since the preparation of the restriction report (2010) e.g. the German study on PAHs from articles (2017), the JRC report (2018) and information in the restriction proposal from the Netherlands on PAHs in rubber granules (2019) – showed that the relationship between PAH content in articles and its migration from articles is not directly proportional.

A number of variables such as molecular structure of individual PAHs, thickness of the material, presence and influence of coating, type of matrix as well as deterioration may influence the migration. However, the impact of these variables on migration is to be further investigated to assess exposure risks and define whether actual limits should be kept or further lowered.

2.6.2. Methodologies for assessment of PAH migration and considerations on possible migration limit.

At the request of the Commission, the JRC has developed an inter-laboratory validated method for assessing the migration rate of PAHs through skin and oral exposure. In its study, the JRC used 20 % ethanol solution as the migration media to simulate migration through skin and aqueous simulants (artificial saliva) and through the oral cavity.

The report presenting the validated methodology for the measurement of the migration of PAHs from plastic and rubber consumer articles was published by the JRC in August 2018. Its findings are presented in the Section 2.4.4. Tests performed on different plastic and rubber matrices using aqueous simulants and 20 % ethanol as the migration media, showed no PAH releases from any of the material (above the LoQ of the method used) when aqueous simulants were used and limited migration with 20 % ethanol was used as the migration media from rubber produced using DAE as an extender oil.

The method with 20 % ethanol, although developed to measure migration through skin, is considered to also cover migration through the oral cavity as it is more conservative than methods using artificial saliva as the migration media. It showed good performance and it was subject to an inter-laboratory comparison study to assess repeatability and reproducibility. Detailed information on findings and uncertainties are discussed in Section 2.5.2.

Overall, the method developed by the JRC as well as the results of the tests performed by them, can be considered as a starting point to further discuss the introduction of possible migration limits. Also in this case, as for the reduction of the content limit, additional information is needed to better understand the migration behaviour of PAHs in plastics and rubber matrices, in particular, concerning the impact on migration of variables such as thickness, matrix type, sources of PAHs (e.g. carbon black), type of PAHs present in the articles, content, and deterioration of the material.

However, the introduction of a migration limit, as an exemption from the content limit or in addition to it, requires further assessment before it could be considered as a better option to control the risks.

2.6.3. Availability of alternatives

The information provided in response to the call for evidence is too limited to allow definitive conclusions to be drawn on the availability of alternative materials with PAH content lower than those currently used.

It seems that there may be alternatives with lower PAH content for some consumer articles, but not for all. There were some remarks made indicating that the use of such alternatives is not economically viable. However, none of the alternatives or the applications for which they may be available were specifically identified by the respondents.

However, the results of the migration testing confirms that use of the low-PAH extender oil TDAE instead of DAE leads to reduced potential for exposure: it was also indicated that TDAE has already replaced DAE in the production of articles made of rubber with potential for skin contact. Extender oils had limited use in plastics as plastic additives (e.g. soft-PVC).

According to information received in the call for evidence, they are not used anymore in these applications.

2.6.4. Other issues

The newly classified PAHs (dibenzo[b,def]chrysene and benzo[*rst*]pentaphene, see Table 3) have similar classifications to the existing eight substances and, in principle, these could be considered to be added to the restriction.

It could even be considered if PAHs classified as Cat. 1a or 1b could in general be added to the restriction. However, the impact on industry and benefits to human health of these changes (on the scope of applicability of the restriction) has not been further considered.

2.6.5. Overall conclusions

In response to the requests from the Commission to

- assess availability, reliability, performance and applicability of validated analytical methods to establish content and migration of PAHs from articles;
- investigate availability of these methods in commercial labs;
- review availability of alternatives low-PAH raw materials; and
- advise on possible more stringent PAHs content limits in articles.

ECHA concluded that:

1. An analytical methodology to determine the **content** of PAHs (listed in entry 50) in articles at a very low level is available. The method, although not validated, has been developed by the JRC in the context of the STANPAH[47] project and their limit of quantification is in a range between 0.6 and 3.6 ng/ml, with a sample-specific limit of 0.001 to 0.007 mg/kg for a 500 mg sample. This methodology allows significantly lower concentrations of PAHs (up to two orders of magnitude) to be tested than any of the other methods currently used[48].

   The in-house validated method developed by the JRC to measure **migration** of PAHs (listed in entry 50) from plastic and rubber matrices showed good performance, although high variability was observed in the inter-laboratory comparison study attributed to the fact that the determination of PAHs is close to the LoQ. Tests were performed by the JRC on the same rubber and plastic specimen (representative of the most common commercial articles) using both artificial saliva (to assess migration in the oral cavity) and 20 % ethanol solution (to assess migration to skin) as the migration media.
   Migration was observed only when 20 % ethanol was used as the migration media, while no migration was observed in artificial saliva. Therefore, it has been concluded

[47] Information provided in section 2.4.3 of this document

[48] The most widely used method to determine PAHs content in plastics and rubbers was developed by German AfPs in 2014. This method has been recently updated in 2019 (see section 2.4.4. of this document for additional information) and it has a limit of quantification of 0.2 mg PAH/kg material. Other methods are also available to measure PAHs content in specific materials (see section 2.2. of the JRC report for more information).

that the use of 20 % ethanol as the migration media can be considered as a conservative approach to assess both migration to skin and in the oral cavity.

2. Methods developed by the JRC for determining PAH **content** and **migration** are considered sufficiently reliable, easily available in all Member States and also outside the EU. Costs of content testing seem to be acceptable to industry. Minor shortcomings of the JRC method for determining PAH content could be addressed by the ongoing development by CEN of a harmonised method for determining PAH content in rubbers and plastics upon mandate by the Commission[49]. In relation to the method to measure migration of PAHs from articles, the JRC has identified possible actions (not implemented in the method) that may contribute to reduce the variability. These methods (content and migration) can be easily deployed in commercial laboratories and testing costs can be considered comparable with the costs of the method used for PAHs quantification.

3. Information obtained in the call for evidence is not sufficient to identify **alternatives** to currently used PAH-containing substances. However, information in the Annex XV restriction report from Germany (2010) and information obtained from industry shows that alternatives are available to high PAH-containing materials. Such alternatives include low-PAH carbon black and low-PAH extender oils as well as carbon black/extender oil-free alternatives that can be used to produce consumer articles (e.g. thermoplastic elastomers, and PAH-free plasticisers). However, some of these alternatives may pose health related concerns and availability issues in applications where high quantities of extender oils are used.

4. In relation to **content limits**, based on the German Annex XV report (2010) on migration of PAHs from articles (2017), actual content limits may not guarantee a low level of migration of PAHs from consumer articles and safe use for all types of plastic and rubber matrices. Germany has, therefore, recommended that the current limits are kept or even reduced.

   A similar conclusion was drawn by RIVM, in their study on the assessment of PAH content limits in rubber articles (2016). More recently, the JRC (2018) showed that detectable migration of PAHs from plastic and rubber matrices was only observed in rubbers with high PAH content. The JRC also concluded that there is no linear relationship between PAH content in the article and their migration.

   The Fraunhofer Institute (2017) on mandate from industry, studied the migration of PAHs from articles made from recycled tyres. Based on the tests performed on a number of commercial articles, showing very low migration of PAHs from analysed articles, the Fraunhofer Institute concluded that the contact area and not the PAH content in the article, determines the extent of migration. Based on this study, Professor Hoffman (University of Mainz) published (in June 2020) an expert opinion commissioned by industry on the toxicological risk assessment of PAHs in rubber articles and safety slabs made of granulate from recycled rubber tyres. In his opinion, Professor Hoffman concluded that toxicological effects of PAHs in rubber tiles do not depend on the quantity of PAHs which are present in the article, but on the

[49] https://ec.europa.eu/growth/tools-databases/mandates/index.cfm?fuseaction=search.detail&id=579

quantities that migrate from the contact area of the article to the human body through the skin. Professor Hoffman also concluded that, in the case of the tiles (considered in his study), the migration of PAHs was very low and did not pose any additional risk to human health.

Based on available information, ECHA concludes that the current content limits for PAHs in plastic and rubber articles are still considered effective as a risk management measure to control consumer exposure. However, work done by the JRC along with other literature information has provided better knowledge on the migration behaviour of PAHs from articles compared to the Annex XV restriction report from Germany (2010).

Although some uncertainties still exist in determining the influence of certain parameters on migration of PAH content in articles (e.g. thickness of the material, use pattern and deterioration), reliable methods are available to measure migration.

Overall, taking all available information into account, ECHA is of the opinion that it is necessary to perform a risk assessment to conclude if a migration limit could be set in addition to or as an alternative to the content limit.

However, if the Commission requests it, ECHA is ready to assess the risks for consumers from migration of PAHs from plastic and rubber articles and to analyse whether a migration limit could be established to control risk and, in addition, if the current content limit value is protective enough against risks from exposure to PAHs.

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