The pathway for enforceable restrictions of chemicals present in rubber goods

Laia Perez Simbor
Head of Sustainability, Chemicals and Materials

Agenda

1. Introduction
2. Methods to quantify the content in weight of substances in rubber matrices are complex and expensive.
3. Migration methods have allowed successful compliance and enforcement for rubber goods in contact with food.
4. Way forward

General Rubber Goods are essential for many sectors

General rubber goods (GRG) are found in the sky, deep in the earth and everywhere in between!

Major markets are :

63% — **Transport** (automotive, rail, ships, aviation, aerospace, ...)

10% — **Household appliances**

8-10% — **Industrial applications** (construction, mining, agriculture, farming, machinery, ...)

10-12% — **Energy/offshore**

4-5% — **Food contact** (drinking water, baby care, medical devices, ...)

1-2% — **Leisure and sports equipment**

An innovative and technology driven industry:

Drivers for innovation include high technology customers, high performance requirements and regulatory pressure.

As much as 5% of the industry's investments are in R&D.

A fragmented sector

More than **6000** companies present in Europe

98% are SMEs and many are micro-enterprises (<10 employees).

However, most of the GRG turnover is produced by about 20 companies organised in several small units (50 to 100 people in each factory supported by technical centre) according to their product-lines.

A highly integrated value chain

in order to respond to the requirements of its customers, the sector needs to develop a very close relationship with its customers. This is a growing trend.

The sector provides employment for 160.000 employees

and many of these have very specific know how to respond to the technological needs of the industry.

Turnover about 30 Billion

European, American and Japanese companies dominate the world market.

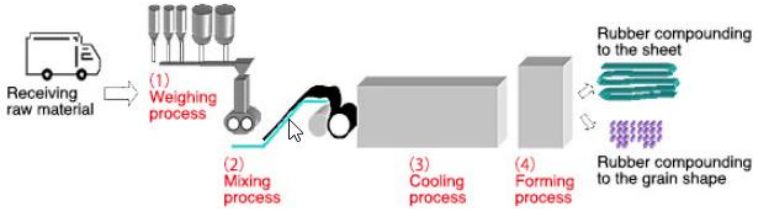
These include 46 of the first 50 ranking GRG producers in the world, with 17, 15 and 14 companies respectively. This is linked to the high technological value added provided by companies in these countries. In 2014, the top three companies were European.

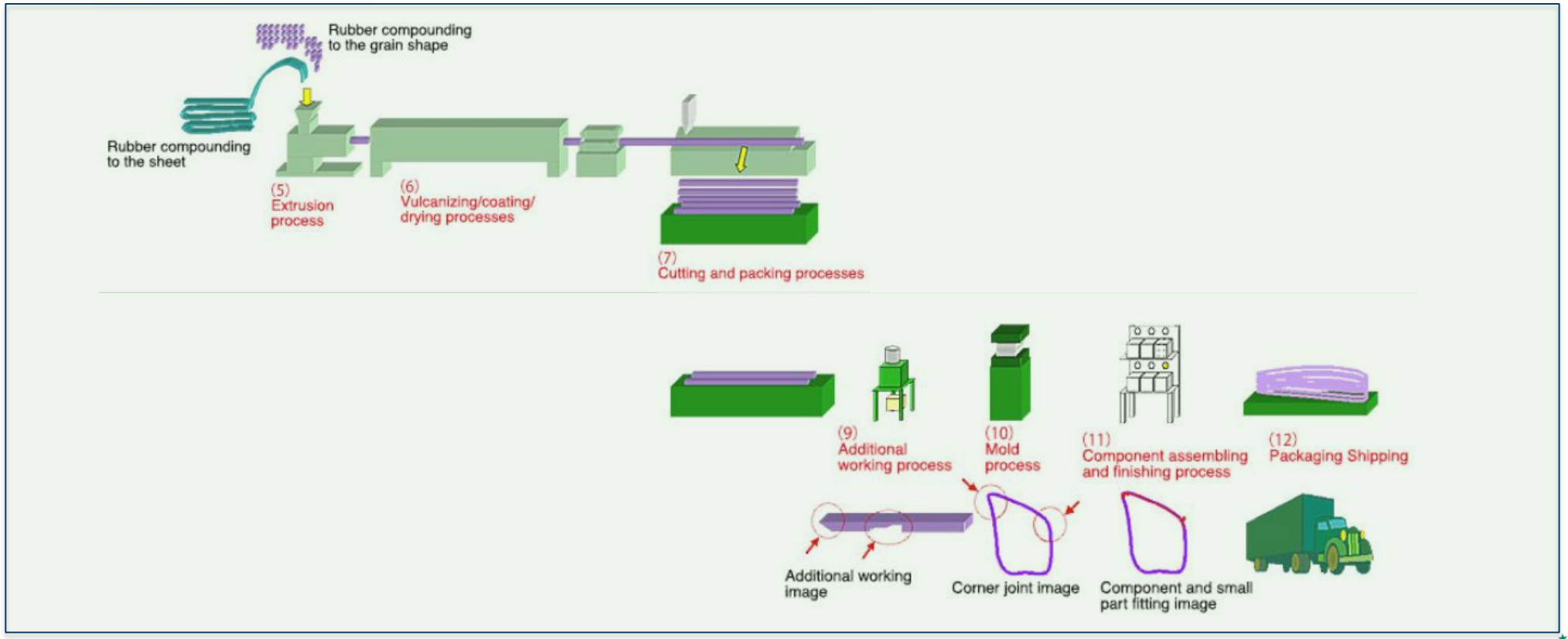
The trade balance is positive

With €4.3 B of exports compared to €3.4 B of imports

This is driven by the high value added products.

Rubber Goods manufacturers are downstream users of substances and mixtures that produce articles





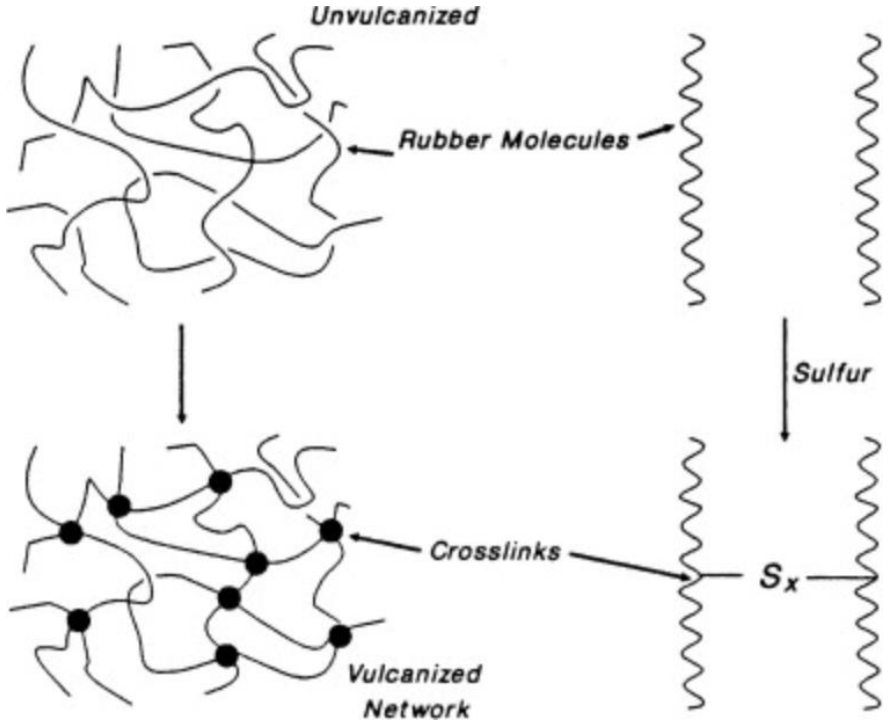
SOURCE: https://www.nishikawa-rbr.co.jp/english/technology_manufacturingline.php

2. Methods to quantify the content in weight of substances in rubber matrices are complex and expensive

The vulcanization, curing state, creates cross-linked matrix were components are trapped in the matrix

When a rubber matrix is vulcanised, substances can be either bounded or trapped / imprisoned, both presenting challenging testing. When a substance reacts during the vulcanization, a covalent link with rubber matrix may be generated (for example with sulphur), and in that case, it would not be possible to extract it, whatever the duration of the solvent extraction.

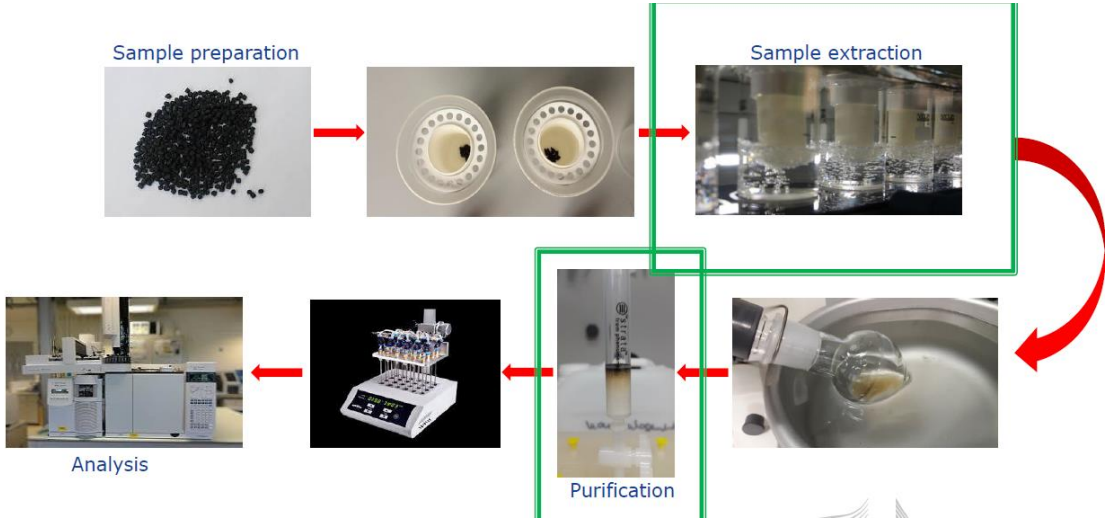
In the case where a substance is trapped/imprisoned inside the rubber vulcanized matrix, its extraction with a solvent is possible, provided the development of a specific method which implies the identification of the ad-hoc solvent, the temperature and the duration of the extraction, to secure that all the substance is well completely extracted.



Source: A.Y. Coran, in The Science and Technology of Rubber (Fourth Edition), 2013

Test methods to quantify the quantity and presence of substances in vulcanised rubber require an extraction step

Test methods to quantify the quantity and presence of substances in vulcanised rubber usually foresee the following steps: a preparation of the rubber sample, an extraction of the substance with a selected solvent, a concentration of the substance, a clean up of the solution, and the final determination of the concentration using a gas chromatograph or equivalent technics.



SOURCE: STANPAH presentation to stakeholders (Barrero, J. et all 2018)

For substances in vulcanised rubber that are trapped, the extraction step is essential to secure that the substance is later present in the whole amount and therefore measured.

- The extraction step includes introducing the sample solvent-based solution, for instance, toluene for hydrophobic substances, then heat the solution for a period of time in order to extract all the material.
- The longer the extraction period, the higher the precision and the accuracy of the detection limits.
- High trueness and accuracy is essential and crucial in order to meet the requirements of restrictions with thresholds on content in weight for rubber articles

Case study: enforcement of restriction on PAH in rubber articles in contact with the skin - Entry 50 p 5-8 of Annex XVII REACH

50. Polycyclic-aromatic hydrocarbons (PAH)

(a) Benzo[a]pyrene (BaP) CAS No 50-32-8

(b) Benzo[e]pyrene (BeP) CAS No 192-97-2

(c) Benzo[a]anthracene (BaA) CAS No 56-55-3

(d) Chrysen (CHR) CAS No 218-01-9

(e) Benzo[b]fluoranthene (BbFA) CAS No 205-99-2

(f) Benzo[j]fluoranthene (BjFA) CAS No 205-82-3

(g) Benzo[k]fluoranthene (BkFA) CAS No 207-08-9

(h) Dibenzo[a,h]anthracene (DBAhA) CAS No 53-70-3

5. Articles shall 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 amongst 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, wrist-bands, masks, head-bands

6. Toys, including activity toys, and childcare articles, shall 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.

7. By way of derogation from paragraphs 5 and 6, these paragraphs shall not apply to articles placed on the market for the first time before 27 December 2015.

8. By 27 December 2017, the Commission shall review the limit values in paragraphs 5 and 6 in the light of new scientific information, including migration of PAHs from the articles referred to therein, and information on alternative raw materials and, if appropriate, modify these paragraphs accordingly.

There were no tests methods to achieve the levels of precision for the proposed *1 mg/kg (0,0001 % by weight of this component) of any of the listed PAHs*

There are test methods available for measuring the content of PAH in rubber, but no methodology was available for compliance for the analysis of the eight listed PAHs in rubber components due to:

- The sensitivity required: The detection limit of the method for each of the eight individual PAH in rubber in order to comply with the restriction has to be in the range of in 0.2 mg PAH/kg at the minimum.

- The accuracy: The trueness and precision of the PAH methods available is not set to the minimum requirements established in general standards such as ISO 5725. Thus, meaning that the methods could not be replicable across laboratories or were dependent of the use of a specific machinery brand.

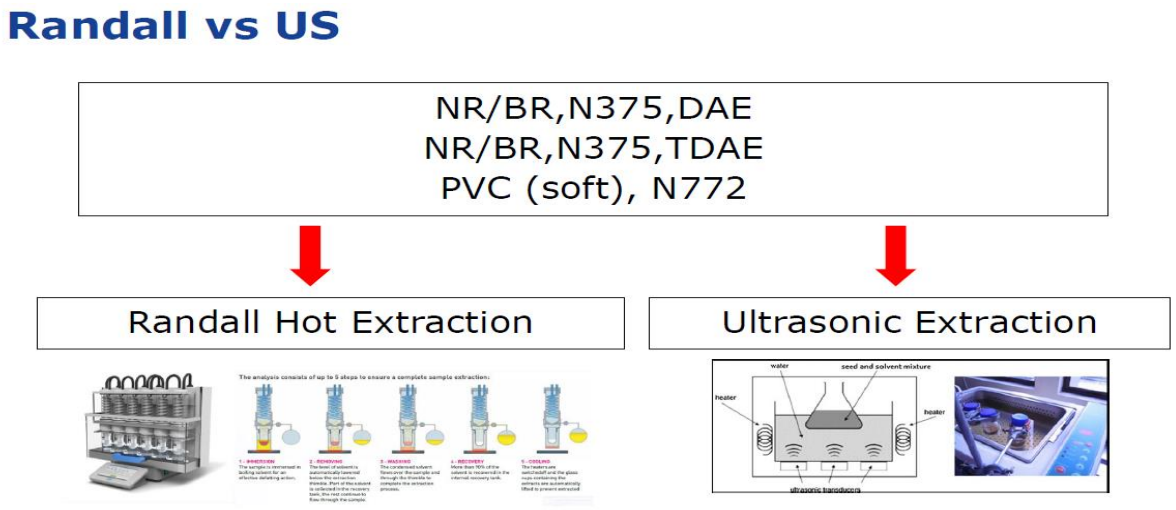
The Joint Research Centre of the EU published in 2018 the results of STANPAN study that compared several available methods to measure PAH content in Rubber matrices

STANPAHs Objectives were to:

A) Better understanding of the migration behaviour of certain PAHs in plastic and rubber components of articles, and

B) Develop a reliable methodology to determine PAH migration from these matrices, under conditions simulating, to the extent possible, dermal contact (including the oral cavity)

STANPAH compared the hot extraction method (3h) with ultrasonic extraction methods (1) - the latter commonly used for PAH extraction in current standardized methods

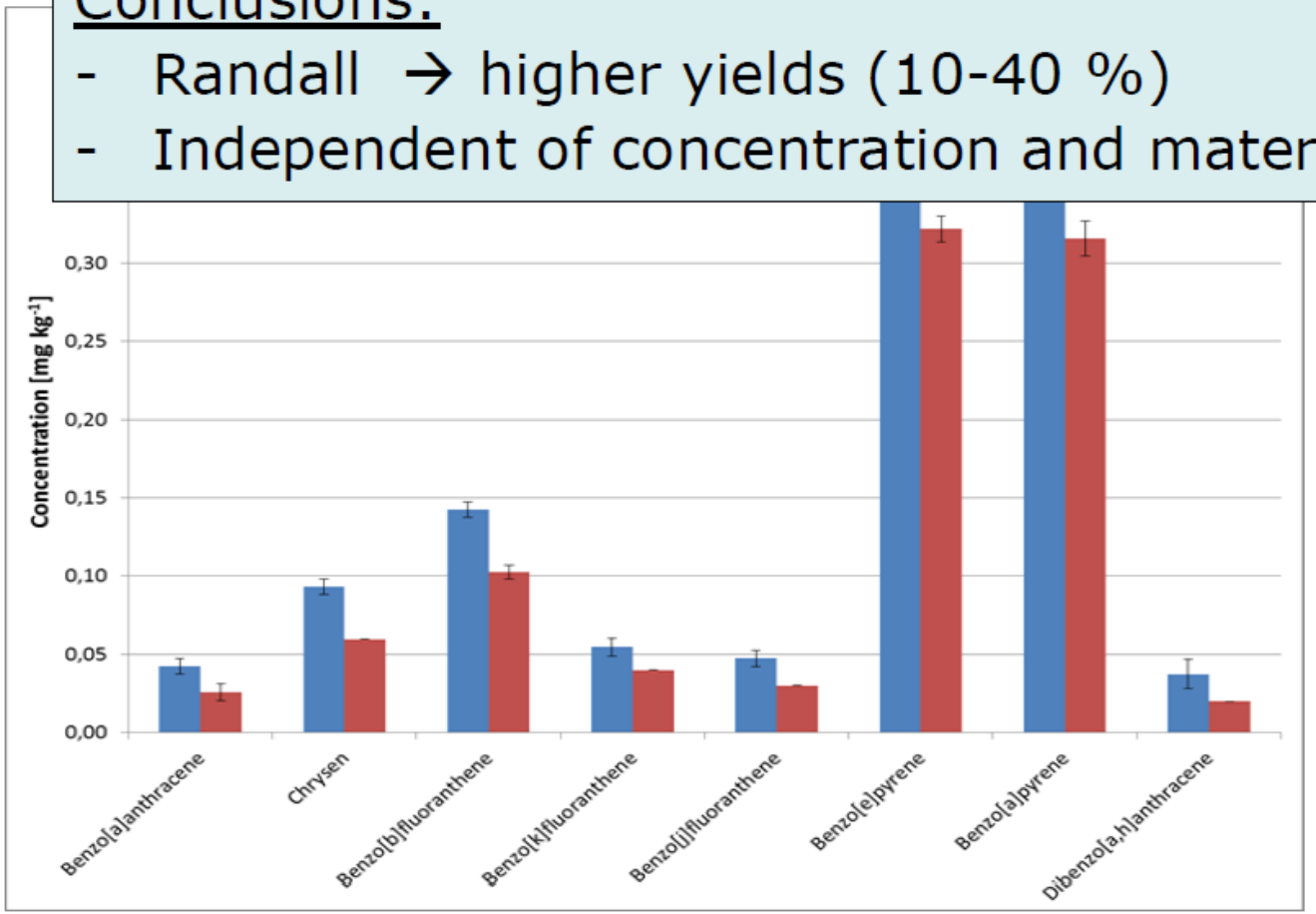


SOURCE: STANPAH presentation to stakeholders (Barrero, J. et al. 2018)

Extraction Efficiency – Randall vs Ultrasound

Conclusions:

- Randall → higher yields (10-40 %)
- Independent of concentration and material



Randall:

- 3 hours *(all steps)*

Ultrasound:

- 1 hour
- 800 W
- Frequency: 59 kHz
- Temp. 60°C

SOURCE: STANPAH presentation to stakeholders (Barrero, J. et all 2018)

STANPAH concluded that standards used for measure PAH in rubber matrices were not accurate enough

Table 1
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			
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.
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
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.
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.
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 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

SOURCE: (Otmar, J. et al. 2018)

The European Commission mandated CEN to develop a test method that would be used to enforce the restriction in 2017 (M556)

EC request to draft harmonised standards for the analytical determination of the individual concentrations of the 8 carcinogenic PAHs, listed in entry 50 of Annex XVII to Regulation (EC) No. 1907/2006 (REACH), in the plastic and rubber components of articles, in support to the enforcement of the provisions in paragraphs 5 and 6 of the restriction. Requested standards shall meet the requirements set out in Annex I and are listed in Annex II.

Although a number of methodologies exist for the analysis of PAHs in environmental matrices3 and specific industrial4 and consumer products5 , no such methodology is available for the analysis of the eight listed PAHs in plastic and rubber components in the broad range of consumer articles within the scope of the restriction.

The Mandate requested CEN to perform a:

- Scoping study,
- Selection of reference rubber and plastic materia
- Development and optimisation of a PAH content method (or methods)
- In house validation of test method
- Inter-laboratory validation (round-robin testing).

The work at CEN is still on-going with the final standard expected to be published in 2023 – seven years after the entry into application of the restriction.

PAH case study conclusions

- Setting thresholds for content in weight for rubber matrices require to have available test standards
- The accuracy of the test standards is determined by the threshold, for PAH at least in 0.2 mg PAH/kg precision was needed for a threshold of 1 mg/kg
- For rubber matrices the extraction step is essential to secure high sensitivity and precision
- Longer extractions increase the time and cost of the standard, but secure high precision
- The process of developing EU harmonised standards is long, require resources from industry and regulators.
- 7 years after the Entry into application (2015) there is not an available method trustable to enforce the restriction

The proposed restriction on PFHxA include thresholds for rubber articles, without a method publicly available and reliable

ECHA Published in December 2021 its final opinion on the restriction on *undecafluorohexanoic acid (PFHxA), its salts and related substances,* PFHxA (see image)

It proposes several thresholds for rubber goods in the range of 2 mg/kg. In order to prove compliance the detection limit of the test used has to reach levels of at least 0.2 mg/kg per salt

There are not publicly available methods that can measure the content of PFHxA in rubber matrices.

Private methods are available but can only be used under certain conditions and in specific laboratories. Further, with not guarantee that the results are precise and accurate

Are we heading towards a long and expensive process to allow GRG producers and authorities to enforce?

11. The concentration limit referred to in paragraph 2 shall be
    (a) 2000 ppb for the sum of PFHxA and its salts in fluoropolymers;
    (b) 150 ppm for the sum of PFHxA and its salts in fluoropolymers used in the following usage groups: Engine parts in automotive, aerospace and shipping industry.
    (c) 10 ppm for the sum of PFHxA and its salts in fluoropolymers used in coating of electronic devices until XX XX XXXX [7 years after entry into force]
    (d) 100 ppm for the sum of PFHxA related low molecular[1] substances in fluoropolymers.
    (e) 2500 ppm for the sum of PFHxA related low molecular substances in fluoropolymers used in the following groups: Engine parts in automotive, aerospace and shipping industry.
    (f) 500 ppm for the sum of PFHxA related substances in fluoropolymers used in coating of electronic devices until XX XX XXXX [7 years after entry into force].

3. Migration methods have allowed successful compliance and enforcement for rubber goods in contact with food

Migration methods have allowed successful compliance and enforcement for rubber goods in contact with food

- Rubber goods need a coherent approach to be able to enforce, test and show compliance with restrictions for PAH, PFHxA and the further restrictions to come such as Bisphenol AF.
- An approach based solely on the content of substances by weight in rubber goods will not succeed in securing efficient and practical enforceability.
- A comprehensive approach is needed for rubber goods.

The rubber sector is already acquainted with compliance of chemical substances in the area of Food Contact Materials.

For instance, Germany's Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) published three interrelated recommendations for natural and synthetic rubber commodities intended to come into contact with food. Articles in contact into food are classified in 3 categories from category 1, what includes rubber goods that are in contact with food for more than 24 hours, to category 3 – where rubber goods are in contact with food only for a period of 10 minutes.

Then, migration tests on specific simulants have to be performed to show compliance. With the conditions of the test, and the time of migration adapted to each category, from 24 h of category 1 to 10 minutes on category 3.

In France, Arrêté N° 196 of 11/08/2020 also follows a similar approach, where rubber goods are distributed across categories A to D, and with specific migration test defined for each category..

Federal Institute for Risk Assessment
XXI/1 'Commodities based on natural and synthetic rubber in contact with food', as of July 1, 2021

	Food contact consumer goods made of natural and synthetic rubber (when used as intended)*		
Category	**Category 1 (Long-term contact)**	**Category 2 (Medium-term contact)**	**Category 3 (Short-term contact)**
Time in contact with food	More than 24 hours and up to several months	24 hours maximum	10 minutes maximum
Example of commodity	- Storage containers - Container linings - Sealing rings for cans, jars, bottles and similar items - Bottle stoppers and caps	- Sealing rings for pressure cookers, hoses for coffee machines - Lid seals e.g. for milk cans - Valve balls	- Gloves and aprons worn during processing of food - Roller covers for fatty food
Simulants	1) deionized water, 2) 10% ethanol, 3) 20% ethanol, 4) 3% acetic acid, 5) 50% ethanol, 6) poly(2,6-diphneyl-p-phenylene oxide) particle size 60-80 mesh, pore size 200 nm and 7) vegetable oil with less than 1% unsaponifiable matter		
Test conditions** for migration	40 °C, 10 days***	40 °C, 24 hours	40 °C, 10 mins

Source: SGS https://www.sgs.com/en/news/2021/09/safeguards-13221-germanys-bfr-issues-guidelines-for-natural-and-synthetic-rubber-commodities

Migration tests present advantages for general rubber goods producers compared with content in weight methods

Migration tests are simpler to implement than content in weight methods on rubber matrices, because they do not require an extraction. Instead, a standardized protocol for migration is used. The advantages of not needing an extraction step from the rubber matrix are:

- The reduction of the time of the test for the majority of articles. As opposite to the 3-4 hours extraction process, migration test for most of the articles are in the range of 10 minutes
- The laboratory equipment needed is widely available
- The temperature is in the range of 40ºC, allowing for less costly security provisions in the laboratories.

The migration tests have allowed rubber goods producers to effectively enforce and comply with the requirements, without costly or complex procedures. It reassures manufacturers of rubber goods with clear provision and supports SMEs with acquainted process.

4. Way forward

4. Building a way forward: How can the forum help to secure enforceable restriction of general rubber goods?

- The number of restrictions on substances present in rubber goods is increasing, with the PFHxA restriction and the BPFA restriction under development and with other wide restrictions expected over the coming years.
- Thresholds on the content in weight are difficult to test in vulcanised rubber matrices. For some substances, that PFHxA, there are no test methods available. When test methods are available such as for PAH, the specificities of rubber matrices rend long and expensive to test with high precision.
- This hampers a proper enforcement and sends confusing messages to the sector, largely dominated by SMEs.
- Enforceability for general rubber goods based on already available test methods that set migration as basis have many advantages. Those methods are well now by laboratories and already implemented for food contact materials´ compliance.
- An approach for compliance based on migration will allow an efficient, fast and economically possible implementation of rubber goods restrictions. It will allow rubber producers to address compliance in a timely manner and at the end secure enforcement and protection for users

References

References:

Otmar Geiss, Chiara Senaldi, Ivana Bianchi, Ana Lucena, Salvatore Tirendi, Josefa Barrero-Moreno, A fast and selective method for the determination of 8 carcinogenic polycyclic aromatic hydrocarbons in rubber and plastic materials, Journal of Chromatography A, Volume 1566, 2018, Pages 13-22, ISSN 0021-9673, https://doi.org/10.1016/j.chroma.2018.06.047

Barrero, J., Senaldi, C., Bianchi, I., Geiss, O., Tirendi, S., Folgado De Lucena, A., Barahona Ruiz, F., Mainardi, G., Leva, P. and Aguar Fernandez, M., Migration of Polycyclic Aromatic Hydrocarbons (PAHs) from plastic and rubber articles, EUR 29282 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-89749-8 (online),978-92-79-89748-1 (print), doi:10.2760/41492 (online),10.2760/637211 (print), JRC111476.

M/556 COMMISSION IMPLEMENTING DECISION C(2017) 7926 of 1.12.2017 on a standardisation request to the European Committee for Standardisation and to the European Committee for Electrotechnical Standardisation as regards compliance with maximum content criteria of Polycyclic Aromatic Hydrocarbons in rubber and plastic components of articles placed on the market for supply to the general public in support of Regulation (EC) No. 1907/2006 of the European Parliament and of the Council

Thank You.

Contacts: Laia Perez Simbor, l.perez@etrma.org

ETRMA