

CARBON BLACKS WITH LOW AMOUNT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Product Application PA R514-GL



INTRODUCTION

Carbon black is an industrial product which is produced under precisely defined processing conditions and which consists essentially of elemental carbon. Carbon black contains small quantities of hydrogen, oxygen and sulfur in the form of functional groups. Due to the production process, traces of polycyclic aromatic hydrocarbons (PAH) exist and are tightly bonded to the surface. They can only be extracted from the surface of the carbon black itself under vigorous laboratory conditions such as Soxhlet extraction with strong organic solvents e.g. toluene, at elevated temperatures¹.

This product application gives a brief overview of a selected number of regulations and standards, related to carbon black and PAHs. It also presents Orion's product portfolio that is eligible for use in rubber applications.

ABOUT POLYCYCLIC AROMATIC HYDRO-CARBONS (PAH)

PAHs consist of condensed benzene rings which occur as by-products of combustion of organic substances like coal, oil, fuel, wood, fat, etc. They are not only formed in side reactions during carbon black production but are also present in food like grilled and smoked meat or fish. Several hundreds of PAHs exist with different toxicity: some PAHs were identified as carcinogenic, mutagenic and teratogenic. Nevertheless, the assessment of hazardous potential of individual PAHs can vary significantly between legislations and institutes. Commonly, benzo[a]pyrene is seen as the PAH with the highest toxicity and thus often used as a reference substance.

SELECTED REGULATIONS FOR THE PAH CONTENT IN RUBBER ARTICLES

Several regulations and standards, depending on the respective country or sector, have set limits regulating the amount of PAHs allowed in finished rubber goods or in raw materials like carbon black used for the manufacture of rubber goods. While hundreds of PAH exist, only some are concerned. Depending on the regulation, different PAH substances and limits are listed. A further complication is that, often, either no applicable test method is given or the cited test method is not applicable to carbon black. The following selected regulations concern rubber applications and carbon blacks:

The Commission Regulation (EU) No. 1272/2013 sets limits for the PAH content of accessible plastic or rubber parts of consumer articles; each of the so-called 8 EU-PAHs may not exceed 1 ppm (mg/kg). For toys and childcare articles, the limit for each of the 8 EU-PAHs is 0.5 ppm. No method to test PAH levels and verify compliance is specified by the regulation. Commission Regulation (EU) No. 1272/2013 applies to parts of articles that come into direct, prolonged or short-term repetitive contact with the human skin or the oral cavity under normal or reasonably foreseeable conditions of use. Articles or parts thereof which are only in short and infrequent contact with the skin or oral cavity should not be included within the scope of the restriction as the resulting exposure to PAHs would be insignificant.

Although, the GS Specification AfPS GS 2019:01 PAH is a voluntary certification of the so-called "GS mark" for technical articles in Germany, it has now also become a global reference. The GS mark certification can only be provided by authorized institutes. It does not apply to raw materials like carbon black but to the finished article. Depending on application and usage, three categories with different PAH levels for 15 PAHs are defined.

PAH-containing extender oils in car tires are restricted by the European Chemicals Regulation REACH (Regulation (EC) No. 1907/2006). This restriction bans the use of extender oils for producing car tires or tire parts if these contain more than 1 ppm of Benzo[a]pyrene or if the overall contents of all PAHs listed is more than 10 ppm. Carbon black is not part of this regulation.

The automotive industry has established a list of declarable substances, the so-called GADSL (Global Automotive Declarable Substance List); the last edition is from February 2021. Since carbon black is not a hazardous substance, it is not listed in the GADSL. However, PAHs are included and reference is made to EC 1272/2013 for rubber and plastics articles in contact with skin. As mentioned above, the limit in the final article is 1 mg/kg for any of the 8 REACH PAHs.

¹ Stephan Hamm, Thomas Frey, Rudolf Weinand, Gilles Moninot, and Nicole Petiniot (2009) "Investigations on the Extraction and Migration behavior of Polycyclic Aromatic Hydrocarbons (PAHS) from Cured Rubber Formulations Containing Carbon Black as Reinforcing Agent", Rubber Chemistry and Technology: May 2009, Vol. 82, No. 2, pp. 214-228; http://dx.doi.org/10.5254/1.3548246

SELECTED REGULATIONS FOR THE PAH CONTENT OF CARBON BLACK USED IN RUBBER ARTICLES

In Germany the Federal Department for Risk Assessment ("Bundesinstitut für Risikobewertung, BfR''') has defined the purity requirements for carbon black in food-contact commodities in the BfR Recommendation XXI (Food Commodities on the Basis of Natural and Synthetic Rubber, effective July 01, 2021). Carbon black is part of the "evaluated starting materials" and the requirements for carbon black used as a filler are defined in Table 1. Besides limits for toluene extractables and for the UV absorption of a cyclohexane extract, there is now also a limit for the benzo(a)pyrene content: max. 0,25 mg/ kg carbon black (ppm). Former editions of this recommendation did not consider polycyclic aromatic hydrocarbons (PAH). This new requirement is only matched by very few carbon black grades¹.

For elastomer products in contact with drinking water, the German Elastomer Guideline as of March 16, 2016 applies². The Positive List has been revised on December 3, 2019. For carbon black it now refers to the purity criteria of the EU Regulation 10/2011 on plastic materials and articles intended to come into contact with food. The criteria are basically the same as described above for BfR XXI. For the final articles, migration tests shall be carried out to determine PAHs according to the TrinkwV 2011.

In France the "Arrêté du 05.08.2020 Rubber articles in contact with food" has adopted the same limits for toluene extract, absorbance of a cyclohexane extract and benzo[a]pyrene content as the German BfR XXI. In China the National Food Safety Standard GB 9685-2016 has implemented limits for use of additives in food contact materials and products. Carbon blacks with a benzo[a]pyrene content of less than 0.25 ppm are approved for use in rubber food contact applications with a maximum level of 50% in the compound.

PRODUCT PORTFOLIO FOR LOW PAH CARBON BLACKS FOR RUBBER APPLICA-TIONS

Orion offers a family of products, DUREX[®], CORAX[®] and the PUREX[®] RP grades, which have a particularly low PAH content. These products have been designed to meet the requirements of several regulations related to PAH (see table 1 and figure 1).

For more information on food-contact applications please refer to our product application PA R506-GL.

Figure 1

Orion's low-PAH grades in OAN-STSA-map



Table 1

Maximum content of selected PAHs (in ppm)

GRADE	ASTM EQUIVALENT	DESCRIPTION	BENZO[A]PYRENE	EACH OF THE 8 EU PAHs	SUM OF THE 15 AfPS PAHs
DUREX® 0	-	lamp black	<0.03	<1	<10
		forma en la la alc	-2.5	-2.5	.100
PUREX® LS 30 RP	N772 (clean)	furnace black	<2.5	<2.5	<100
PUREX [®] HS 45 RP	N550 (clean)	furnace black	<0.25	<1	<10
PUREX® HS 75 RP	close to N330 type	furnace black	<0.03	<2.5	<100
PUREX® HS 95 RP	N200 series	furnace black	<0.03	<2.5	<50
CORAX [®] N550 RP	N550	furnace black	<0.25	-	<20

¹ https://bfr.ble.de/kse/faces/resources/pdf/210-english.pdf

² https://www.umweltbundesamt.de/sites/default/files/medien/5620/dokumente/20160316_elastomerleitlinie.pdf

THE AMERICAS

EUROPE/ MIDDLE EAST/ AFRICA

ASIA PACIFIC

Orion Engineered Carbons LLC AMERICAS@orioncarbons.com

Orion Engineered Carbons GmbH

INCORPORATED IN LUXEMBURG

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