European regulation (EU) No 1272/2013 has now been in force for over two years, restricting polycyclic aromatic hydrocarbons (PAHs) in some rubbers and plastics depending on their end use. But, why are they restricted, which PAHs have been detected in consumer products and where could they be found?

PAHs in footwear

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Polycyclic aromatic hydrocarbons, (PAHs) are organic molecules that consist of two or more adjacent aromatic rings. Although they only contain the elements carbon and hydrogen, these atoms can exist in many different structural arrangements, so there are in fact many different PAHs. They occur naturally in coal, crude oil and petrol, and can be formed during the incomplete burning of fossil fuels. Generally speaking, the less efficient the burning, the more PAHs will be formed.

Studies have shown there are possible short-term and long-term health effects from PAH exposure and this has resulted in national and international legislation. SATRA has been testing rubbers and plastics for the presence of PAHs since before EU 1272/2013 updated REACH (Regulation EC No 1907/2006) Annex XVII entry 50 and this article will help to explain why they are restricted, why they could be present and identify some of the specific PAHs that have been detected when samples have been tested.

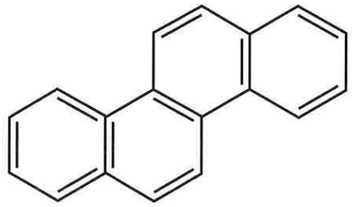
EFFECTS ON HEALTH

PAHs may pose a risk to human health by ingestion, skin absorption and inhalation. Studies with animals have shown exposure may cause eye irritation and vomiting and also long-term effects such as an increased risk of cancers in the stomach, skin, bladder and liver. It is this increased long-term risk of causing cancers that has justified the introduction of PAH legislation.

From 27 December 2015, the eight PAHs listed in table 1 have been restricted to a maximum concentration of 1 mg/kg (ppm) in rubber or plastic components that come into contact with the skin or oral cavity. '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' is the descriptive text in REACH Annex XVII and footwear is specifically listed as one of the articles included in the scope of the restriction.

IMAGE: SATRA

Figure 1 - chrysene is a PAH that has been detected in flip-flops on sale in the UK



PAHs IN FOOTWEAR

Some of the main styles of footwear where rubbers and plastics may come into direct contact with the foot are sandals, jelly shoes and flip-flops. It is likely that polyvinyl chloride (PVC), ethylene-vinyl acetate (EVA) and polyethylene (PE) could be in direct contact with the foot in all these styles, so the REACH restriction would be directly applicable to these plastics in those types of footwear. In the summer of 2017, a major UK high street retailer instigated a product recall as a result of chrysene *(Figure 1)* being detected above the maximum allowable limit.

Of the eight restricted PAHs, chrysene, benzo[a]pyrene and benzo [b]fluoranthene are the ones most commonly detected at SATRA, although it is rare that they are present above 1 mg/kg. Some brand and retailer specifications have restricted PAHs in all rubbers and plastics, regardless of whether they are in contact with the skin or not. Examples are synthetic uppers and synthetic soling materials, with the blanket inclusion of PAHs on restricted substances lists a sign that brands and retailers wish to ensure their suppliers meet a wider restriction than just the minimum legislative requirements.

WHY MIGHT PAHs BE PRESENT?

PAHs are not intentionally added to plastics or rubbers but instead could be present as impurities. A commonly used pigment in black rubbers and plastics is carbon black. As previously mentioned, PAHs can be formed through the burning of fossil fuels and carbon black can also be manufactured in a similar way by the partial combustion of oil or natural gas. Black rubbers and plastics generally contain carbon black as a pigment, so they are therefore more likely to contain PAHs than other colours. However, all coloured rubbers and plastics may contain process oils, plasticiser oils or extender oils (which are added to modify and cheapen processing or plasticiser oils), which may also be manufactured from coal, crude oil or petrol and could again contain PAH impurities.

TESTING FOR THE PRESENCE OF PAHs

SATRA has developed an internal testing procedure to identify and quantify PAHs in rubbers and plastics based on two published standards. The first is PD CEN ISO/TS 16190:2013 – Footwear (critical substances potentially present in footwear and footwear components) test method to quantitatively determine polycyclic aromatic hydrocarbons (PAH) in footwear materials. The other is the German national standard ZEK 01.4-08, Testing and Validation of Polycyclic Aromatic Hydrocarbons.

The principle of the SATRA procedure is the test specimens are extracted with toluene at elevated temperature in an ultrasonic bath. Trials showed that toluene, the extraction solvent specified in ZEK 01.4-8, has a higher propensity to extract PAHs than hexane, the one specified in the PD CEN test, so the former was selected for the SATRA procedure. Once the extraction is completed, the toluene containing the PAHs is filtered to remove any particulate matter and the resulting extract analysed by Gas Chromatography with Mass Spectrometry (GC-MS). This separates, identifies and quantifies any of the 18 PAHs (those listed in *Tables 1 & 2* which may be present in the test specimen.

Analysing the results of various samples tested, SATRA has detected the PAHs listed in *Table 2* more often than the eight shown in *Table 1*. Phenanthrene, pyrene and naphaline are the most common PAHs identified in rubbers and plastics.

OTHER PAH LEGISLATION

Before 27 December 2015, there were already existing European restrictions in REACH (EC 1907/2006) Annex XVII entry number 28, which banned the sale of PAHs to the general public in substances or mixtures, and entry number 50 which banned their presence in vehicle tyres. There were also some specific national requirements. Within Germany, there are limits on the amounts of PAHs present in consumer products. Clause 30 of the LFGB (the food and feed code) restricts the amount of 18 PAHs that can be present in food contact items such as packaging or plastic utensils. Clause 30 of the LFGB is also applicable to toys for children under 36 months that are intended to come into contact with the skin. Product on sale within Germany wishing to be labelled with the GS mark (a voluntary certification mark to indicate the product has passed essential safety requirements) must also meet with specific PAH requirements. Many PAHs, including seven of the eight restricted by EU Regulation (EU) 1272/2013, are also listed in Californian Proposition 65, so warning labels must be attached if products on sale in the state of California contain these chemicals.

TABLE 1 - RESTRICTED PAHS LISTED IN REACH ANNEX XVII ENTRY 50

PAH	CAS Number
Benzo[a]anthracene	56-55-3
Chrysene	218-01-9
Benzo[b]fluoranthene	205-99-2
Benzo[k]fluoranthene	207-08-9
Benzo[j]fluoranthene	205-82-3
Benzo[e]pyrene	192-97-2
Benzo[a]pyrene	50-32-8
Dibenzo[a,h]anthracene	53-70-3

TABLE 2 - ADDITIONAL PAHS RESTRICTED IN THE GERMAN FOOD AND FEED CODE (LFGB)

PAH	CAS Number
Naphthalene	91-20-3
Acenaphthylene	206-96-8
Acenaphthene	83-32-9
Fluorene	86-73-7
Phenanthrene	85-01-8
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Indeno[1,2,3-c,d]pyrene	193-39-5
Benzo[g,h,i]perylene	191-24-2