

# **REACH Compliance for Rubber Products**

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# The REACH Directive

The REACH Directive is: Regulation (EC) No 1907/2006 of The European Parliament dated 18<sup>th</sup> December 2006 concerning the **Registration, Evaluation, Authorization and Restriction of Chemicals** (REACH), establishing a European Chemicals Agency.

This requires all manufacturers or importers of chemicals or articles containing certain specified chemicals or substances into the EU (one tonne or more per annum) to register these substances with the European Chemicals Agency (ECHA) and comply with certain limits. These are listed in a number of Annexes to the Directive

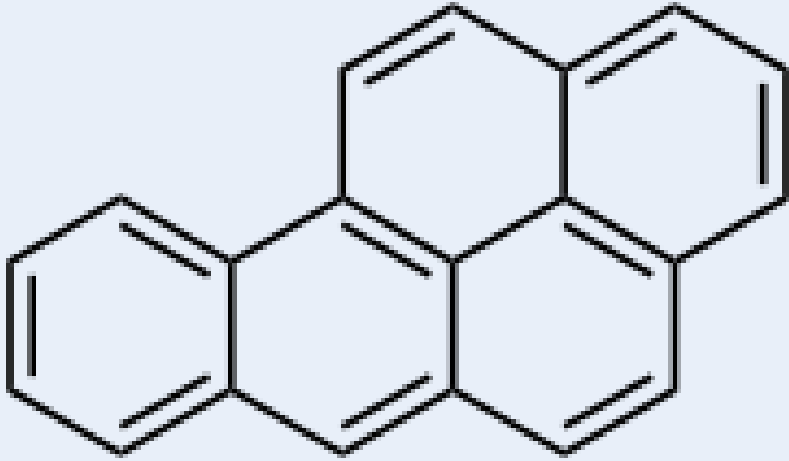
# Impact of REACH directive on rubber product and additive manufacturers / suppliers

## Polycyclic Aromatic Hydrocarbon Compounds (PACs)

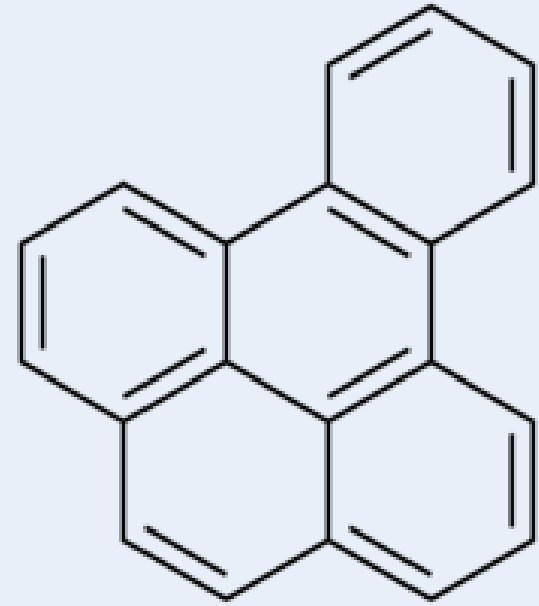
PACs are naturally-occurring substances formed whenever carbon containing compounds are burned at low temperatures in uncontrolled conditions.

PACs occur naturally in crude-oil and, being easily formed and stable, accumulate during the early stages of cracking and distillation of the oil.

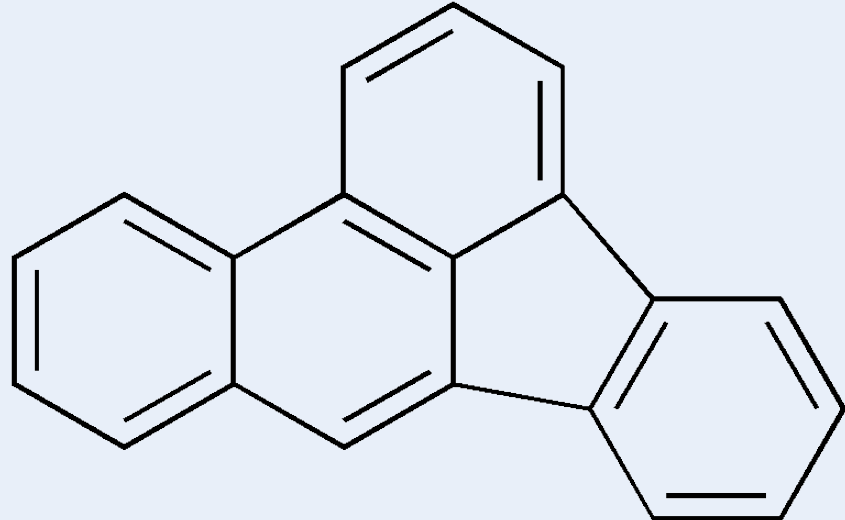
This process of partial oxidation results in a mixture of components with **linked unsaturated five and six-member carbon rings**, called Polycyclic Aromatic Hydrocarbons.



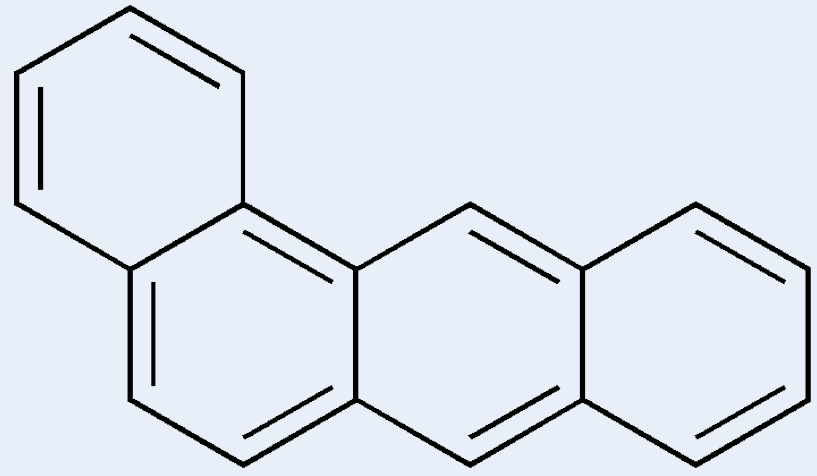
**Benzo [a] pyrene**



**Benzo [e] pyrene**



**Benzo [e] fluoranthene**



**Benzo [a] anthracene**

Some PACs have been shown to be carcinogenic to animals, it is reasonable to classify the mixtures of PAHs as likely to cause cancer in humans. Oils known to contain PAHs therefore require risk and safety labeling.

Rubber compounds require extender oils to facilitate processing. In the tyre tread compound oil is an essential component for the technical performance of the tyre, in particular for its road adherence (grip) and wear & endurance characteristics.

Highly aromatic oils ([DAE or Distillate aromatic extract oils](#)) have traditionally been used in tyres because of the excellent compatibility with natural and synthetic rubbers and also because of their lower cost vis-à-vis other oils.

In 2005 the European Commission adopted Directive 2 restricting the marketing and use of certain PACs in extender oils used in tyre production. Tyres produced after 1 January 2010 have to comply with the requirements of the Directive.

In the Directive a list is mentioned of eight different PACs which the European Union has classified as carcinogenic. One specific PAC, benzo(a)pyrene is proposed as a qualitative & quantitative marker for the presence of other PAHs.

Extender oils are not be used for the production of tyres if they contain more than 1.0 mg/kg B(a)P and / or more than 10 mg/kg of the sum of all listed Eight - PACs.

These limits are regarded as maintained, if the polycyclic aromatics extract is less than 3% by mass, as measured by standard method IP346. Finished rubber products including tyre & re-tread should not contain extender oils exceeding the limits indicated above.

These limits are regarded as maintained, if the vulcanized rubber compounds do not exceed the limit of 0.35% Bay hydrogen (protons) as measured by ISO 21461 (2012)

Other sources of PACs besides extender oils may be

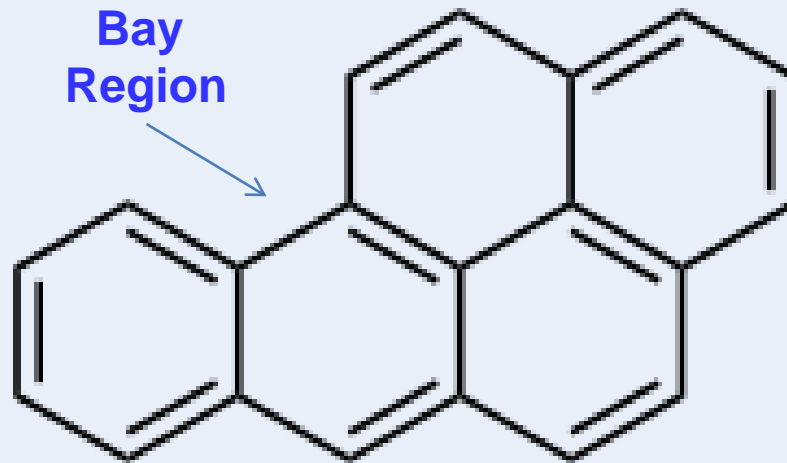
- Reclaimed Rubber
- Carbon Black
- Other additives like petro based waxes

## TEST FOR PACs in FINISHED RUBBER PRODUCTS

Analysis according to [ISO 21461: 2012-06\(E\)](#) vulcanized rubber article is cut into small pieces and is extracted using acetone for 8 hours in a soxhlet apparatus. After drying by a stream of nitrogen the dried extract is dissolved in methylene chloride.

The dried non-polar eluate of the solid phase extract is used for the NMR spectroscopy. With [NMR spectroscopy the percentage of Bay Region Hydrogen's \(%Hbay\)](#) is determined. This gives an indication of the aromaticity of the oil. REACH limits are regarded as maintained, if the %Hbay as measured by ISO 21461(2012) does not exceed the limit of 0.35%.





**Benzo [a] pyrene**

The NMR method provides a measure of polyaromaticity in a purified dry residue extracted from the rubber. The molecular structure of certain non-linear PAHs with 3 or more fused rings contains a characteristic 3-sided concave area at the periphery of the molecule. The hydrogen atoms in this area are called bay region hydrogen's. The level of these 'bay protons' is used as an indication of aromaticity for compliance with EC 552/2009 REACH (EC 1907/2006 Annex XVII amendment).

**GC-MS method (Gas Chromatography – Mass Spectrometry) to analyze individual PACs, as defined in Annex XVII of REACH Directive EC/1907/2006**

For tyres the limits are as follows:

< 1.0 mg / kg Benzo (a) pyrene

< 10 mg / kg in total of all the following PAHs

- 1) Benzo (a) pyrene
- 2) Benzo (e) pyrene
- 3) Benzo (a) anthracene
- 4) Chrysene
- 5) Benzo (b) fluoranthene
- 6) Benzo (j) fluoranthene
- 7) Benzo (k) fluoranthene
- 8) Dibenzo (a,h) anthracene

## TEST FOR PACs IN EXTENDER OILS

**Method IP346** - a weighed amount of oil (~ 4 g) is dissolved in cyclohexane, then the resulting solution is extracted twice in succession with dimethyl sulfoxide (DMSO). Saline solution is added to the combined DMSO extracts to precipitate the extracted compounds, which are then back-extracted into cyclohexane. The resulting solution is processed to remove water, then transferred to a tared flask and the cyclohexane is removed by rotary evaporation. The flask is weighed, and the weight of residue determined by subtraction of the tare weight from the final weight.

The resulting value is expressed as the **weight-percent of DMSO-extractables**. The standard requires that oils with PAC contents greater than or equal to 3% (w/w) be labeled as potentially carcinogenic.

## REACH - Substances of Very High Concern - Annex XIV

REACH Annex XIV has introduced controls on Substances of Very High Concern (SVHC) because of their potential harm to human health or the environment. From 1 Jun 2011, ECHA must be informed of the presence of SVHCs in a wide range of products if the total quantity used is > 1 tonne per annum and the SVHC is > 0.1% of the product by weight.

The first 'Candidate List' of SVHCs was published by ECHA in October 2008. **Currently there are 163 substances declared on the SVHC candidate list** published by ECHA as of 15<sup>th</sup> June 2015. This list is regularly updated as member states suggest more substances for inclusion.

## Some substances in the SVHC list

Fatty acids, C16-18, lead salts (e.g. Lead Distearate)

Alkanes, C<sub>10-13</sub>, chloro (Short Chain Chlorinated Paraffin's)

Bis (2-ethylhexyl)phthalate (DEHP or DOP)

Dibutyl phthalate (DBP) / Dihexyl phthalate / Dipentyl phthalate (DPP)

2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (UV-328)

2-benzotriazol-2-yl-4,6-di-tert-butylphenol (UV-320)

Heavy metals - cadmium, lead, cobalt & strontium and their salts

Cadmium fluoride / sulphate / chloride / oxide

Lead oxide / lead tetroxide / Diboron trioxide / Cobalt dichloride

Strontium chromate / Lead di(acetate) / Dibutyltin dichloride (DBTC)

4-methyl-m-phenylenediamine (toluene-2,4-diamine)

Biphenyl-4-ylamine / Diethyl sulphate / Dimethyl sulphate

## WHAT SHOULD YOU DO AT YOUR END FOR REACH COMPLIANCE

- 1) Closely scrutinize the TDS and MSDS of all ingredients and study whether any of these contain PACs and SVHCs and at what levels
- 2) Request suppliers to provide detail material test reports
- 3) Request suppliers for REACH compliance documentation
- 4) Prepare a [detailed chemical ingredients inventory](#)
- 5) If the chemical ingredients inventory points to presence of PACs and SVHCs at unacceptable levels – use alternative raw materials.
- 6) Test product sample at accredited third party laboratory
- 7) Prepare Technical Dossier for REACH compliance
- 8) Product sample testing / prepare report / communicate to all stakeholders non-presence of any SVHC in the product at above 1000 ppm (0.1% w/w) level.

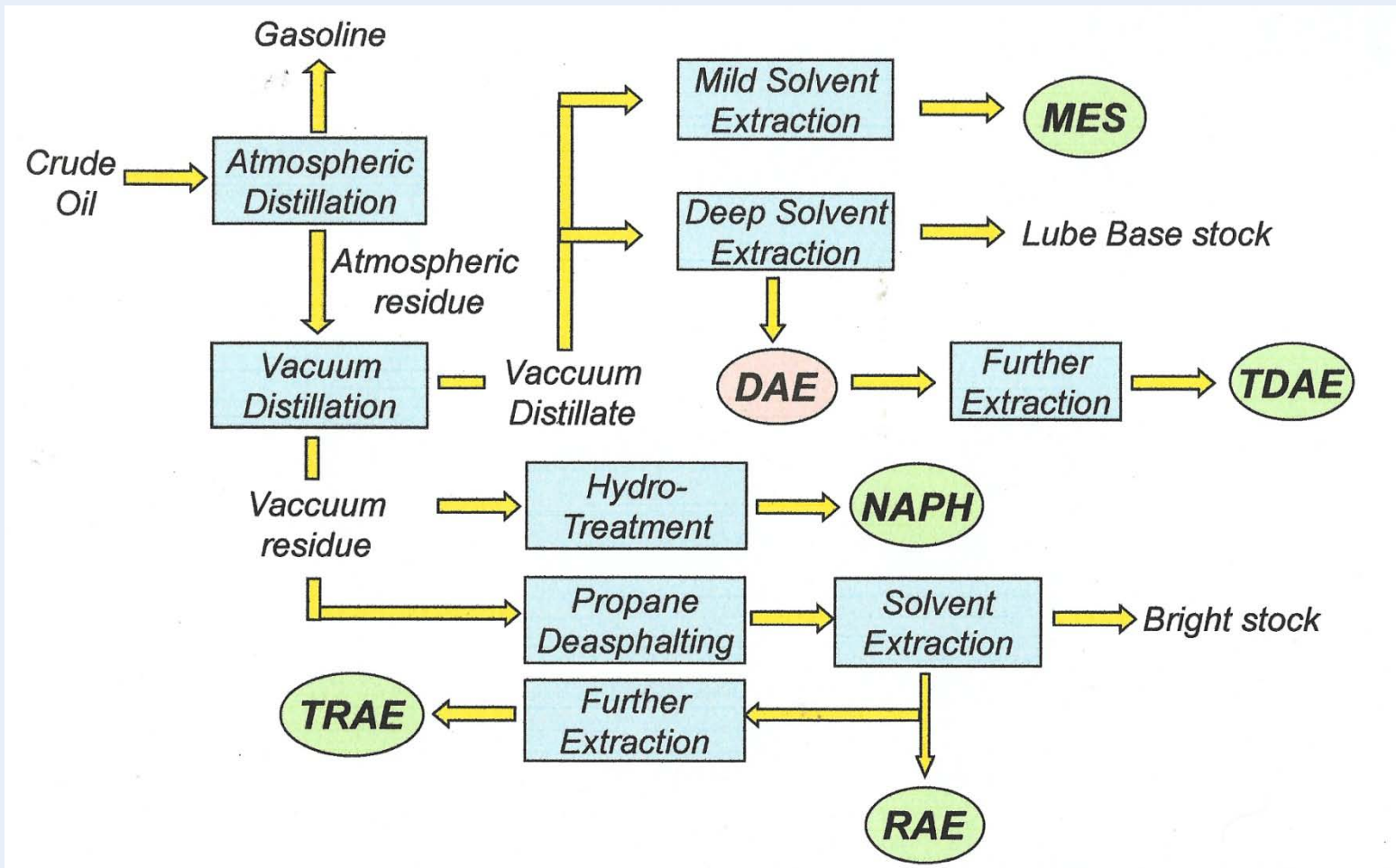
## Individual ingredients

**Extender Oils** - use appropriate alternative oils which comply with REACH directives (PAC / DMSO extractibles < 3% by wt. and sum of 8 PACs < 10 mg/kg) instead of traditional distillate aromatic extract (DAE) extender oils. These alternatives can be

- a) **Treated Residual Aromatic Extract (TRAE)** Oils like  
HP Elasto Supreme, Shell Flavex 595, Total Palaxolen 50
- b) **Treated Distillate Aromatic Extract (TDAE)** like  
Total – Palaxolene TD346
- a) **Mild Extraction Solvate (MES)** like  
Total Palaxolene MS 132, Gandhar - Divyol low PCA 360
- a) **Napthenic Oils** - miscibility, loading, properties?

Extensive research activity is necessary to make sure that the required compound properties and product performance is achieved with the new extender oil used and dosage.

# Refining Process Flowchart for New Generation Oils



Ref: European tire industry compliance with REACH, Goodyear Dunlop Tires Europe, June 2014.



## Individual ingredients (cont.)

**Plasticizers** – do not use chlorinated paraffin's & phthalates (sulfonated fatty acid esters, vegetable oil based, alkyl phosphates etc.)

**Reclaimed Rubber** – NMR spectroscopy (%Hbay < 0.35%)

**Carbon black** – sum of 8 PACs < 10 mg / kg (by GC-MS)

**Sulphur, Accelerators, Activators** - heavy metal & salts (SVHCs < 0.1%)

**UVA** (if used) - should not be of bezotriazole class

**Anti-oxidants & Anti-ozonants** - SVHCs < 0.1%

**Silica / Clay / CaCO<sub>3</sub>** – heavy metal & salts (SVHCs < 0.1%)

**Colour Pigment** – should not contain lead & heavy metals

Please note the author does not intend to promote any product or trade name in this presentation

## Testing of SVHC in rubber products

- > **Inorganic Compounds** - acid digestion / aqueous extraction followed by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry)
- > **Hexavalent Chromium** (Cr6+) by UV – Vis Spectroscopy
- > **Organic Compounds** (semi-volatile & non-volatile) – solvent extraction followed by GC - ECD or HPLC - DAD or LC - MS / MS
- > **Organic Compounds** (volatile) by Gas Chromatography – Mass spectrometry (GC-MS)
- > **SCCP** – MS in ECNI (Electron Capture Neg. Ionization) mode

# THANK YOU

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