ENVIRONMENTAL FRIENDLY CHEMICALS AND RECYCLED PET

New approach and effects

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Archroma – Global leader in Textile, Paper and Emulsions

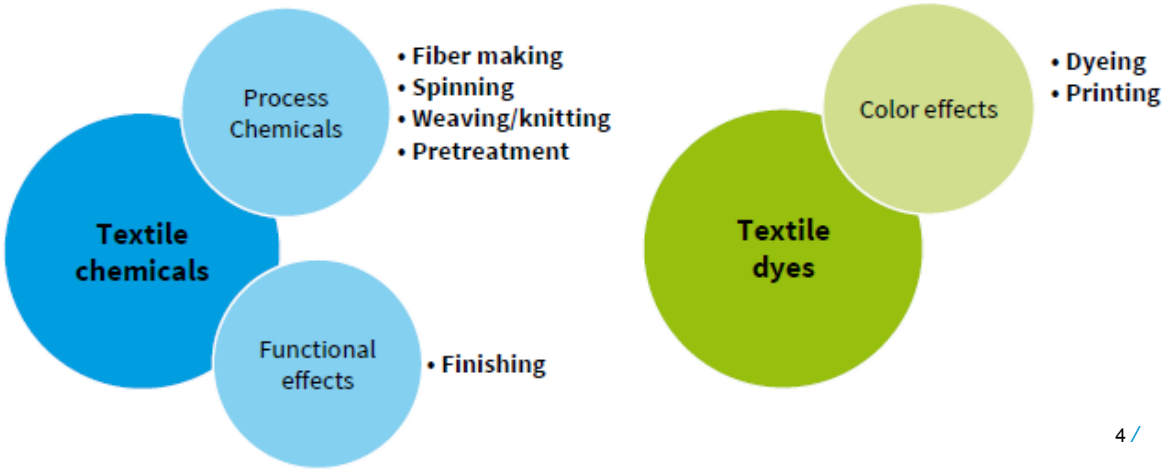
Archroma – Global leader in Textile, Paper and Emulsions

- global leader providing colors and specialty chemicals to sectors such as fibers and fabrics, paper and packaging, as well as adhesives, coatings and construction
- A company with proven innovation power, strong core technologies and a global footprint
- Experts with a rich tradition of working side by side with customers as long-term partners, developing tailored solutions that help them deliver business success in their local markets

Textile Technology

Broad product offering supporting the entire textile value chain

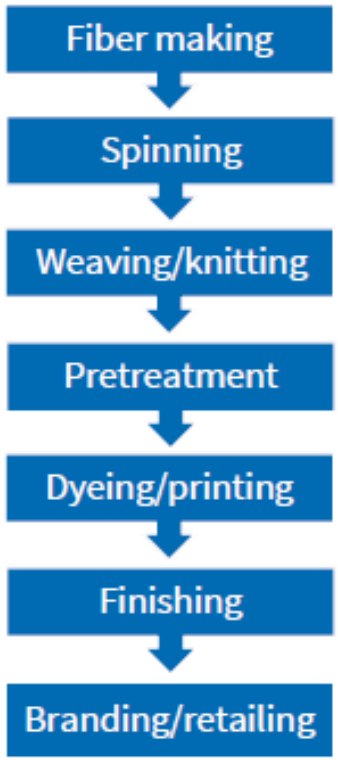
- Specialty chemicals for pretreatment, dyeing, printing and finishing
- Full range of colors of disperse, reactive, direct, acid and sulfur dyes, as well as pigment preparations



Archroma – Global leader in Textile, Paper and Emulsions

Supporting the entire textile value chain

From fiber to finish

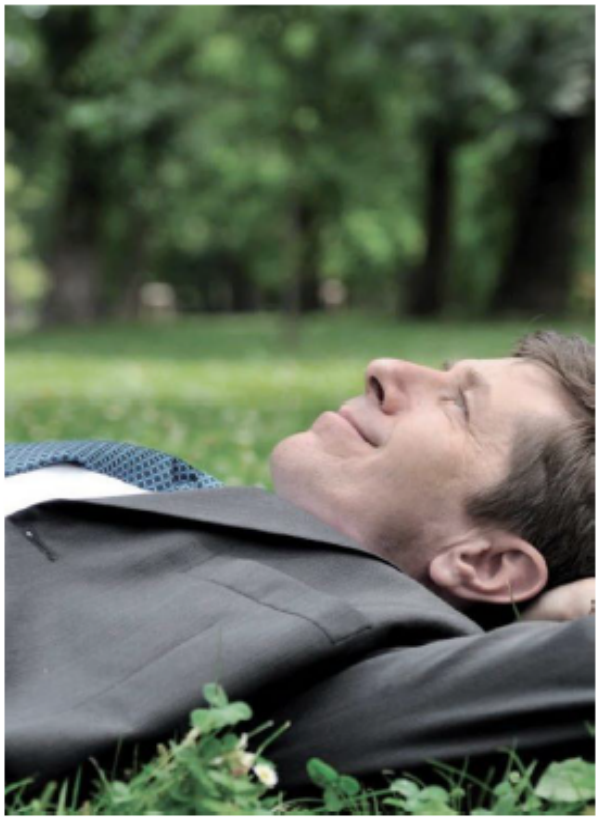


Products to support the entire production chain

- Process chemicals to improve carding, spinning, weaving, dyeing and printing
- Dyes and functional chemicals to deliver color and special effects such as moisture management, easy-to-iron properties and UV protection
- Color-matching technology to help customers get products to market quicker

Archroma – Global leader in Textile, Paper and Emulsions

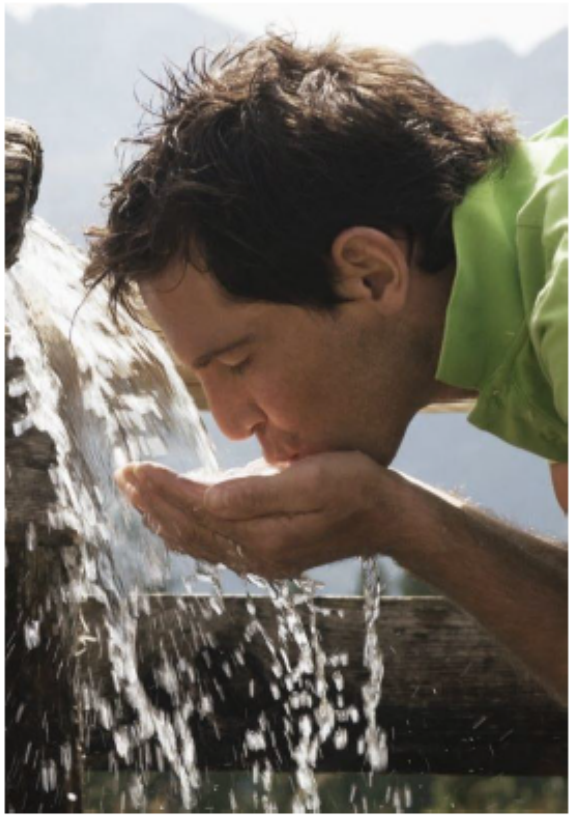
Sustainability By Innovation



- Archroma's Textile Specialties Business is committed to develop products and processes that are safer and gentler for the consumer and for the environment
- We strongly believe - and our experience demonstrates - that sustainability can generate innovation, performance and even cost savings for our customers

Archroma – Global leader in Textile, Paper and Emulsions

Sustainability Efforts



- We are a member of:
  - Textile Exchange
  - Sustainable Apparel Coalition
- We integrate as much as possible certifications and labels such as:
  - bluesign®2 (Archroma is a system partner)
  - Oeko-Tex®3, GOTS
  - RSLs of brands and retailers
- Awarded the EU Ecolabel for our Advanced Denim collection

Recycled PET materials

Ecofriendly chemicals for PET
Recycled PET materials

Datas on PET fibres

- Represents 40-45% of the global annual production
- PET production is energy intensive and uses non renewable natural resources.
- About 65-70% of global PET production is used for textile (65% in China).
- Remaining quantity is used for manufacture of PET bottles.

Ecofriendly chemicals for PET
Recycled PET materials

Steps for PET recycling

- **Sorting** (collecting, compacting, …)
- **Processing**
  - Mechanical recycling
  - Chemical recycling (molecule breakdown, glycolyisis, methanolysis, …)

- **Purity** is the main parameter and issue during PET recycling, as it impacts directly the performances.
  - Macroscopical physical contamination: glass and stone fragments, soils, papers, glue, …
  - Microscopical physical contamination: more difficult to remove!
  - Chemical contamination, like oil, surfactants, …

Ecofriendly chemicals for PET Recycled PET materials

End use markets for recycled PET

- **Fibers**

  In 2011, 39% of all recovered European PET was used to produce polyester fibers.

  - Fibers for weaving
  - Fibers for for nonwovens production (hygiene, wipes, industrial, …)
  - Fillers for upholstery, anoraks, … as alternative to PU foams
  - Spundonded nonwovens for building, geotextiles, filtration, shoe linings, …

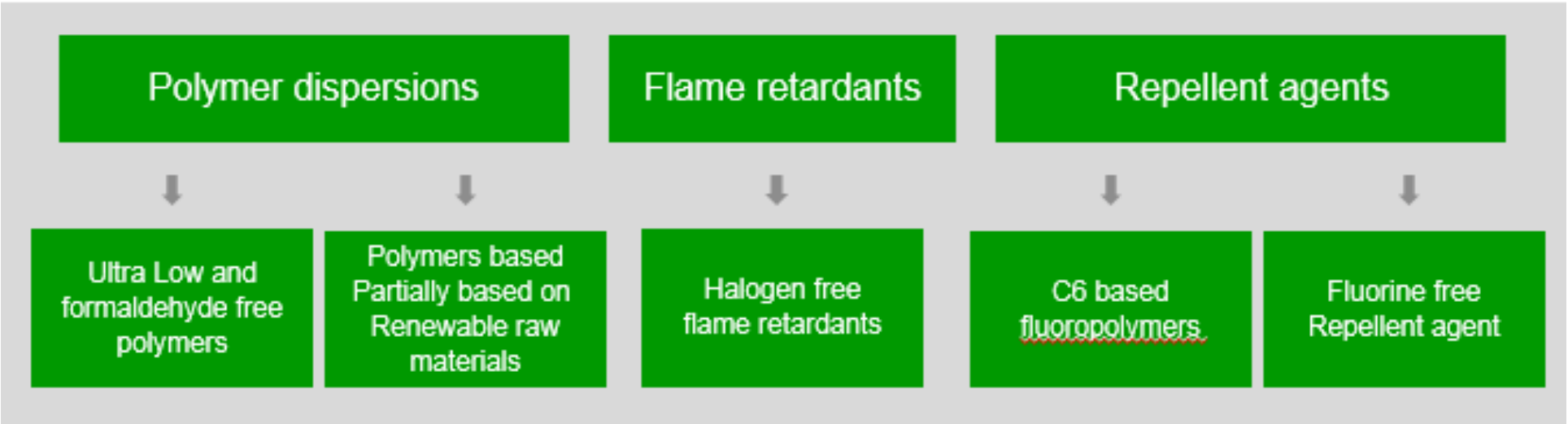
- **Packaging**
  - Preformed plastic boxes, containers for drinks, household products, …

Ecofriendly chemicals for PET

Ecofriendly chemicals for PET

- Market requires more and more ecofriendly chemicals for technical textile applications and particularly the nonwoven industry.

- Archroma offers a broad range of textile chemicals, including for recycled PET materials:
  - Polymer dispersions for chemical bonding
  - Flame retardants
  - Repellent agents for water and oil repellent treatments



Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

- **EC 605/2014**: The new classification represents the broadest amendment to regulation **EC 1272/2008** on the classification, labelling and packaging of substances and mixtures (CLP Regulation). It has been published in the Official Journal of the European Union on the 6th of June.

- The regulation classifies formaldehyde as carcinogenic (category 1B) and mutagenic (category 2) and requires companies to label it accordingly in the future.

- The new regulation goes into effect on April the 1st, 2015.

- The new classification of formaldehyde will have a direct effect on numerous rules and regulations, and will also require modification of Safety Data Sheets.

DANGER, H350 May cause cancer

Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Classification of formaldehyde

- Formaldehyde is classified in the group 1 by the IARC
  - **Group 1: “Carcinogenic to humans”**
  - Group 2A: “Probably carcinogenic to humans”
  - Group 2B: “Possibly carcinogenic to humans”
  - Group 3: “Unclassifiable as to carcinogenicity in humans”
  - Group 4: “Probably not carcinogenic to humans”
- Exposure limits to be reduced
  - TWA: the time weighted average (TWA) concentration of a substance in air which may not be exceeded over a normal 8 hour work period.
  - STEL: the time weighted average (TWA) concentration of a substance in air which may not be exceeded over any 15 minute period, limited to no more than 4 such periods in an 8 hour work shift with at least one hour between any 2 successive 15 minute excursion periods.
- Hazardous labelling for products containing > 1000 ppm of free formaldehyde (0,1%)
- Global trend to reduce the limits of free formaldehyde on various substrates

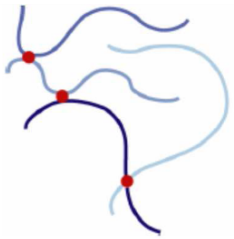
Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Sources of formaldehyde in polymers

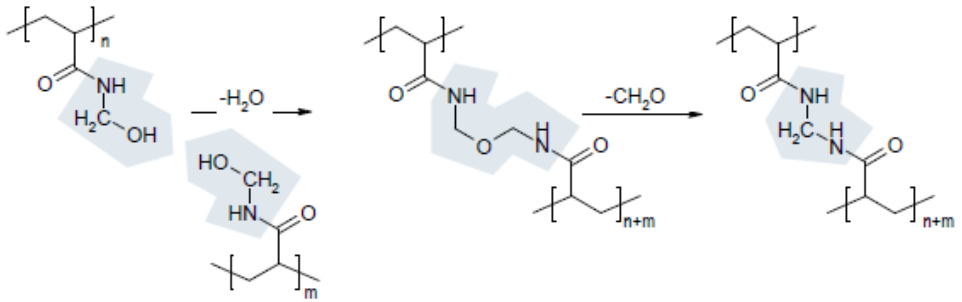
- **Methylol acrylamide monomers** — ***Difficult to remove!***
  - Used for the crosslinking
  - 500 to 1500 ppm
- **Reducing agent** — ***Easy to remove!***
  - Reduction of residual monomers
  - < 150 ppm
- **Biocide** — ***Easy to remove!***
  - To avoid bacteria and fungi overgrowth
  - 20 to 500 ppm
- **Additional crosslinkers based on MF** — ***Optional***
  - If used to improve water/solvent resistance
  - 1000 to 20000 ppm

Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Classical water based self crosslinking acrylates contain free formaldehyde



- In order to achieve good water and solvent (wash and dry cleaning) resistant coatings, need to work with specific monomers like NMA and NMMA
- Those monomers release free formaldehyde
- Free formaldehyde is found at different steps in the process:
  - In the dispersion itself (HPLC method)
  - In the air during the industrial application (TWA and STLE in mg/m3)
  - On the substrate after the application, in ppm, mostly according to the Japan Law 112 (for Oekotex), but many measurement methods exist



Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Archroma polymers range

- Standard self crosslinking polymers: contains less than 1000 ppm of free formaldehyde
  - **Appretan N**

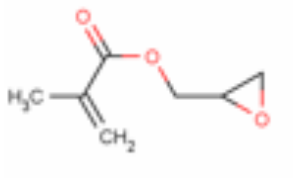
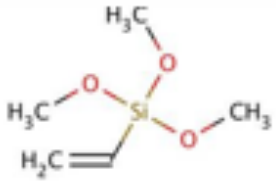
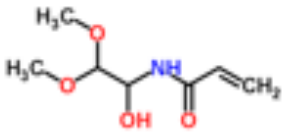
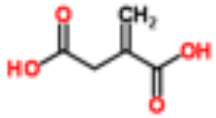
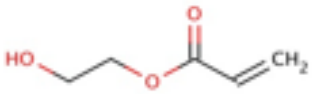
- Ultra low formaldehyde self crosslinking polymers: formaldehyde free on the substrate after the application is less than 16 ppm according to Japan Law 112
  - **Appretan E**

- Formaldehyde free self crosslinking polymers
  - **Appretan …**

Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Technical possibilities for formaldehyde free self crosslinking polymers

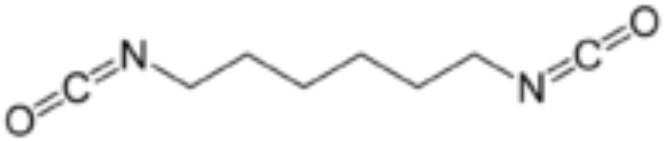
- Replacement of standard NMA and NMMA by other formaldehyde free crosslinking monomers
  - **Epoxy:**
  - **Alkoxy:**
  - **Carboxy:**
  - **Hydroxy:**

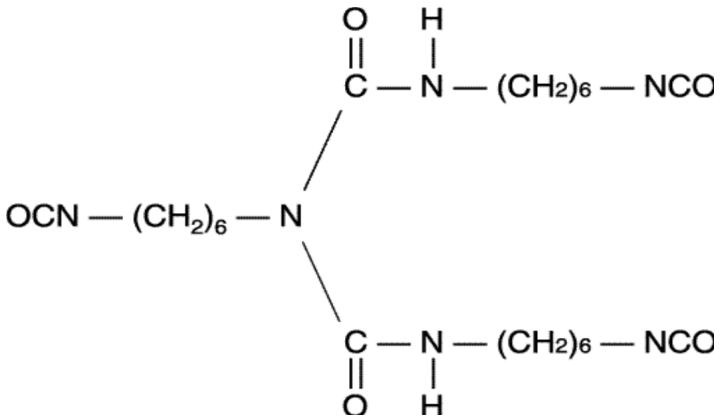






Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Technical possibilities for formaldehyde free self crosslinking polymers

- Use of polyisocyanate chemistry as formaldehyde free crosslinker, to enhance properties like water and solvent resistance





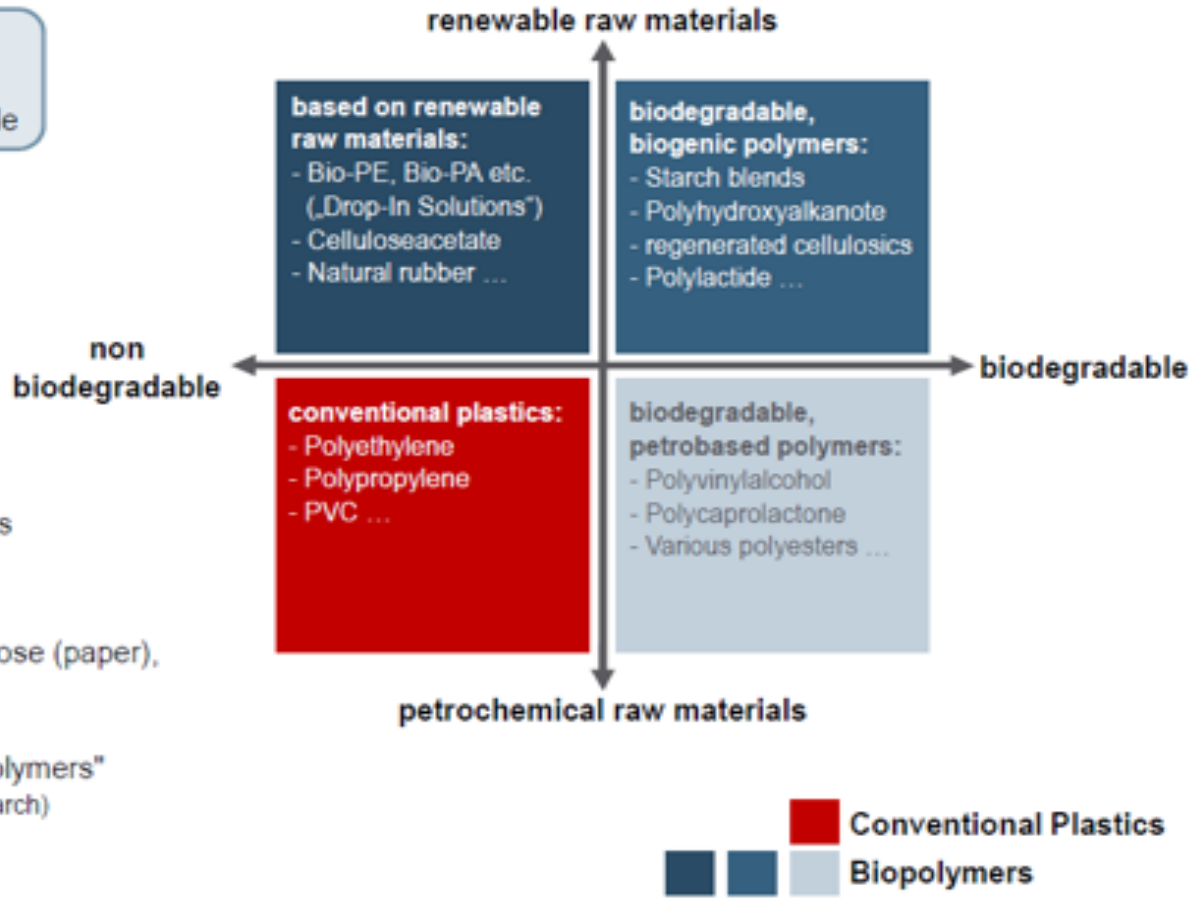
Ecofriendly chemicals for PET
Ultra low formaldehyde and formaldehyde free polymers

Polymer	Tg	Chemistry	Application fields
Appretan NF liq	-13°C	Styrene acrylate copolymer	Automotive
Appretan PL 10077 liq	+33°C	Styrene acrylate copolymer	Filtration, building
Appretan N 93200 liq	0°C	Vinyl acetate, vinyl versatate, acrylate terpolymer	Automotive, building
Appretan N 93250 liq	+35°C	Vinyl acetate, vinyl versatate, acrylate terpolymer	Automotive, filtration

Ecofriendly chemicals for PET
Biopolymers

Definition Biopolymer:
Biopolymers are made from biogenic raw materials **and/or** are biodegradable

- Biopolymers are not necessarely made from renewable ressources
- The definition of a Biopolymer does not tell us anything about its chemistry
- Not all biogenic polymers are biodegradable (e. g. natural rubber)
- Processes converting biomonomers into polymers are normally conventional chemical processes
- Biopolymers like e. g. starch, cellulose (paper), cotton, wool, cellulosic fibers etc. are well known since a long time
  → all others are called "New Biopolymers"
  (incl. e. g. the use of thermoplastic starch)

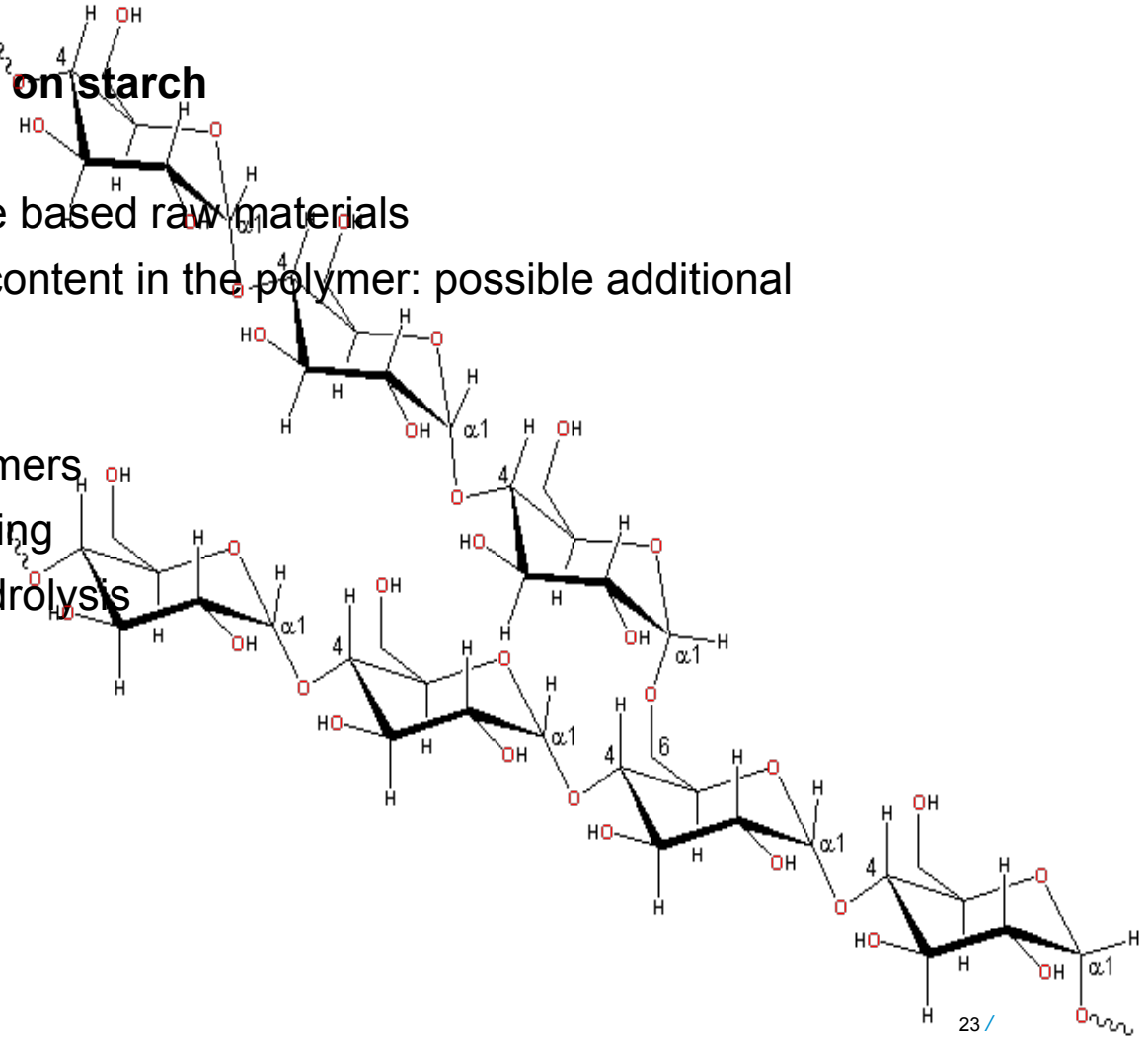


Ecofriendly chemicals for PET
Biopolymers

Grafting of acrylic copolymers on starch

- Partial use of renewable based raw materials
- Presence of high –OH content in the polymer: possible additional crosslinking

- Limitations for soft polymers
- Possible thermal yellowing
- Sensitive to alkaline hydrolysis



Ecofriendly chemicals for PET
Biopolymers

Polymer	Tg	Self crosslinking / formaldehyde free	Application fields
Appretan PL 6472 liq	+20°C	Yes / No	Building, filtration
Appretan PL 10101 liq	+48°C	No / Yes	Filtration, automotive
Appretan PL 6480 liq (FDA and BfR)	+25°C	No / Yes	Food filtration

Ecofriendly chemicals for PET
Halogen free flame retardants

Market segments for flame retardant textiles

FR technology is required when fire is a safety hazard of high concern and strict regulations have to be met, with certain optical and physical aspects to be considered for textile related applications.

Public transportation

Military

Hospitals/Public buildings

Automotive interior

Home furnishings

Protective wear

Construction

Ecofriendly chemicals for PET
Halogen free flame retardants

Regulatory requirements for flame retardant textiles

Flame retardants are used in areas with limited means of escape and often in direct contact with human skin. To protect consumers potentially harmful chemicals various RSL's and many eco-standards blacklist specific substances with some exemplary listings given below:

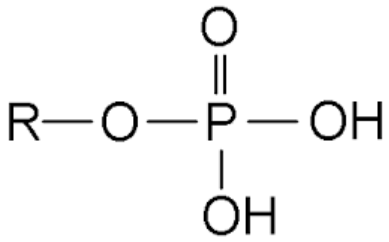
- **TCEP (Tris-2-chloroethyl-phosphate):** used as flame retardant softener and rheology modifier in PUR foams for upholstery/mattresses/car seats and in PVC coatings; mutagen & suspected carcinogen, EPA phase out in 2010, SVHC listed with sunset date in August 2015, prohibited under Oeko-Tex
- **HBCD (Hexabromo-cyclododecane):** used in coating and finishing of car interior fabrics, mattresses, upholstery, curtains and blinds; PBT (persistent, bio-accumulative, toxic) substance, SVHC candidate, sunset date August 2015, prohibited under Oeko-Tex
- **DecaBDE (decabromo-diphenylether):** used in back-coating of upholstery, carpets, automotive interior, awnings, industrial and military applications, U.S. EPA initiative enforced total phase out end of 2013 in the US, prohibited under Oeko-Tex

Ecofriendly chemicals for PET
Halogen free flame retardants

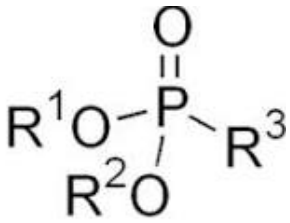
- Halogen based flame retardants have been baned for a long time from Archroma products range.

- Archroma prohibits the use of any of the substances listed in SVHC, and only uses raw materials compliant with the current edition of OekoTex® Standard 100.

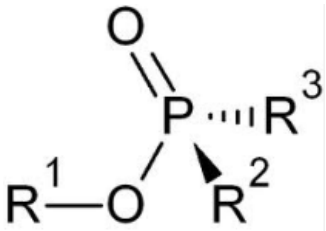
- All flame ratardants are based on the phosphorus chemis



  - **Phosphate**



  - **Phosphonate**



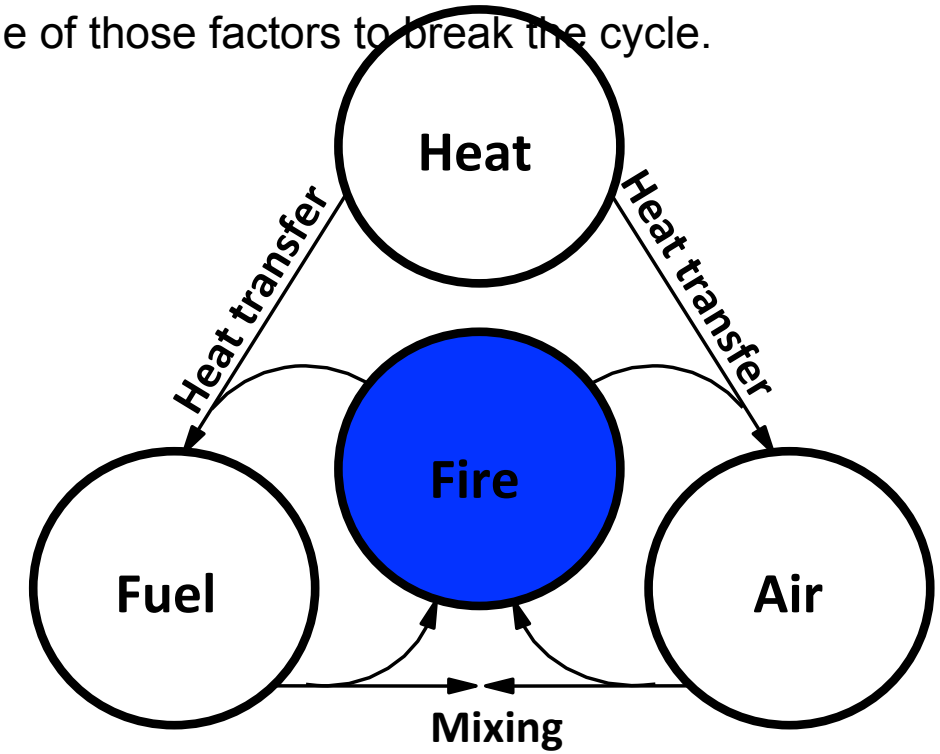
  - **Phosphinate**

Ecofriendly chemicals for PET
Halogen free flame retardants

Emmon's fire triangle

The fire triangle demonstrates that 3 factors must coincide in order to propagate a fire: the fuel (means the substrate which may burn), the air (the oxygen), and the heat.

It's enough to interfere on one of those factors to break the cycle.



Ecofriendly chemicals for PET
Halogen free flame retardants

Mode of action of flame retardants

There are mainly 3 modes of action for flame retardants:

- **Chemical effect on the gas phase**

The FR stops the radical mechanism of the combustion process and the supply of flammable gases is reduced and eventually suppressed.

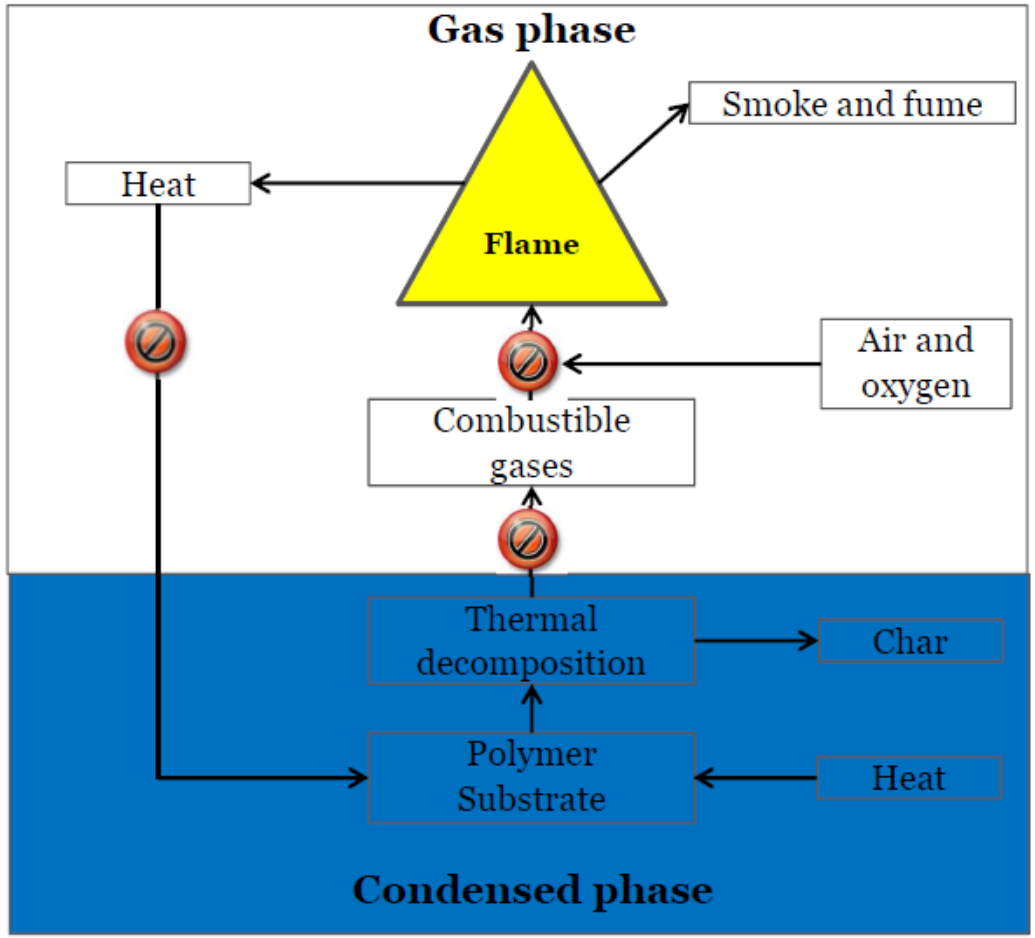
- **Chemical effect on the condensed phase**

The FR generates a layer of carbon (or charring) on the fuel's surface.

- **Physical effect**

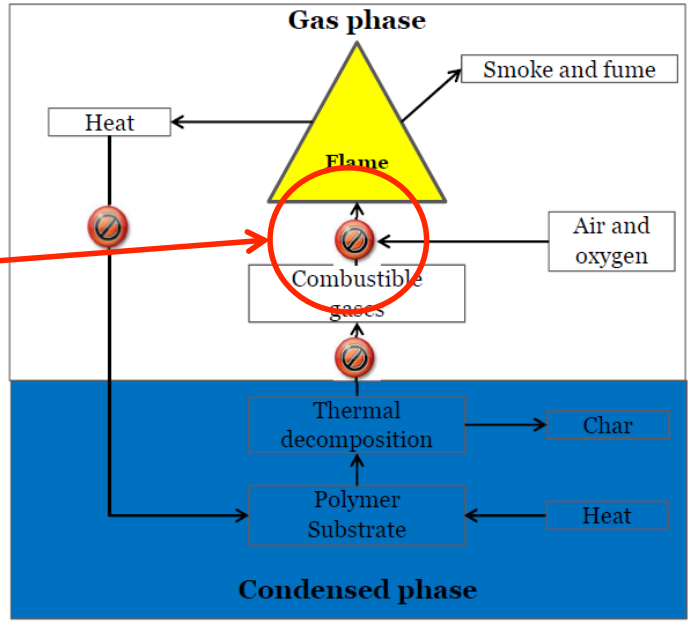
Various physical effects like cooling effect (heat sink) or dilution with inert substances

: main approaches to extinguish a fire scenario



Ecofriendly chemicals for PET
Halogen free flame retardants

Chemical effect on the gas phase



Inhibition of the exothermic oxidation reaction in the flame via radical scavenging, reducing the energy feedback to the substrate surface. Typical scenario with halogenated flame retardants.

$$X^\circ + RH \longrightarrow HX + R^\circ$$

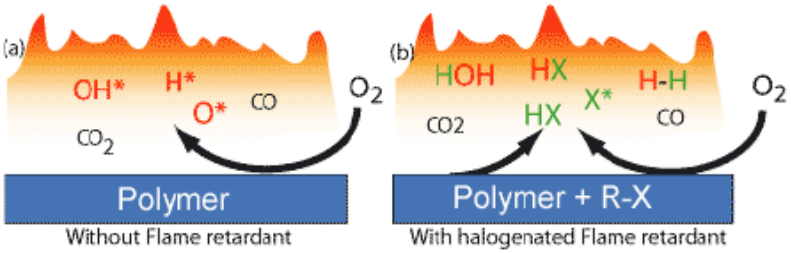
$$H^\circ + HX \longrightarrow H_2 + X^\circ$$

$$HO^\circ + HX \longrightarrow H_2O + X^\circ$$

Halogen free FR based on phosphinate chemistry have a similar effect

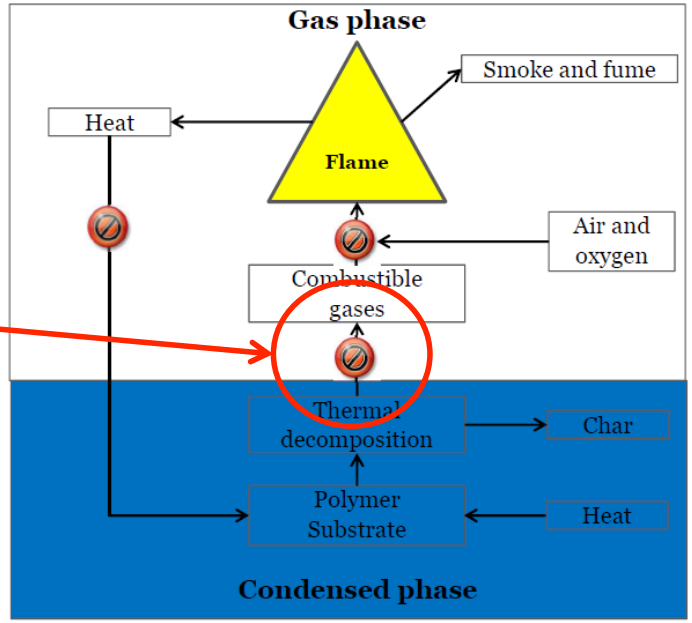
$$H^\circ + HPO^\circ \longrightarrow H_2 + PO^\circ$$

$$HO^\circ + HPO^\circ \longrightarrow H_2O + PO^\circ$$



Ecofriendly chemicals for PET
Halogen free flame retardants

Chemical effect on the condensed phase



Formation of a thermal barrier (charring) at the surface of the condensed phase, which blocks the release of gaseous fuel and prevents the transfer of heat back to the burning substrate.

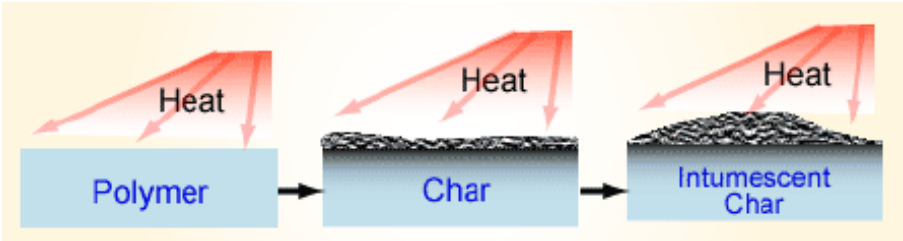
Phosphorous based flame retardants tend to form polyphosphoric acids under thermal stress, promoting the formation of thermally stable polymers (charring).

Formation of “poly“-phosphoric acid

$$(NH_4PO_3)_n \xrightarrow[-\,n\,NH_3]{>250°C} (HPO_3)_n$$

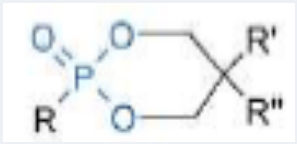
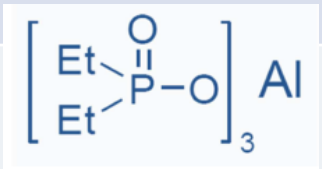
Formation of a protective carbon layer due to generation of polyphosphoric acid and carbonisation, e.g. by release of water

$$(HPO_3)_n + C_x(H_2O)_m \longrightarrow ["C"]_x + (HPO_3)_n.mH_2O$$



Intumescent effect is an additional case of condensed phase mechanism. Typical combination is polyol, catalyst and N source (pentaerythritol, APP and melamine)

Ecofriendly chemicals for PET
Halogen free flame retardants

Chemistry	Formula	Products
Water soluble inorganic ammonium phosphate		**Pekoflam THA liq**
Organic cyclic phosphonate		**Pekoflam PES liq conc new**
Non water soluble inorganic ammonium polyphosphate	 n > 1000	**Pekoflam TC 203 p (standard)** **Pekoflam TC 204 p (micronized)** **Pekoflam TC 303 p (melamine micro-encapsulated)** **Pekoflam TC 503 p (intumescent)**
Aluminium phosphinate		**Pekoflam ATC p (standard)** **Pekoflam STC p (micronized)** **Pekoflam HFC p (synergies)**

Ecofriendly chemicals for PET
Halogen free flame retardants

Global range for textile applications

Our focus on ‘greener’ chemistry results in an efficient range of eco-advanced products that are globally available wherever halogen-free FR solutions are needed.

Automotive interior & nonwoven

Pekoflam ATC p / STC p
Pekoflam THA liq

Protective & military wear

Pekoflam HFC p
Pekoflam TC503 p

Furnishings & decorative materials

Pekoflam PES liq conc new
Pekoflam HFC p
Pekoflam TC503 p

Construction materials & industrial nonwoven

Pekoflam TC203 p / TC204 p
Pekoflam TC303 p
Pekoflam THA liq

Ecofriendly chemicals for PET
Repellent agents

3M initiated a voluntary phase-out of PFOS (perfluorooctyl sulfonate) based fluorochemicals (ScotchgardTM) beginning in 2000 because data indicated that PFOS is persistent in the environment, accumulates in biological systems and is toxic in tests with laboratory animals

Data on PFOA (perfluoro octanoic acid), which is used as a polymerization aid in the production of PTFE was provided to government regulatory authorities. Regulators wanted more information about PFOA and how it was getting into humans

Blood data show the presence of PFOA at extremely low levels in humans

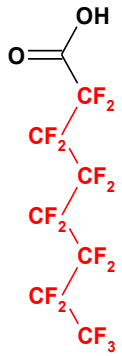
PFOA is known to be persistent in the environment. There is published literature on the toxicity of PFOA indicating that it causes reproductive toxicity and is a carcinogen in animals

Ecofriendly chemicals for PET
Repellent agents

What is the origin of ubiquitous PFOA and PFOS in the environment?

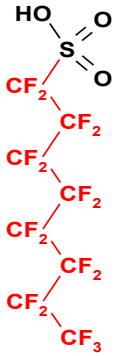
Use as a surfactant in different industry sectors:
electroplating, fire-fighting foams, fluoropolymers (PTFE), etc…

PFOA



- Persistent
- Bioaccumulative
- Carcinogenic in animals

PFOS



- Originates only from electrochemical fluorination
- Persistent
- Bioaccumulative
- Suspicion of carcinogenic properties
- EU restriction of application

However, they are not actively used to finish textiles, and only trace amounts are present as by-products from the synthesis of raw materials

Ecofriendly chemicals for PET
Repellent agents

Archroma produces high molecular weight polymeric fluoro compounds which are toxicologically safe. Archroma neither uses PFOA nor PFOS during manufacturing

Fluoro telomer alcohol (C8-2-OH) may metabolize into PFOA under certain circumstances; unclear if telomer products significantly contribute to PFOA found in the environment

Archroma participates in the voluntary emission and residual reduction stewardship program of the Environmental Protection Agency (EPA), USA. As part of this program Archroma is committed to reduce emissions by 95% until 2010

Further impurity reduction of C8 chemistry and launch of new C6 chemistry 2007

Classical Nuva range below 1 ppm PFOA and Nuva N serie PFOA free*.
The whole range does not contain PFOS!

Almost complete range of Nuva N series: Soil release product,
nonionic repellent product and fluorine-light repellent product successfully launched in 2012

* below limit of detection

Ecofriendly chemicals for PET
Repellent agents

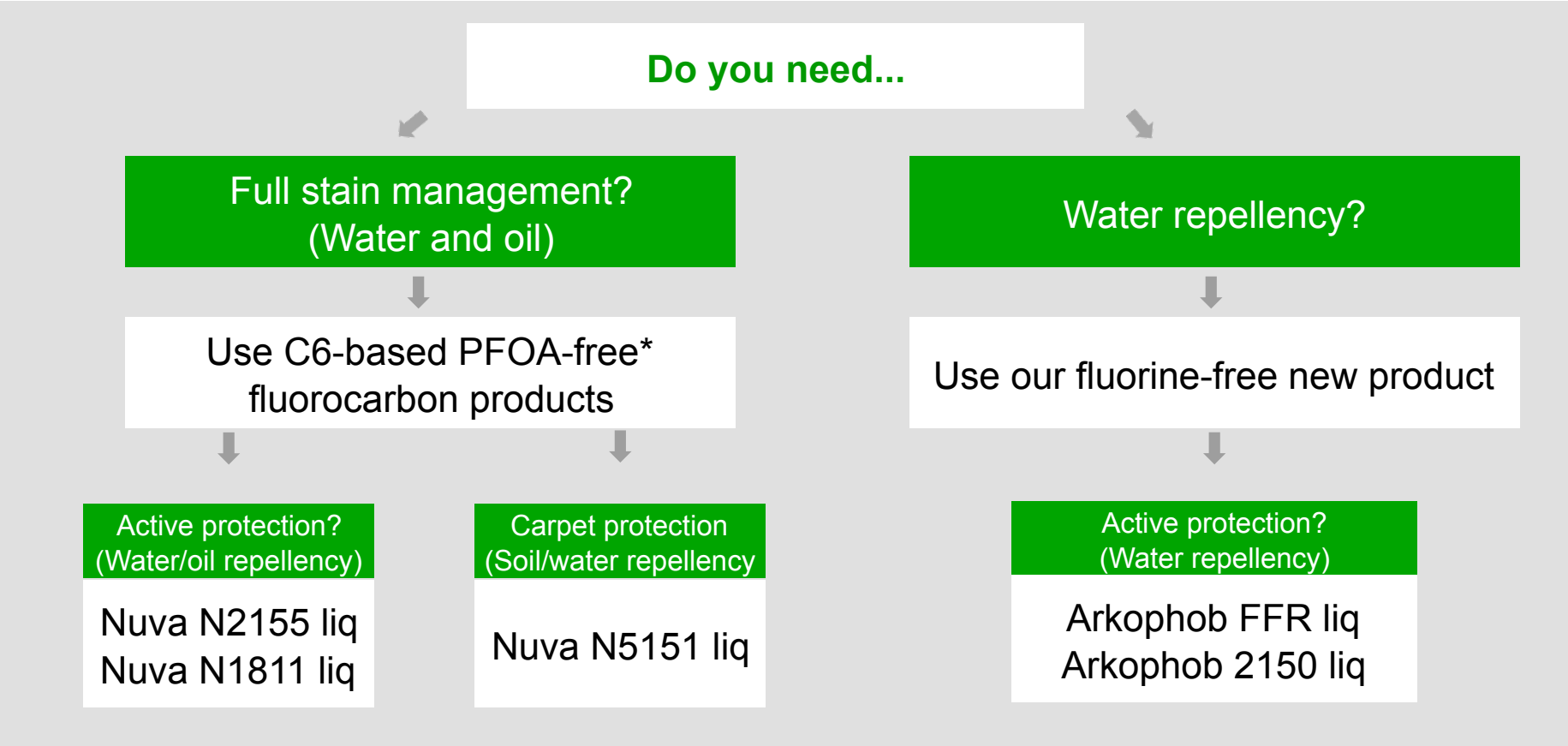
Situation and forthcoming steps

- US EPA: 2010/15 PFOA Stewardship Program:
  - Commit to achieve, no later than 2010, 95% reduction in both facility emissions to all media and product content of PFOA, PFOA precursor chemicals, and related higher homologue chemicals
  - Commit to working toward elimination of these chemicals by 2015
- Restrictions already exist in countries like Germany, or Norway from mid 2014
- Further restrictions in Europe will be implemented in 2016
- No more C8 available after end 2015
- Many brands have already switched to C6 or to fluorine free

PFOA-Restriction in Norway (Product regulation FOR 2004-06-01 Nr. 922, § 2-32):

Applicable products	Limit	Date of application
Substances and Mixtures	10 mg/kg	1st June 2014
Textiles, Carpets and other coated consumer products	1µg/m²	1st June 2014
Other consumer products	0,1%	1st June 2014
Adhesive foil or tape in semiconductors; photographic coatings for film, paper or screen.	0,1% for foil and tape, 10 mg/kg for coatings	1st January 2016

Ecofriendly chemicals for PET
Repellent agents



* = below limit of detection with current analytical methods (20 ppb)

Ecofriendly chemicals for PET
Repellent agents

Product	Chemistry	Features	Application fields
Nuva N 2155 liq	C6 fluoropolymer Acrylic backbone	Non ionic High WOR properties, even at low curing temperature	Automotive
Nuva N 5151 liq	C6 fluorpolymer PU backbone	Non ionic Good oil repellence Medium water repellence Low flammability Dry soil repellent	Filtration Building
Arkophob 2150 liq	Fluorine free Polymer dispersion	Weakly cationic Very good water repellence Wash durable with crosslinker No yellowing	Filtration Building

Other possibilities

Ecofriendly chemicals for PET
Other possibilities

Polyester chemistry to be used on polyester fibers…

- **Arkofil PES gr**
  - Polyester resin
  - Easily water soluble in warm water (80°C) up to 20% (low viscosity)
  - Stiffening agent with low yellowing
  - Heat sealable
  - Compatible with fluoropolymers

- **Hydroperm SRHA liq**
  - Modified polyester copolymer, water soluble
  - Hydrophilizing agent, with antistatic effect
  - Soft

Questions?

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