Worauf es jetzt ankommt?

U. Giese

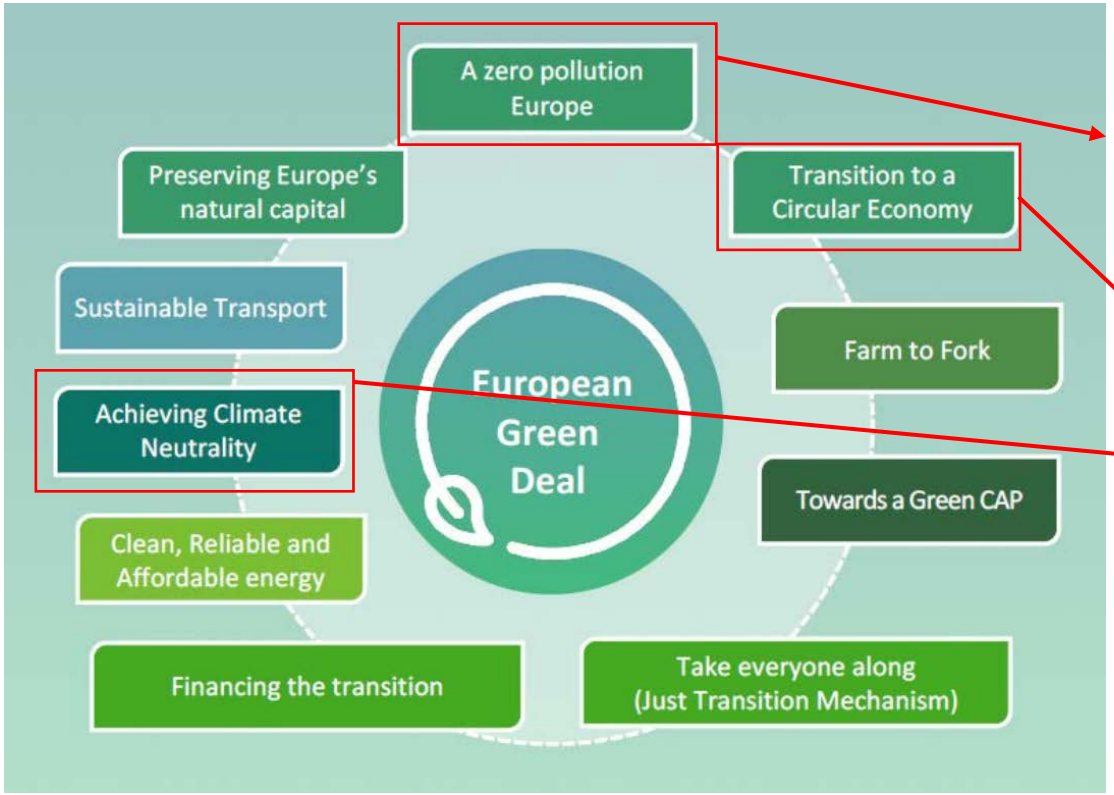
Tag der Kautschukindustrie

Berlin

23. April 2024

Deutsches Institut für Kautschuktechnologie e.V.
DIK- Prüfgesellschaft mbH
Leibniz Universität Hannover

Green deal – main elements



- Zero pollution action plan for water, air and soil
- Revision of measures to address pollution from large industrial installations
- **Chemicals strategy for sustainability – regulatory measures**

- **Circular economy**
- **Climate neutral and circular poducts**
- **Recycling**

Published:
EU-The European Green Deal, Brussels, 2019

Chemicals strategy for sustainability – regulatory measures

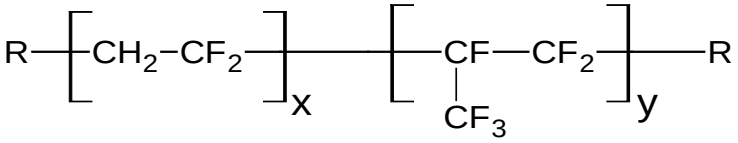
Part of Green Deal: Commission adopts new Chemicals strategy towards a toxic-free environment

Important raw materials for rubber industry under special concern and discussion:

- **Fluoro rubbers (PFAS)**
- Diphenylguanidine (DPG)
- Cobalt (Cobalt-naphthenate-adhesion systems)
- **N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylene diamine (6PPD)**
- Resorcin-formaldhyde phenolic resins (RFK-adhesion systems)
- Polycyclic aromatic components – ELT-materials, rubber crumb as raw material?
- (Bisphenol AF)

Situation - Fluorinated polymers (FKM)

Properties - Use:



- Heat stability up to 230 °C
- High resistance against oil
- High resistance against fuel and hydraulic liquids
- Stable against acids (aqueous systems)
- Ozon- and weather resistancee
- Low permeability against gases
- Not stable against prim. and sec. aminea
- ⇒ Dehydrofluorinatiion
- Not stable in aqueous with high pH-value

https://www.google.de/search?q=Motor+Daimler+E-+Klasse&client

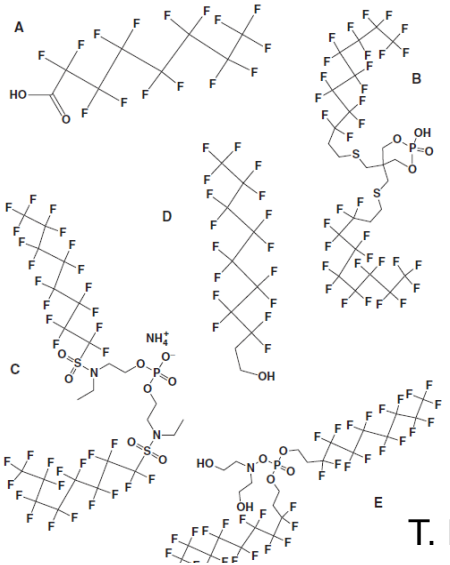
Fuel systems:

- Tank/sealings/tubes
- Motor lubrication
- Exhaust systems
- Turbo charger hoses
- Aviation
- Electric mobiltiy
- Medical applications

Source: U. Giese/DIK

Per Fluoro Alkyl Substances (PFAS)

PAFS are aliphatic organic components, where minimum at one C-atom the hydrogene atoms at the carbon backbone is completely substituted by fluoro atoms
(Organisation for Economic Co-operation and Development (OECD))



T. H. Begely et al

Food Additives and Contaminants, October 2005; 22(10): 1023–1031

EUROPEAN FOOD SAFETY AUTHORITY

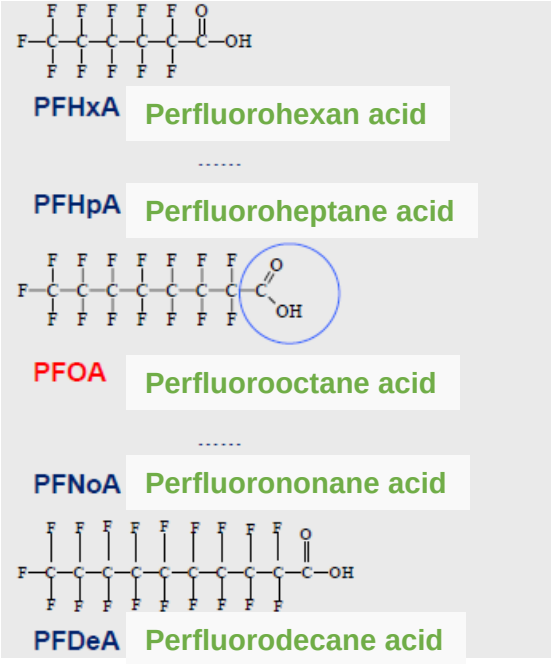
In 2020 for PFAS in food efsa had published: Substances, or PFAS, that accumulate in the body: **The threshold – a group tolerable weekly intake (TWI) of 4.4 ng per kg body weight per week** – is part of scientific opinion on the risk to human health from the presence substance in food.

PFAS Restriction – Submitted to ECHA

- Public consultation on the PFAS restriction dossier submitted by 5 EU member states
- Proposed restriction envisages a total ban of PFAS in the EU after 2038/20239
- Chemical scope of the restriction proposal is extremely broad, more than 10000 substances are under concern
- **No distinction between polymers (PTFE, FKM) and low molecular substances**
- Temporary derogations are proposed for very specific applications, (Requirement of reporting obligations and management plans)

Application and properties of PFAS

- Tensid and precursor for other perfluorinated materials
- Additive in synthesis of fluoro containing polymers
- Surface protection of textiles, leather, paper etc.
- In cleaning chemicals, lubricants, paints



Selected properties

- High stability of C-F-bonding
- Solubility in water: 3400 - 9500 mg/L
- Bp.: 188 °C (PFOA)
- pH-value: 2.6 at 20 °C (PFOA)
- Partition coeff.$_{Octanol/water}$: 2.69 at pH7, 25°C (PFOA)
- Biodegradation: > years (persistent)

Intended threshold for materials and articles: 25 ppb
For C9 - C14 PFAS and salts (valid in 2025 ??)

Umweltbundesamt, Dr. N. Theobald et al., Forschungsbericht 20222213, 10/2007

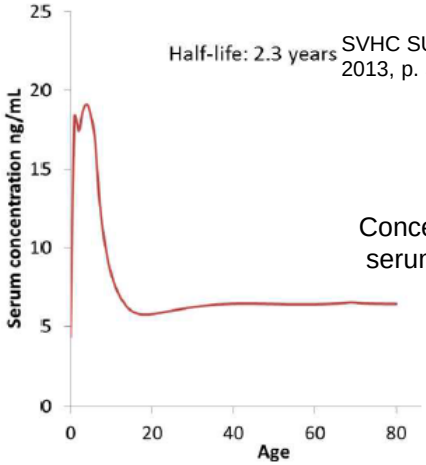
SVHC SUPPORT DOCUMENT – PFO, 2013

Toxicity and classification of PFOA and PFAs

Pentadecafluorooctanoic acid (PFOA)
CAS no.: 335-67-1
Mol. formula: C8HF15O2

- Substance may damage the unborn child,
- Causes damage to organs
- Harmful if swallowed,
- Causes serious eye damage, is harmful if inhaled,
- Suspected of causing cancer

CLP-directive: Toxic for reproduction, classified as PBT substance



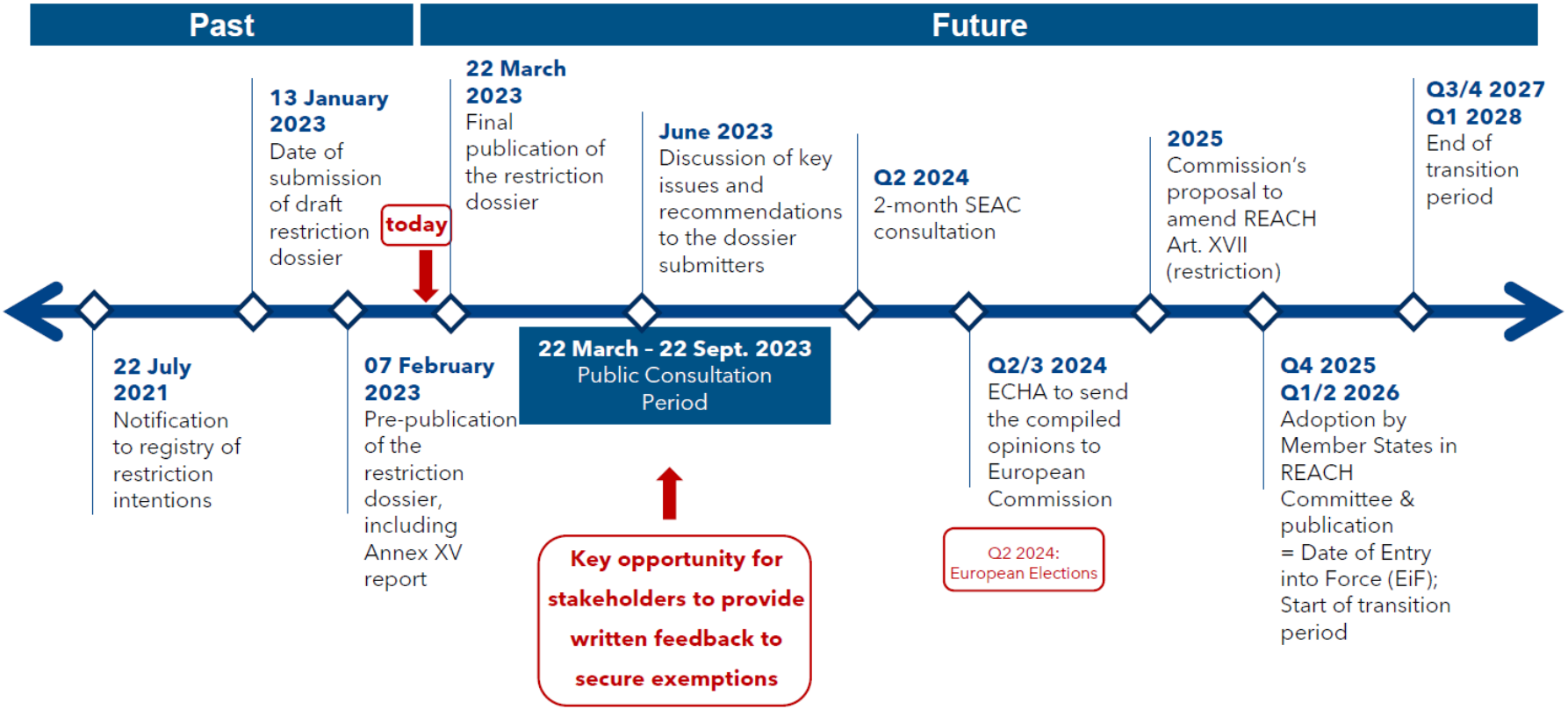
Concentration in human serum (model)

Since 2013 in SVHC candidate list

25 ppb = 0,025 mg/kg in mixtures/preparations
or 1 mg/kg for sum of PFA s and salts.
In GADSL: declaration limit 0.1 %

No. 68 Annex XVII, REACH (in force for C_8, C_9, C_{10}, in 2021):
Restriction intended for C_6,C_9-C_{14}-PFCA, their salts and C_9-C_{14}-PFCA related components.

PFAS REACH Restriction – indicative time line



RAC: Committee for Risk Assessment
SEAC: Committee for Socio-Economic Analysis

PFAS Restriction – Actual Status

Status March 2024:

ECHA receives more than 5600 comments on PFAS restriction proposal up to 26 September 2023 – Topics:

- Restriction on the manufacture, placing on the market and use of PFAS
- Restrictions process
- Risk Assessment
- Socio-Economic Analysis

Scientific committees of RAC, ECHA and SEAC are working on the Comments

Revision of the originally submitted restriction report is expected

RAC: Committee for Risk Assessment
SEAC: Committee for Socio-Economic Analysis

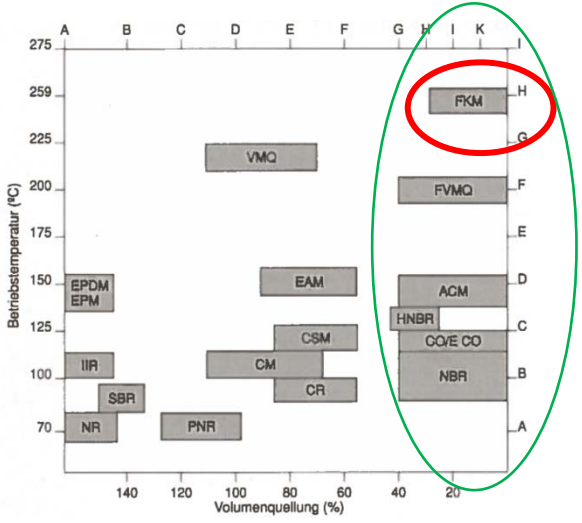
PFAS- What can be done -measures

Measures at polymer industry:

- Withdraw from market
- Changing polymerization process
- Cleaned FKM types

Consequences:

- Reduced portfolio of products
- Polymer quality??
- New compounding
- New approval by customer/OEMs
- Use of alternative polymers
  (list of proposed materials is available at wdk)



Kleemann, Gupta Verlag

- Distinction between polymers and low molecular substances from toxicity effects is necessary
- Regulation with derogations for selected application of fluoro polymers
- Threshold limit values in materials ???; Biological availability in contact media ?
- Validated analytical methods

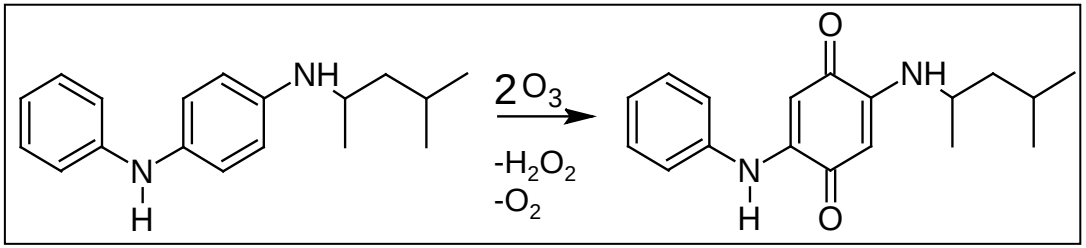
Situation: Antioxidants/Antiozonants

First release: 3 December 2020

Cite as: Z. Tian *et al.*, *Science* 10.1126/science.abd6951 (2020).

A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon

Zhenyu Tian[1,2], Haoqi Zhao[3], Katherine T. Peter[1,2], Melissa Gonzalez[1,2], Jill Wetzel[4], Christopher Wu[1,2], Ximin Hu[3], Jasmine Prat[4], Emma Mudrock[4], Rachel Hettinger[1,2], Allan E. Cortina[1,2], Rajshree Ghosh Biswas[5], Flávio Vinicius Crizóstomo Kock[5], Ronald Soong[5], Amy Jenne[5], Bowen Du[6], Fan Hou[3], Huan He[3], Rachel Lundeen[1,2], Alicia Gilbreath[7], Rebecca Sutton[7], Nathaniel L. Scholz[8], Jay W. Davis[9], Michael C. Dodd[3], Andre Simpson[5], Jenifer K. McIntyre[4], Edward P. Kolodziej[1,2,3*]



6PPD

Source: Tian et al. , *Science* 371 (2021)

6PPD-quinone

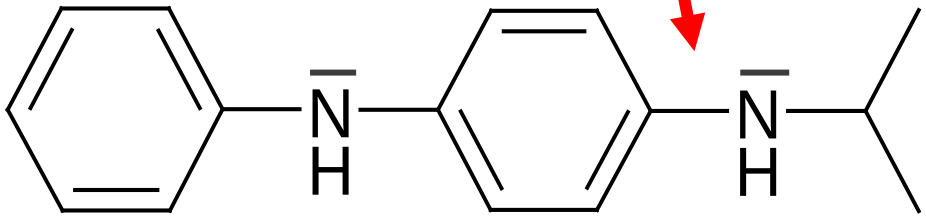
- High toxicity against salmons
- Identified in roadway runoff and storm water
- Impacted creeks at USA West Coast: conc. 0.3 -19 µg/l
- Authors: Origin mainly from TWP/TRWP

US-market (California): Tires containing 6PPD designated as Priority Products by Department of Toxic Substances Control (10/2023)

Mechanism of N-Antioxidants/Antiozonants

Asym. subst.
Aryl-alkyl-N-Atom:
Higher e$^-$-density

High effectiveness as **antiozonant**



Heat of H-radical formation for 6PPD, IPPD:

aryl-alkyl	149.4 kJ/mol
aryl-aryl	141.5 kJ/mol

Sym. subst.
Aryl-aryl-N-Atom:
Easy H-abstraction

Component	Consumption t/a in tires	Consumption t/a in tire wear
6PPD	> 3500	>350
IPPD	>460	>46

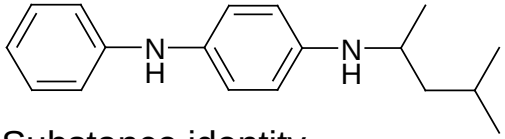
Source: WDK, industry (W. Baumann, M. Ismeier, 1998), data valid for Germany

High effectiveness as **antioxidant**

Z. Cibulkova, E. Klein. V. Lukes
Petroleum & Coal 46 (2), 42-48, 2004

Manufactures and imported in European Economic Area, at ≥ 10 000 to < 100 000 tonnes per annum. (ECHA 2024)

Toxicological aspects of p-PPs



Substance identity
EC / List no.: 212-344-0
CAS no.: 793-24-8
Mol. formula: $C_{18}H_{24}N_2$
H302, H317, H360FD
H400, Long time (chronic) H41

Component	LD_{50} [mg/kg weight] (oral, rat)	Skin and eye irritation	Skin sensitation
6PPD	3580	-	+
IPPD	900	-	+

Source: A.R. Nutt, Toxic Hazards of Rubber Chemicals, 1984

Discussion:
CLP-regulatory - article 12 :
rubber mixtures cont. 6PPD
classified as Repro 1B H360

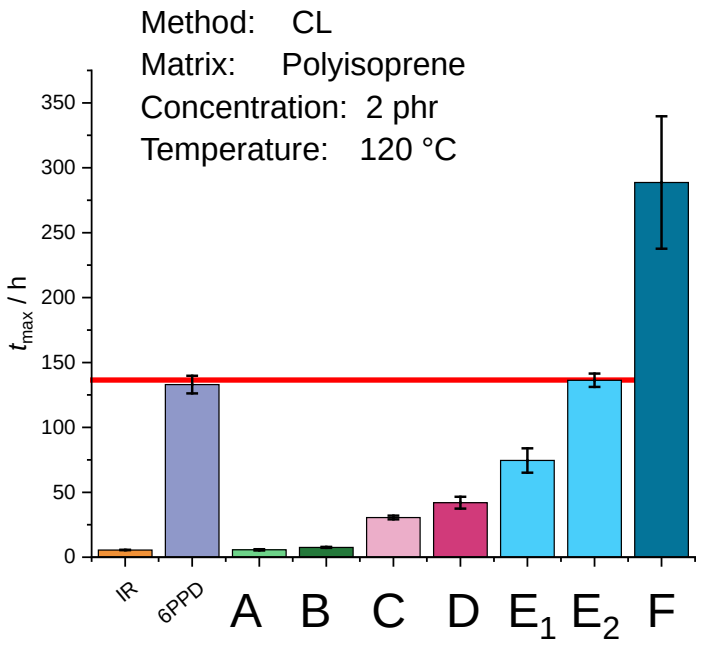
- **On SVHC-list, pre registration REACH**
- **Restriction ??**

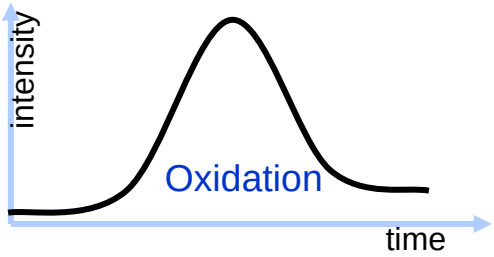
6PPD, IPPD, DPPD

- May cause sensitation by skin contact,
- High allergic potential
- Very toxic to aquatic system
- Harmful to aquatic system
- AGW in Germany - 6 PPD: 2 mg/m^3 (TRGS 900)

Substitutes for 6PPD - CL-results

CL: Time of intensity maxima t_{max}





Positive Results
from wdk/DIK-multi client project
for Antioxidant alternatives

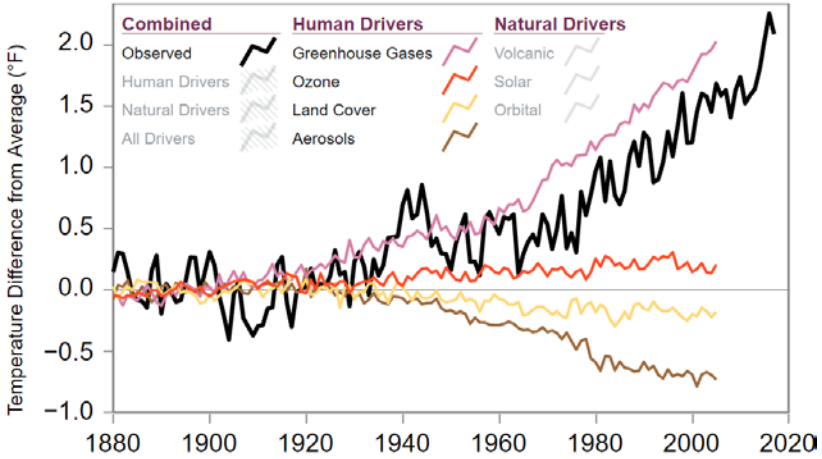
Substitute for Antiozonant effect
is on market shortly
(DIK-multi client project)

N. Borgartz, DIK 2023

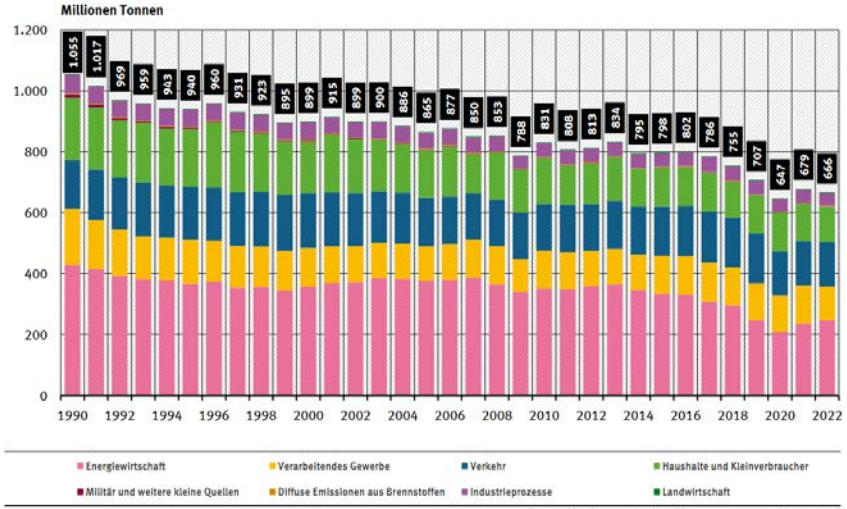
Climate change – CO_2 – footprint

- Human activities alter factors (radiative forcings) that affect the earth‘s climate

- Radiative forcings include:
  - Changes in greenhouse gases
  - Aerosols
  - Land-use and land cover changes



Source: Nca2018.globalchange.gov/chapter/2/



Source: https://www.umweltbundesamt.de/daten/umweltindikatoren/indikator-emission-von-treibhausgasen#wie-ist-die-entwicklung-zu-bewerten

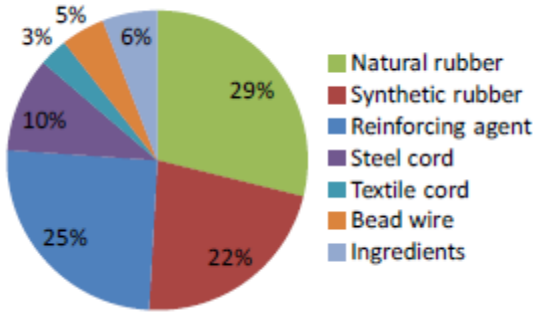
Reduction of GHG emissions 1990 - 2022 :

- COVID-19 pandemic
- Reduction of emissions in transport and energy sectors
- Carbon pricing
- Expansion of renewable energy resources
- Phasing out of coal

How is the Rubber Industry affected?

- ≈ 24 % (2020) of the global GHG emissions can be attributed to the transport sector

  Automobile manufacturers have committed to Paris Climate Agreement:
  - Transparency in the supply chain is a necessity
  - CO_2-neutral components & raw materials from suppliers play an important role
  - VW plans to reduce GHG emissions from passenger cars by 30 % by 2030 compared to 2018
  - Audi also plans to be CO_2 neutral in 2050 while Daimler aims for a CO_2-neutral supply chain by 2030
- E-mobility shifts GHG emissions from the use phase to the production phase & supply chain (Electric cars are only as clean as the electricity



Materials in tires (Japan)

M. Kunioka et al. , Polymers 2014, 6, 423-442

- **Suppliers must take measures to reduce GHG and identify emission sources along their own supply chain → Reduction of fossil components and of energy**

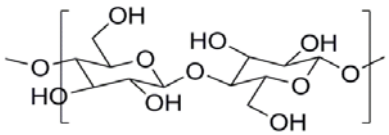
Sources: https://www.volkswagenag.com/en/news/stories/2019/02/clean-mobility-starts-with-suppliers.html# https://www.iea.org/reports/tracking-transport-2020 https://www.volkswagenag.com/en/news/stories/2020/10/29-climate-measures-of-the-volkswagen-group.html https://www.daimler.com/sustainability/climate/global-mercedes-benz-supply-chain-is-becoming-co2-neutral.html

Selected topics for CO_2 -product footprint optimization

Renewable materials as substitutes

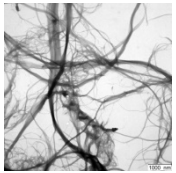
Polymers:
Biochem. synthesis (enzyms), renewable resources, Monomers („Green EPDM“), **NR**

Fillers:
cellulose, lignin, rice husk silica, etc.



repeating unit of cellulose

1.4-β-D-glucose



DIK, I.Weilert

Nanofibrillated cellulose

Additives
Plasticizers (oils)
Antioxidants, etc.

Compounding/Processing

High energy process
"Mixing" , “Vulcanization“

- Latex/masterbatch technology
- Tandem mixing up to 35 % CO_2 reduction

H. Keuter, I. Fynn, U. Giese, Kautsch. Gummi Kunststoffe 4/2022, S. 34 – 46

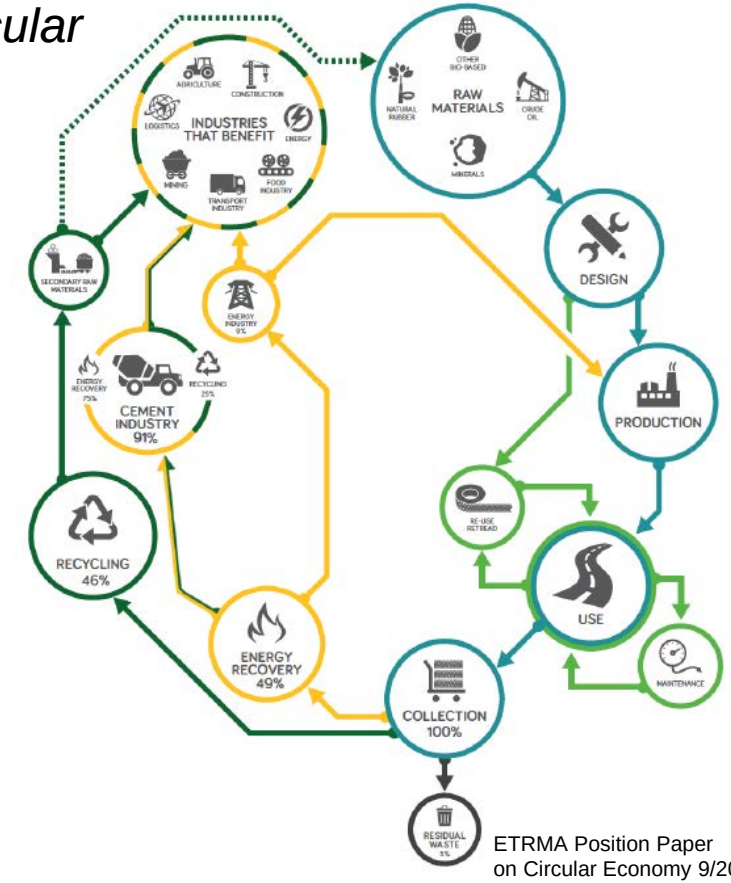
Crosslinking systems, Addition mechanisms (lower Temperatures)

Circular economy act - "Kreislaufwirtschaftsgesetz"

Section 1: *"The purpose of the Act is to promote circular economy in order to conserve natural resources and to ensure the protection of human health and the environment in the generation and management of waste."*

Directive 2008/98/EC - Waste hierarchy:

1. Prevention (e. g. Increase of life time/use)
2. Re-use (e.g. Retreading of tires)
3. Recycling
4. Use for other purposes (e. g. energy)
5. Removal/Disposal



ETRMA Position Paper on Circular Economy 9/2015

Waste Rubber - Recycling

Waste rubber/used tires

582,000 t tires in 2012, Germany
> 3.9 Mill. t/a EU
>13.5 Mill. t/a world wide
(data bases on stat. from 2000 and ETRMA/2016)

Advertisement from 1909
„Gummi-Lohnmüllerei“
for re-plastification or
producing reclaim

Requirements from the EU Directives:

- 2000/53/EC on End of-Life Vehicles for rubber materials

80 %	→	material recycling
5 %	→	for energy
15%	→	landfill

- Landfill Directive 1919/31/EC banned land filling since 2006

→ Producer Responsibility on tire manufacturers

www.tyretradenews.co.uk/news/europe-94-of-all-used-tyres-collected-and-treated-in-2016

Traceability and fate of ELT

How can traceability in the case of used tires help us ?

In 2019, approximately 94% of all ELTs in Europe were collected and treated by material recycling and thermal recycling,
The whereabouts of approximately 5% of ELTs are unclear.

Existing data of 100% on the international market are questionable !

Tracking necessary to counteract uncontrollable utilization!
Consequences: Cheap raw materials from ELT, distortion of competition with respect to countries in which high acceptance fees have to be paid for ELT

ETRMA, "www.etrma.org," 11 3 2021. [Online]. Available: https://www.etrma.org/wp-content/uploads/2021/05/20210511_ETRMA_PRESS-RELEASE_ELT-2019.pdf. [Accessed 21 7 2021].

Retreading - Ecological benefits

Advantages of retreading:

- Longer service life of the tire
- Material savings of up to 70 % (carcass, steel, textile)

Parameter factor
Energy 2.3
Air 1.85
Water 25
Resources 1.4
Atmospher. Emissions 2.2
Waste water load 139

Significantly higher environmental impact for new tire production!

Disadvantage: Minor increase of the rolling resistance ?

Renewal of tread

E. Mugnier and O. Baboulet, "The Socio-Economic Impact of Truck Tire Retreading in Europe," Ernst & Young, 2016.

D. Reichenbach and R. Stark, "Product life cycle assessment of a passenger car tire," Continental AG, 1999.

E. Weidner, M. Hiebel, J. Bertling, J. Nühlen, H. Pflaum, A. Somborn-Schult, M. Franke, K. Reh and S. Kroop, Fraunhofer Institute for Environmental, Safety and Energy Technology Umsicht, 2017

Retreading

Makes retreading of passenger car and commercial vehicle tires economic and ecological sense and should be promoted in the interests of the circular economy?

According to 2001/507/EC, there are uniform rules for retreading:

- Truck tires up to 3 x retreadable; passenger car tires 1 x retreadable
- Carcass not older than 7 years

Market Situation:

- Share of retreaded truck tires in the EU5: 37% in 2010, 30% in 2015
- Share of replacement demand: 15 % in 2008, 7 % in 2012
- Loss of 3200 jobs in EU 5 states
- Reason probably lies in cheap "low end" tires from Asia
- "Low-end" tires are not retreadable

Conclusion: retreading creates twice as much social value
like a complete replacement with non-retreadable "low end" tires

S. Hoyer, 2020.

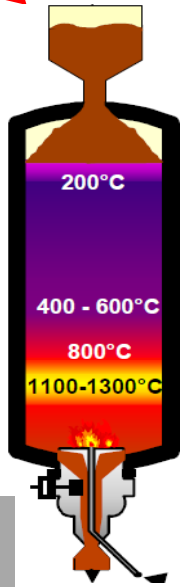
E. Mugnier and O. Baboulet, " Ernst & Young, 2016

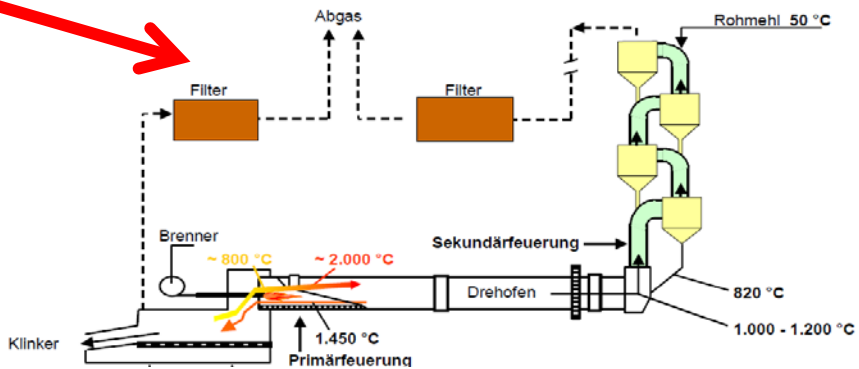
E. Weidner, M. Hiebel, J. Bertling, J. Nühlen, H. Pflaum, A. Somborn-Schult, M. Franke, K. Reh and S. Kroop, Fraunhofer Institute for Environmental, Safety and Energy Technology Umsicht, 2017

Thermal recycling of used rubbers

Aerobe
Thermal processes

Pyrolysis
500 – 900 °C





Cement kiln

- Gases,
- oils
- ash
- Carbon black (r-CB)
- „Feed stock“
  for CB produciton

CO/H_2
Methanol

Residue/ash

Energy
appr. up to 39 MJ/kg
(crude oil 42 MJ/kg)

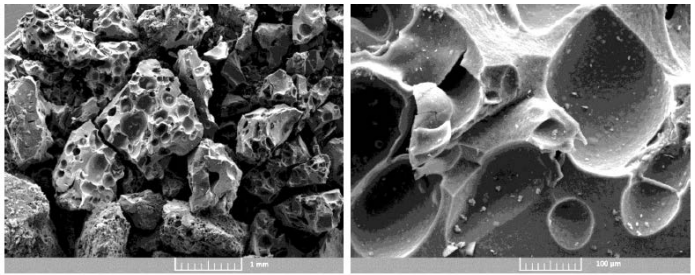
D. Lechner et al.: Makromolekulare Chemie, Bikner Verlag

Blackcycle und Pyrum-Project

New developments in pyrolysis/pilot plants:
Company "Pyrum“

M. Pohl und Q. Peter, „Evaluation neuer Entwicklungen bei alternativen thermischen Abfallbehandelungsanlagen mit Schwerpunkt Verölungsverfahren,“ Umweltbundesamt, 2018

Materials: ELT, all rubber waste, plastics
Quality requirements on feed stock:
Particle size: 1-14 mm
Energy content: 28 -36 MJ/kg
Reaction temp.: 600 - 700 °C for 2.5 - 3.5 h
Products: Gas (10-20 %
Pyrolysis oil: 30 - 50 %
Coke: 40 - 55 %

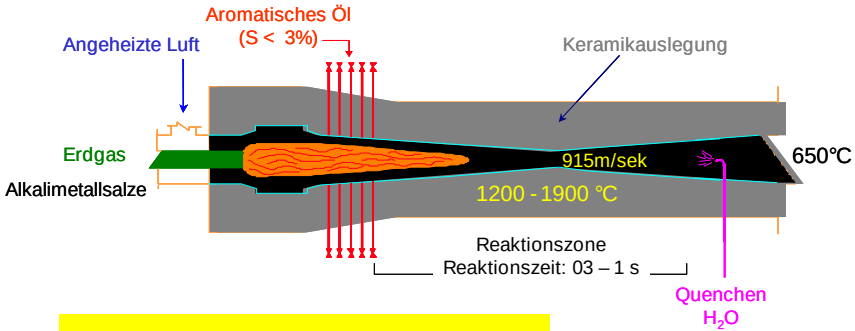


Quelle: Pyrum Innovations AG [14]

SEM-micrograph of the coke from a Tire –pyrolyses - Pyrum Innovation AG

BET: ca. 55 m^2/g

Carbon black production from rubbers
Feedstock: Pyrolyses oil fractions



Result: High CB-quality like N234, N347

H. Westenberg et al., KGK 2021

Material Recycling „ELT“ - Products

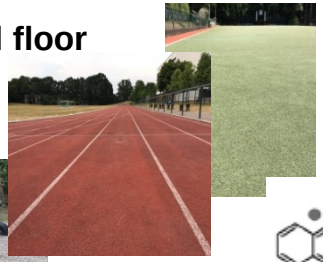
Granules/
Rubber powder

Asphalt additive

Devulcanization
from single components
or rubber powder

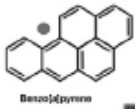
- Selected types of tires
- Original products

- **"Infill"**
- **Artificial floor**



Construction industry
- Floors
- Damping material

Discussion about
toxic characteristics



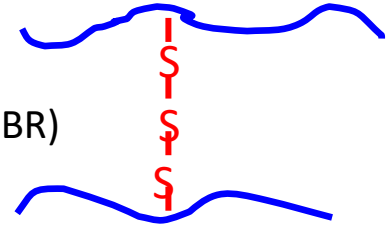
Audited risk assessments
Do not show any conspicuous risk potentials

A. Diekmann, U. Giese*, I. Schaumann,
Polycyclic aromatic hydrocarbons in
consumer goods made from recycled rubber material:
A review, Chemosphere 220 (2019) 1163-1178.

ELT-Material is raw material!

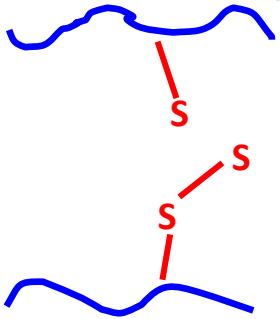
Material recycling - devulcanization

Vulcanizates
(NR, BR, EPDM, SBR)

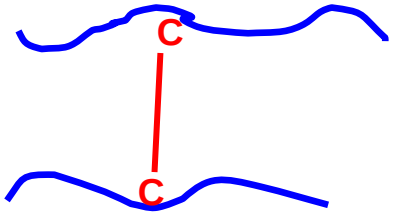


Thermal/Shear/chemicals

Cleavage



Bond	$E_{Diss.}$ kJ/mol
S-S	270
C-S	272
C-Cl	327
C-C	346
C-O	358
C-H	470
C-F	485



Typical for GRG

Vulcanization using peroxide /bisphenols/ catalysts etc., **stable networks**, (EPDM, FKM, HNBR, Q)

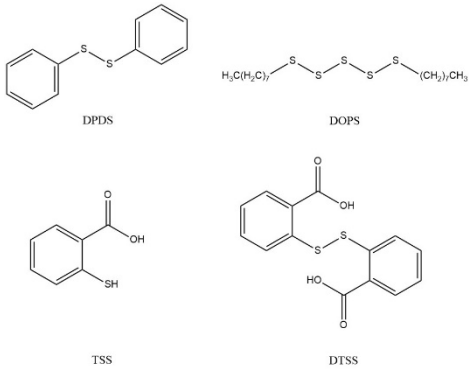
Selective cleavage
of bonds difficult/impossible

Devulcanization NR – SEV, -EV, - CV -systems

- DPDS and DOPS show the best results for NR above 80 % for all systems
- EV system has the most monosulfidic crosslinks which are more stable than disulfidic and polysulfidic crosslinks

→hardest to devulcanize

- 98% reduction in crosslink density for DOPS and SEV system



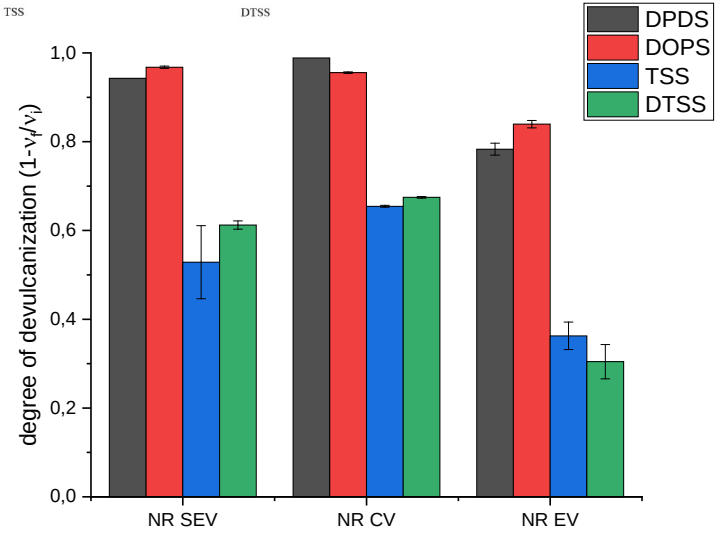
devulcanization conditions:

28 mmol/100 g polymer

1h, 160 °C, N_2 heated cabinet

- SBR-Silica-Silane System more stable (devulc degree: < 60 %)

bond type	bond energy [kJ/mol]
C-C	335
C-S-C	310
C-S-S-C	226
C-Sx-C	142



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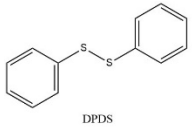
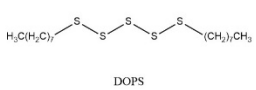
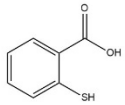
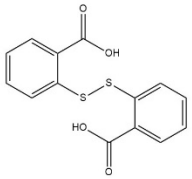
Devulcanization SBR– SEV, -EV, -CV-systems

- DPDS has highest degree of devulcanization of the tested DAs
- The SBR CV sample is dominated by post curing
- EV system has the most monosulfidic crosslinks →more stable than disulfidic and polysulfidic crosslinks (see table)









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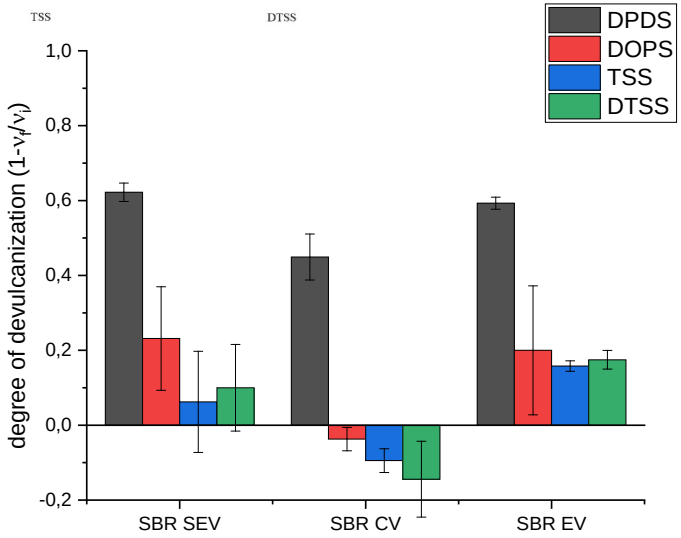

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Summary – What should be done ?

- Green Deal – Chemical strategy/REACH, climate neutral products, energy saving

- Consequences for rubber industry: Substitutes for raw materials,
  renewable resources for monomers, changing of processes,
  evaluation of products – emission behavior

- Regulation with derogations for selected application of fluoro polymers ??
  Development of standard method for analyses

- 6PPD: Substitutes possible, Disadvantage: price and product quality

- Circular economy: - Recycling is to be optimized
  - Products/materials have to be developed for recycling!
  - ELT Materials should be classified as raw material !

Energy saving, searching and developing of substitutes and monomers are main topics!

www.DIKautschuk.de

- Competence in rubber
- Tailor made solutions
- Confidential
- Accreditation: ISO/DIN 17025
- Staff: 80 colleagues
- Non profit organization

Thank you for your attention