Fluoropolymer Production and the use of Processing Aids

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EU Workshop – Outline of presentation

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- What is PFOA and what is it used for
- PFOA use in FP manufacturing
- EPA program and OECD hazard assessment
- Process description of use in FP supply chain
- Learnings from risk assessment
  - C&L industry vs. ECB
  - scope of exposure assessment including all precursors
- Alternatives to PFOA in FP manufacturing

Fluoro-Organics – Fluorinated Polymers - Fluoropolymers - Fluorochemicals

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different chemically & in their uses

- **Fluoro-Organics**
- includes ***Fluorotelomers*** & ***ECF chemicals***
- "short" fluorine chains attached to organic polymer backbones $[F(CF_2)_n-]$ $n \geq 4$
- surface modification & protection
- surfactants
- water & oil repellency

- **Fluoropolymers**
- high MW (10^7)polymers
- PTFE & Melt Copolymers
- fluorinated "backbone"
- chemical resistance
- cookware, CPI linings, aerospace, automotive, apparel, construction, etc

- **Fluorochemicals**
- small molecules
- 1 - 8 carbons
- refrigerants
- cleaning solvents
- blowing agents
- CFC alternatives (e.g. HFC's)

Fluoropolymers: 3M / Dyneon, Daikin, Asahi Glass, DuPont, Arkema, Solvay-Solexis
Fluorotelomers: Asahi Glass, Clariant, Daikin, DuPont and others

What is PFOA?

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- PFOA is a surfactant used as a processing aid to produce long chain fluoropolymer high-performance materials (also called APFO, C-8).
- PFOA is not used to make a different family of compounds, called fluorotelomers. However, it is found at very low trace levels in some fluorotelomer products as a byproduct of their synthesis.
- PFOA is an unintended byproduct of manufacture of POSF-based products (Electrochemical Fluorination—ECF)
- PFOA is a persistent chemical present at very low levels in the environment and the blood of the general population.

PFOA Overview

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- PFOA is persistent in the environment and has been detected at very low levels (average 5 ppb) in the blood of the general population.
  - Industry believes the weight of evidence indicates no health risk to general public
  - Recent studies show blood levels dropping
- In some locations, PFOA has been detected at very low levels in ground and drinking water (current Limit of Detection is ~3 ppt)
- PFOA has been extensively studied (animal toxicology, human epidemiology, environmental)
- Human exposure routes are likely complex (emissions, products, local, global)

Fluorinated Polymers – Fluoropolymers

different chemically & in their uses

Fluorinated telomers

- **“short” fluorinated chains**
- attached to organic polymer backbones $[F(CF_2)_n-]$ n = 4+
- ***surface modification & protection***
- water & oil repellency; soil resistance
- ***Asahi Glass, Clariant, Daikin, DuPont, Nano-tex, Mitsubishi, etc.***

- **Textiles**
- **Home Furnishings**
- **Paper**

Fluoropolymers

- **high molecular weight polymers**
- PTFE & Melt Copolymers
- fluorinated “backbone”
- Material properites : chemical resistance, thermal stability
- ***3M / Dyneon, Daikin, Asahi Glass, DuPont, Arkema, Solvay-Solexis***

- **Aerospace Materials**
- **Hydraulic tubing**
- **Chemical Processing : Valves, Lined Piping, Tanks**
- **Semiconductor Manufacture**

Fluoropolymers: “Super” Polymers

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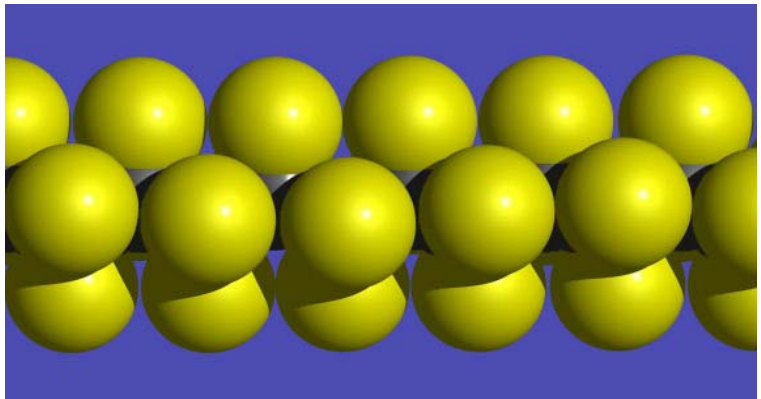
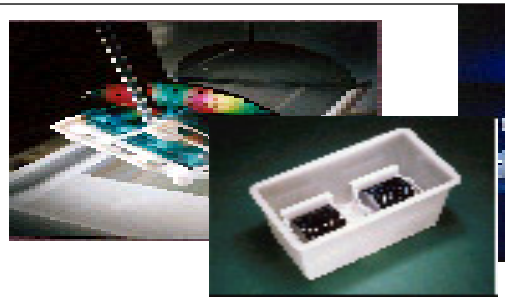
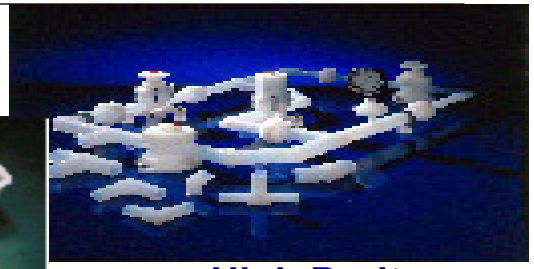
- Chemical resistance across broad temperature range
- “Slipperiest substance known to man”
- Unique properties/High value in use
  - High thermal stability. Working temperature range of -240° c to +240°C. Chemical and electric properties remain stable.
  - Non-flammability and high melting point. Difficult to ignite, self-extinguish once flame is removed. “The plastics that do not burn.”
  - Resistance to chemical attack. Including from acids, bases and solvents. Low chemical permeability.
  - Low coefficient of friction. Creates smooth surfaces resistant to abrasion.
  - Excellent electrical insulation properties.



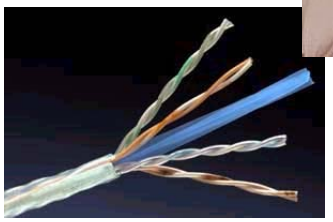
Fluoropolymers Applications - Resins





Semiconductor Manufacture

High Purity
Liquid Handling



Telecomm
Wire & Cabling

Chemical Processing
Valves, Lined Piping, Tanks

Aerospace Materials
Hydraulic tubing
Wire & Cabling Flares

Low Permeable
Automotive Fuel Hose

Fluoropolymer Applications - Dispersions

Non-stick Coatings for Cookware and Small Electrical Appliances

Construction Architectural Fabric

EPA 2010/15 PFOA Stewardship Program

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- Participation in the stewardship program requires voluntary corporate commitment to two goals:

1) To commit to achieve, no later than 2010, a 95% reduction, measured from a year 2000 baseline, in both:
   - facility **emissions** to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and
   - **product content** levels of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals.

2) To commit to **working toward the elimination** of PFOA, PFOA precursors, and related higher homologue chemicals from emissions and products by five years thereafter, or no later than 2015.

- Asahi Glass, Arkema, Ciba Specialty Chemicals, Clariant, Daikin, DuPont, Solvay-Solexis, 3M/Dyneon

Industry Progress

Toward Meeting EPA Stewardship Program Objectives

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Eight major companies participating in the PFOA Stewardship Program reported significant drops in the release of PFOA and related chemicals, putting industry on target to meet the 95 percent reduction goal in PFOA emissions and product content by 2010. Further reductions are anticipated by 2015. These first annual progress reports were submitted to EPA in October 2007, and were measured against baseline data submitted in October 2006. In February 2008, OPPT released summary tables of 2007 progress reports. In December 2008, OPPT released summary tables of 2008 progress reports.

http://www.epa.gov/oppt/ar/2007-2009/managing/potential_risks.htm

Example of Manufacturing Emissions Reductions –

following EPA Stewardship program

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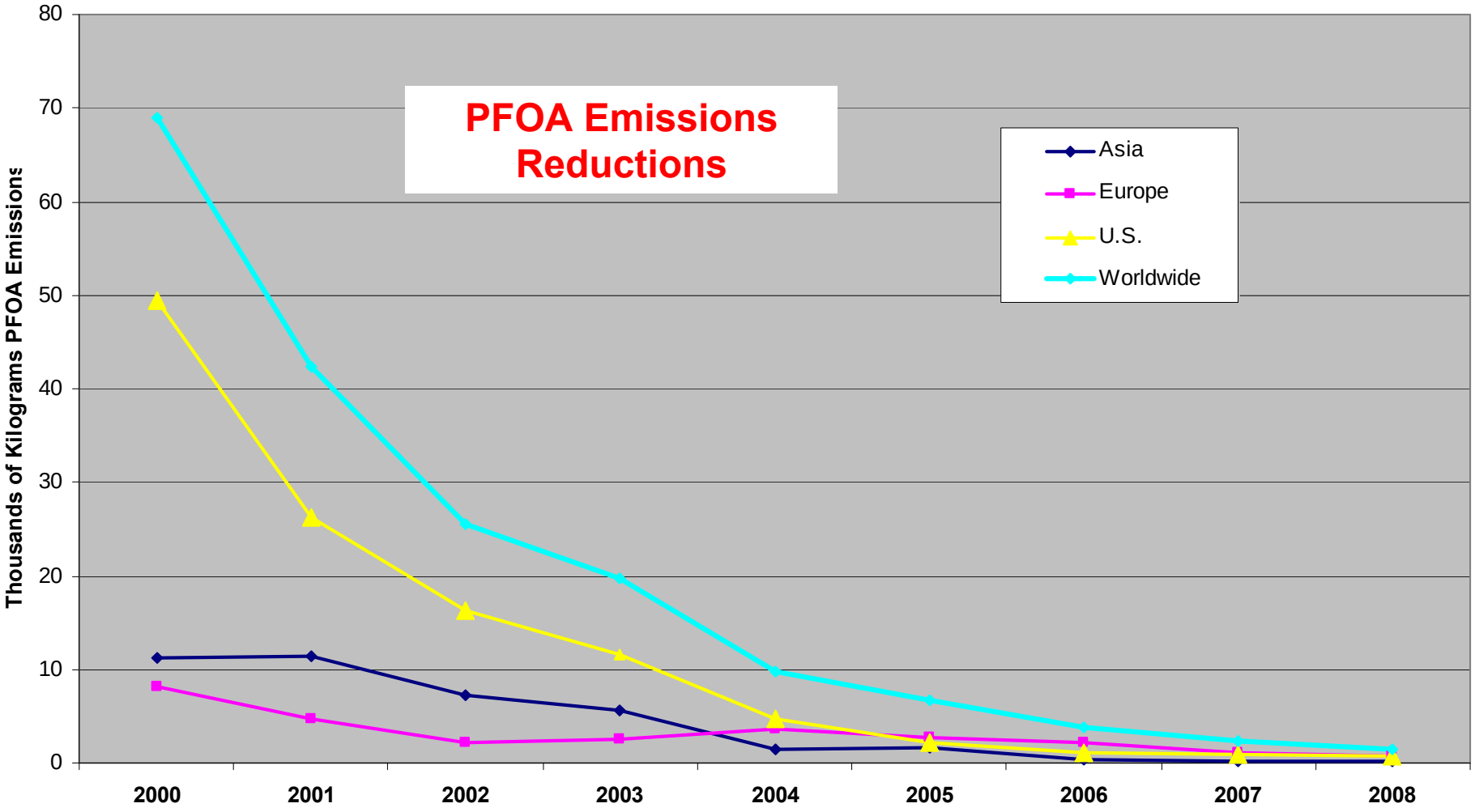

PFCs in the U.S. Population: NHANES 2003-04

Comparisons to 1999-2000 (Calafat et al., 2007)

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	Mean Serum Concentration (ppb)		
	1999-2000	2003-2004	% Change
PFOA	5.2	3.9	-25
PFOS	30.4	20.7	-32
PFHxS	2.1	1.9	-10
PFNA	0.5	1.0	+100

Conclusion:

Reductions related to discontinuation in 2002 of industrial production by electrochemical fluorination of PFOS and related compounds.

Industry participation in PFOS and PFOA Regulatory Assessments

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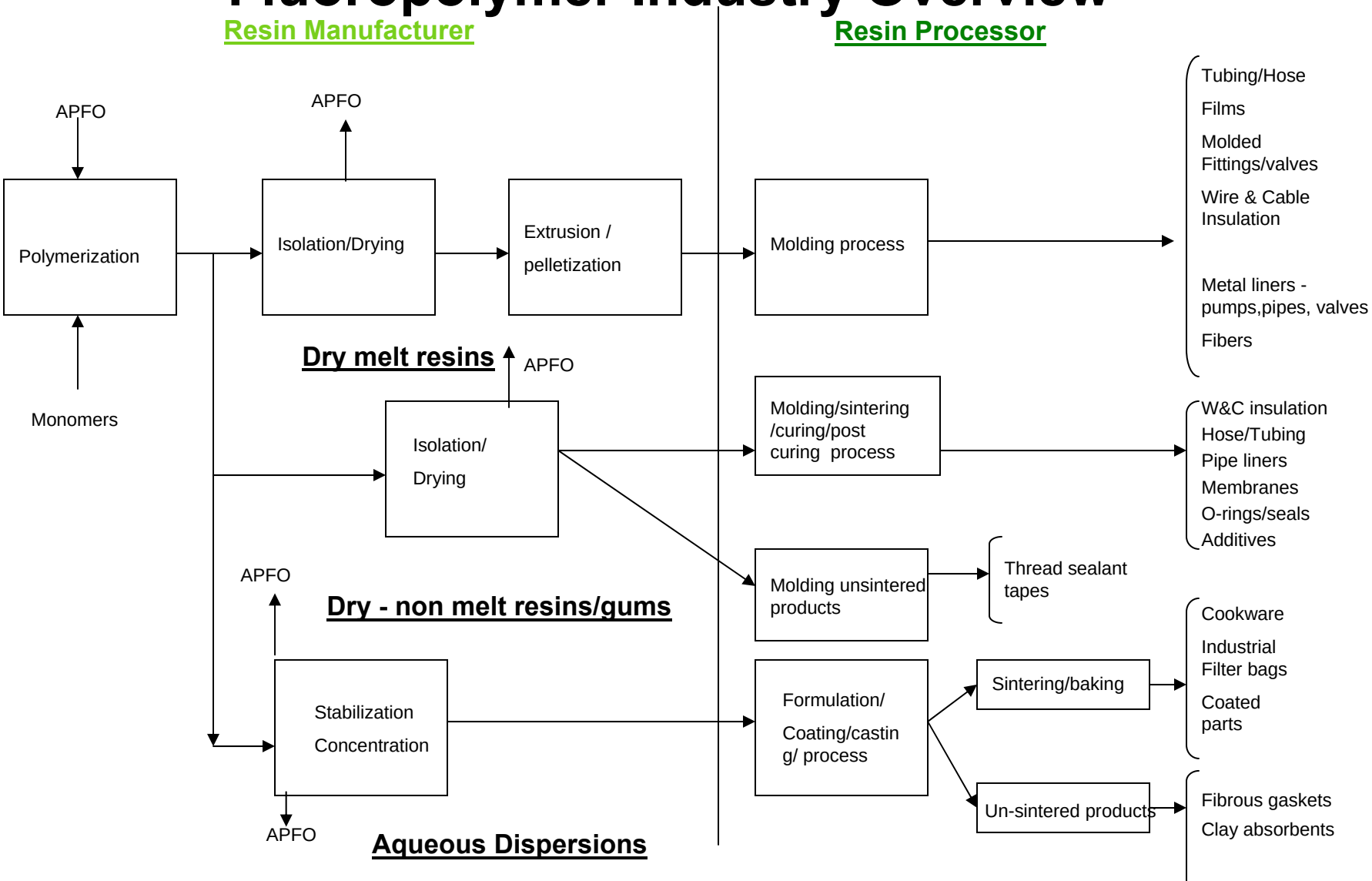
- Marketing & Use Restriction Directive on PFOS – includes revision clause on PFOA requiring a risk assessment but no timeline (Adoption Dec 2006)
- OECD joint PFOA hazard assessment lead by US EPA and UBA Germany (Started in 2006 & completed 2008)
- Harmonized Classification & Labelling decision on PFOA at European Chemicals Bureau: led by Norway (2006)
- German Risk Assessment on PFOA (2008-2009)
- RPS survey (2009)

PFOA Risk Assessment

- PFOA production by EU supplier
- Fluoropolymer manufacture
- Fluoropolymer materials are sold as resin pellets/powder and in aqueous dispersion form to industrial fabricators.
  - Resin pellets/powder contain <15 kg/year PFOA content; PFOA destroyed by thermal processing resin into fabricated articles
  - Aqueous dispersion products contain ~ 50 tons/year PFOA content (worldwide basis pre-2005):
    - Average product content ~2000 ppm (pre-2005)
    - ~60% PFOA destroyed in processing dispersion to final products
    - ~40% emissions to local environment around dispersion processor location
  - Coated products made using aqueous dispersion do not contain measurable levels of PFOA; coatings are sintered at temperatures >350 degrees C which destroys residual levels

Life Cycle

Fluoropolymer Industry Overview



Classification & Labeling – Plastics Europe Tox committee

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Human health from physico-chemical properties & Environmental Health

- Not classified

Human Health

- R-phrase(s)
  - **Xn; Harmful : R20, R22, R48/22**
    - R20 Harmful by inhalation.
    - R22 Harmful if swallowed.
    - R48 Danger of serious damage to health by prolonged exposure.
  - **Xi; Irritant : R36**
    - R36 Irritating to eyes.
  - **Carc. Cat. 3; R40**
    - *Cat 3 is: "Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment. There is some evidence from appropriate animal studies, but this is insufficient to place the substance in category 2."*
    - *R40 Limited evidence of a carcinogenic effect.*
  - **Repr. Cat. 3; R63**
    - Cat 3 is *"Substances which cause concern for human fertility"*
    - R63 Possible risk of harm to the unborn child.

- Label would read:
  - **Xn (Harmful) R20/22 – 36 – 40 – 48/22– 63**

Classification & Labelling – ECB advice to Commission

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Environment - 27 April 2006

- R-phrase(s) : Not classified

Human Health - 6 October 2006

- R-phrase(s)
  - **Xn; Harmful : R20, R22, R48/22**
    - R20 Harmful by inhalation.
    - R22 Harmful if swallowed.
    - R48 Danger of serious damage to health by prolonged exposure.
  - **Xi; Irritant : R36**
    - R36 Irritating to eyes.
  - **T; Toxic : R48/23**
    - R48 Danger of serious damage to health by prolonged exposure.
    - R23 Toxic by inhalation.
  - **Carc. Cat. 3; R40**
    - Cat 3 is: *"Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment. There is some evidence from appropriate animal studies, but this is insufficient to place the substance in category 2."*
    - R40 Limited evidence of a carcinogenic effect.
  - **Repr. Cat. 2; R61**
    - Cat 2 is *"Substances which should be regarded as if they cause developmental toxicity to humans"*
    - R61 May cause harm to the unborn child.

- Label would read:
  - **T (toxic) R20/22 – 36 – 48/22 – 48/23 – 61 S53 – 45**

Comment in the Risk Assessment: The classification recommended by the ECB to the EU Commission but it is recognised that new information may be available based on new animal data/models which may cause a reconsideration of this classification

Submitted: Chapter 8 - PBT Assessment

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- **Persistent** **P** 
- **very Persistent** **vP** 
- **Bioaccumulative** **B** 
- **very Bioaccumulative** **vB** 
- **Toxic** **T** 

- Conclusion: PFOA is not a PBT or a vPvB material

Submitted: Chapter 5 - Human Health

Derived No Effect Level = DNEL

DNEL (in µg/mL = ppm serum)	Workers	General population
Epidemiologically based	**≥ 1.7**	**≥ 0.8**
Animal based:		
- repro – fertility	**≥ 5.2**	**≥ 4.9**
- repro – developmental	**2.1**	**2**
- repro – developmental	**8**	**7.5**
- carcinogenicity	**5.6**	**5.2**
Critical biological DNEL	**≥** *2*	**≥** *0.8*

Both based on extensive human-health data, which is most relevant for humans.

DNELs are consistent with the weight of evidence from animal studies

For the Risk Characterisation the lowest DNEL value will be used respectively for workers and consumers.

Pharmacokinetics: An additional Assessment Factor of 3 should be taken into consideration for interindividual variability in toxicokinetics when calculating tolerated external doses (doses without an effect).

Submitted: Chapter 7 - Environment

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Predicted No Effect Concentration = PNEC

Environmental Protection Target	Value
PNEC	
- aquatic compartment	**0.57 mg/L**
- soil compartment	**0.16 mg/kg ww**
- microorganisms	**> 100 mg/L**

Eventually PFOA is ending in the aquatic compartment

Conclusions from Risk Characterisation

- Communities, the general public and workers are not at risk
  - General public
  - PFOA production
  - Fluoropolymer production & its downstream uses
  - Photographic application

- Assessment supports that this is an issue of persistence in the human blood and the environment
  - Not a health or environmental risk issue

Because of persistence issue, PFOA Stewardship Program participants committed to continued reductions of emissions and exposures

Consideration of PFOA Alternatives for Fluoropolymer production

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Technical Feasibility

- Use in existing manufacturing processes
- Capable of making the full line of existing polymers
- Polymers can work in the same customer applications
- Alternative chemicals possible to produce at commercial scale

Reduced environmental footprint

- Reduced society exposure
  - Environmental engineering control in manufacturing processes
  - Product content control
- Significantly faster bio-elimination/body clearance
- Similar or better toxicology profiles
- Approval by authorities

Economically viable to apply

- Cost of new chemicals
- Capacity of manufacturing process

Available in time

- Commercial conversion possible within each companies timeline

Non Fluorinated PFOA Alternatives

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Fluoropolymers are very high molecular weight products (1 MM Da – 100MM Da)

- very complex to produce and complex to keep stable in resin production
  - forming right amount of polymerization sites is critical – effect particle size
  - building long polymer chains is critical

<u>Issue with non fluorinated Polymer Production Aids (PPA):</u>

- Cannot make the right polymers
- Cannot keep process stable
  - initiators react with non fluorinated PPA vs monomers
    - not enough polymerization sites
    - very big particles that are unstable
  - during polymerization, non fluorinated PPAs react with growing polymer chains (chain transfer effect), molecules too short
  - lower functional performance for critical uses

EU Workshop – Conclusion

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- Industry active participation in the regulatory processes
- Learnings from PFOA risk assessment
  - PFOA is not a PBT or a vPvB material
  - Scope of exposure assessment including all precursors
  - No risk to public, workers or the environment
- Alternatives to PFOA in FP manufacturing are being implemented
- Facility emission to all media will be further reduced on a voluntary basis
- PFOA phase-out in FP manufacturing until 2015 or sooner

Plastics

The Material for the 21st Century