

# **Bromine Flame Retardants – Life Savers or Eco Villains?**

## **The flame retardant users' view**

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**SCI Fire and Materials Group Autumn Meeting**

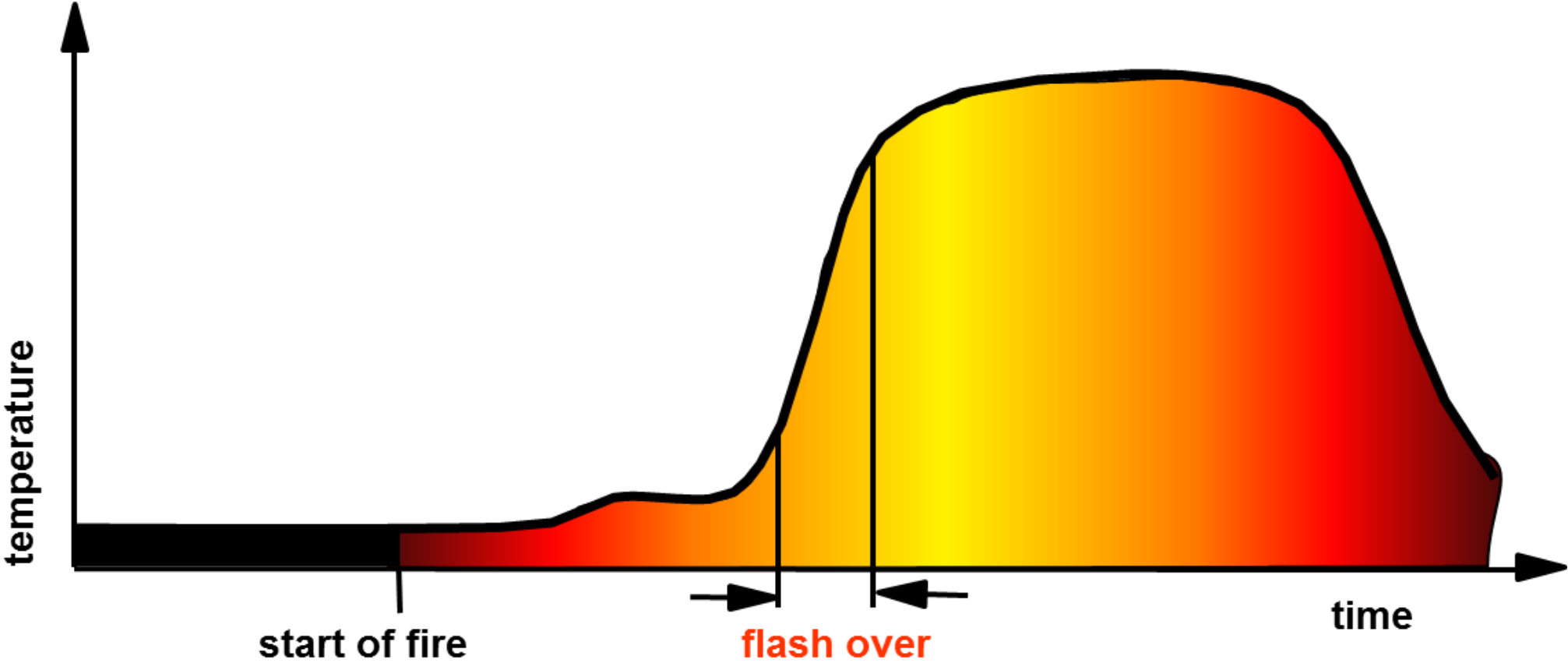
**4-5<sup>th</sup> November 2015**

## The flame retardant “users” view

- EMPHASISE SOME OF THE KEY ELEMENTS OF FR & TEXTILES
- LOOK AT THE BASICS OF WHAT IS NEEDED AND WHAT WE HAVE TO WORK WITH
- TRY TO PUT SOME CONTEXT ON THE SITUATION WE ARE FACING
- LARGE INFLUENCE OF BIS FFR REVIEW THROUGHOUT AS THIS THROWS MANY OF THE QUESTIONS INTO SHARP FOCUS
- TRY AND DETERMINE IF I AM REALLY ADDICTED?
  - ADDICTED TO FR CHEMICALS OR FR STANDARDS THAT DEMAND THEIR USE

# FIRE REPRESENTED AS A GRAPH

TIME vs. TEMPERATURE



## HOW DO WE DEAL WITH A FIRE?

- REDUCE THE INTENSITY
  - Add water – CALL THE FIRE BRIGADE
- HINDER FLASH-OVER AND SPREAD OF FIRE
  - Specify materials - Design and construction - Compartmentalisation
- INHIBIT THE DEVELOPMENT OF A FIRE
  - Reduce the ease of ignitability
  - Use Flame Retardants
  - Especially for Textiles

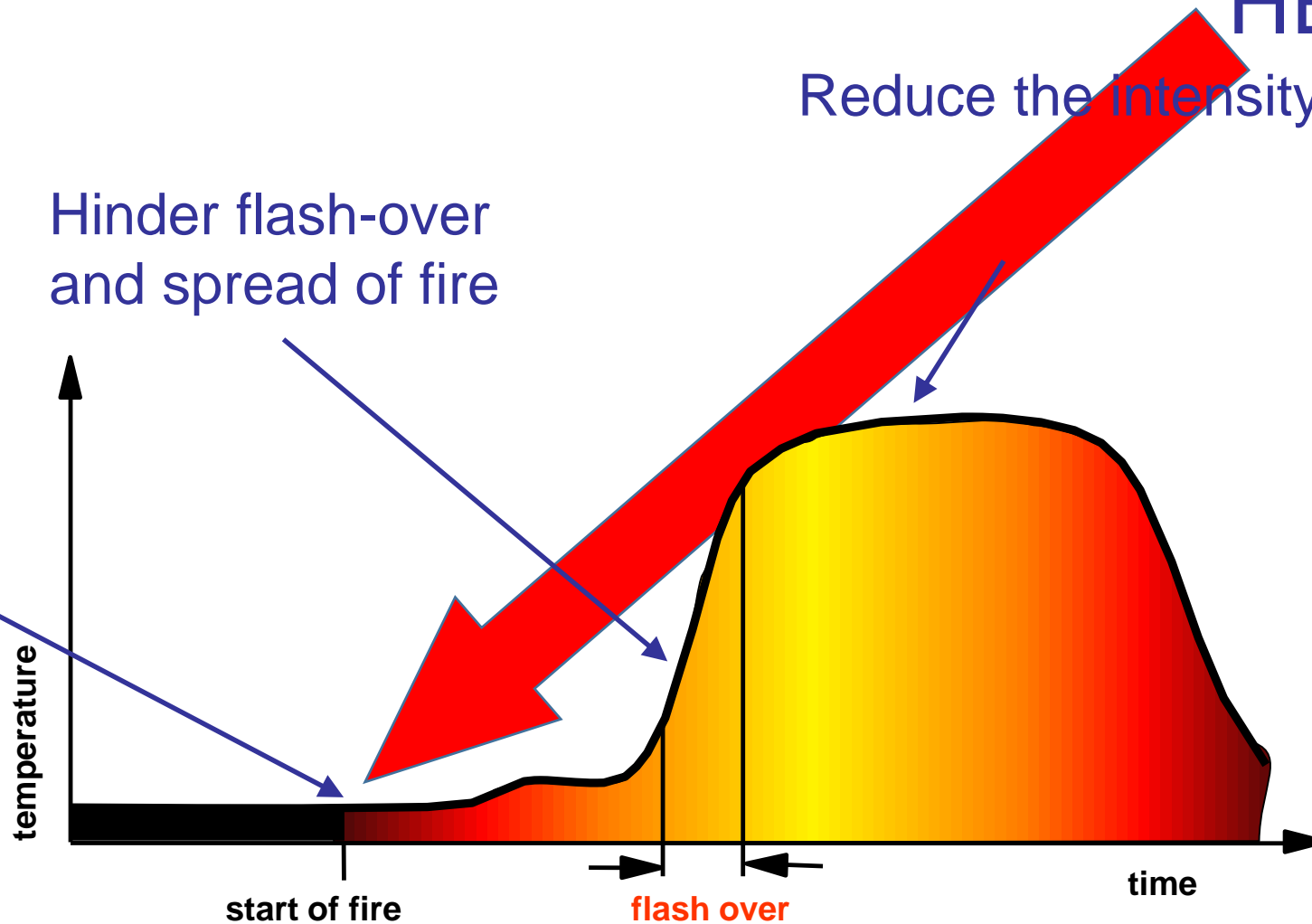
# FLAME RETARDANCY WORKS

HERE

Inhibit the Development of a fire

Hinder flash-over and spread of fire

Reduce the Intensity



## DO FR's WORK?

- IN THE UK A CIGARETTE BURN ON YOUR SOFA MEANS THE FFR WORKED AND A LARGER FIRE WAS PREVENTED
  - AND THAT IS ALL THEY ARE SUPPOSED TO DO.
- INFLUENCE THE RATE OF SPREAD OF FLAME
  - IF THEY DELAY FIRE ONSET THEN THEY BUY TIME FOR PEOPLE TO ESCAPE
  - CONVERSELY: INHIBIT RAPID SPREAD OF FIRE
- THERE IS A DIFFERENCE BETWEEN EASE OF IGNITION AND BURNING BEHAVIOUR
- SAYING FR's ADD TO THE LOAD IN A FIRE USUALLY IS DONE WHEN ALSO IGNORING THE LOAD OF **EVERYTHING** BEING CONSUMED

# DO FR STANDARDS WORK?

- RISK BASED DEVELOPMENT PROCESS
- TEST METHOD
- PERFORMANCE CRITERIA
- EASE OF IGNITION, RATE OF BURN, NATURE OF DAMAGE
- BECOME ARTIFICIAL ASSESSMENT
  - i.e. PASSING THE TEST IS MORE IMPORTANT THAN ACTUAL FIRE SAFETY PERFORMANCE
- DESTRUCTIVE TESTING
  - NO TESTED SAMPLE EVER USED IN PRACTICE(?)

## WHAT INFORMATION DO WE NEED TO FLAME RETARD A TEXTILE?

1. FIBRE TYPE/COMPOSITION
2. TEXTILE CONSTRUCTION
3. TEST REQUIREMENTS
4. DURABILITY REQUIREMENTS
5. END USE FOCUSED REQUIREMENTS
6. AVAILABLE PLANT TO PROCESS



## 1. FIBRE TYPE & COMPOSITION

- CHARRING vs. THERMOPLASTIC
- NATURAL vs. SYNTHETIC?
- NATURE OF MIXTURE
- COMPETITIVE MIXTURES
- THERMAL CHARACTERISTICS OF FIBRES

## 2. TEXTILE CONSTRUCTION

- DENSE OR OPEN CONSTRUCTION
- HEAVY OR LIGHT
- AVAILABILITY OF AIR

## 3. TEST REQUIREMENTS

- IGNITION SOURCE
- ORIENTATION
- PASS/FAIL CRITERIA
- BURN, CHAR, DAMAGE AREA
- TEST METHODS ARE BASED ON A RISK ASSESSMENT APPROACH

## 4. DURABILITY REQUIREMENTS

- SOAK
- WASH
- (DRY CLEAN)
- HARD WATER
- AVOID USE OF WATER SOLUBLE PRODUCTS

## 5. END USE FOCUSED REQUIREMENTS

- HANDLE/FEEL
- AIR PERMEABILITY
- NO INFLUENCE ON OTHER PROPERTIES
  - CORROSION
  - WATERPROOF
- SKIN CONTACT?
- AVOID e.g. SOME CHEMICALS
- AND ETC.

## 6. PLANT AVAILABLE TO PROCESS

- PAD
- COAT
- SPRAY
- LAMINATE

# DURABILITY IN FR TREATMENT OF TEXTILES

1. WATER SOLUBLE PRODUCTS HAVE LIMITED APPLICATION FOR TEXTILES  
ARTICLES NEVER WASHED, DISPOSABLE
2. REACT WITH THE FIBRE  
CELLULOSIC AND COTTON IN PARTICULAR
3. MAKE A SUBSTANCE INSOLUBLE - POLYMERISE/SELF REACT  
FILL FIBRE INTERNALLY - CELLULOSIC
4. USE AN INSOLUBLE SUBSTANCE AND FIX WITH A BINDER (GLUE?)
5. DISSOLVE IN FIBRE (QUANTITATIVE PROCESS?)

# CHEMICAL CHARACTER OF FR's FOR WATER BASED SYSTEMS

- WATER SOLUBLE – IONIC
  - WEAK BASE AND STRONG ACID.
  - ADD HEAT AND YOU HAVE A STRONG ACID (E.G. ammonium phosphate)
  - (NOT GOOD WITH BINDERS/EMULSIONS AND VISCOSITY MODIFIERS)
- CHEMICALLY REACTIVE OR COMBINED INTO REACTIVE MOIETY
- OILS CAN BE EMULSIFIED
  - OK FOR PAD OR COATING FORMULATION
- INSOLUBLE CAN BE DISPERSED
  - OK FOR PAD OR COATING FORMULATION
- EITHER A SYSTEM FOR FORMULATION OR READY-MADE (3 & 4)

## INHERENTLY FR FIBRES

- CO-POLYMER OR SIMPLY ADDITIVE?
- DURABILITY CANNOT BE PRESUMED WITH ADDITIVES
- PERFORMANCE CANNOT BE ENGINEERED
- NOT NORMALLY SUBJECTED TO THE SAME COMPLEX PROCESS OF ASSESSMENT
- ADDED FINISHES CAN COMPROMISE EFFECTS
- HAVE THEIR PLACE BUT ARE NOT A ONE SIZE FITS ALL REPLACEMENT

## WHAT DO WE WANT?

- EASY TO FORMULATE
- MIX WITH BINDERS
- CONTROL STABILITY OF A FORMULATION
- CONTROL RHEOLOGY OF A FORMULATION
- ALL APPLICATION SYSTEMS
  
- COATED TEXTILES COME IN MANY FORMS
  - TEXTILE PLUS COATING ON THE BACK e.g. UPHOLSTERY
  - COATING SUPPORTED BY A TEXTILE e.g. PVC tarpaulin
  - COATING AS THE FACE/OUTER OF A TEXTILE

## SOME OBSERVATIONS:

### NON DURABLE

- Water soluble must not be overheated and are often hygroscopic
- More complex molecules solve issues such as migration to surface and are more stable thermally
- Still water soluble = no durability

### DURABLE

- Degree of reaction = rate of fixation NEVER high in textile processing
- Large effect of fibre properties (TENDERING OF COTTON)
- Enter fibre thus cotton preferred



## OTHER PROBLEMS?

- INERT AND INSOLUBLE BROMINE (BFR's) ARE WHITE PIGMENTS
  - POTENTIAL CHANGE OF SHADE OF TREATED TEXTILE
- INORGANIC PHOSPHORUS SYSTEMS ARE OFTEN NEAR TO CHELATING CHEMISTRY
  - HARD WATER **PROBLEM** IN DURABILITY
  - BUILD UP OF DEPOSITS IN LAUNDERING/IN USE
  - CALCIUM TRIPHOSPHATE IS NOT A FLAME RETARDANT
  - TOO STABLE THERMALLY AND EFFECTIVE NEUTRALISATION OF FR EFFECTS
- ORGANIC OILS MORE LIKELY TO HAVE HH/ENV PROBLEMS?
  - PHYSICOCHEMICAL PROPERTIES ISSUE?

# ANYTHING ELSE?

- WIDE RANGE OF EFFECTIVITY
  - ALL FIBRE TYPES AND MIXTURES
- PROBABLY NEEDS TO BE GAS PHASE
- LOW ADD-ON
- LOW COST
  
- PROBLEM FREE
  - HUMAN HEALTH AND THE ENVIRONMENT

AND THE WINNER IS:

DECABROMO DIPHENYL ETHER

a.k.a. DecaBDE

EXCEPT THERE SOME PROBLEMS

In 2012 the UK government sent DecaBDE off to be sacrificed on the altar of Substance of Very High Concern (SVHC) evaluation

- Based on
  - Discovery in the environment
  - Debromination (to lower congeners – obviously, and Penta was on the way to becoming a POP)
- Quote senior Gov't scientist: “Overwhelming evidence of debromination”
  - 2 studies, 1 not published
- Otherwise its discovery in the environment is the problem
- INSOLUBILITY HERE = PERSISTENCE

## WHAT'S WRONG WITH DecaBDE?

- LARGE MOLECULE AND VERY INSOLUBLE AND NON-REACTIVE
- PRESUMED TO BE INACCESSIBLE TO ANIMAL AND HUMAN
- NOW DISCOVERED “EVERYWHERE” BUT NO KNOWN TOXICITY
- 15 YEARS AND NO “SILVER BULLET”
- HIGHLY TOXIC:

**POLITICALLY**

## Historic industrial practice

- In the 1990's any waste from use of DecaBDE would go straight to sewer.
- At times of high volume flows (it can rain in Manchester) they would effectively discharge direct to the Irish sea – Untreated sewage
- Discovery in the environment is not carbon dated so does not distinguish between new and old
- Discovery also involves ppm -> ppb -> ppt analysis levels
- (WHY ? Because we can)

# MODERN MSDS

## 2 Hazards identification

- Classification of the substance or mixture
- Classification according to Regulation (EC) No 1272/2008  
Carc. 2 H351 Suspected of causing cancer. Route of exposure: Inhalative.

- 
- Classification according to Directive 67/548/EEC or Directive 1999/45/EC  
Xn; Harmful  
R40: Limited evidence of a carcinogenic effect.

- 
- Label elements
  - Labelling according to Regulation (EC) No 1272/2008  
The product is classified and labelled according to the CLP regulation.
  - Hazard pictograms



GHS08

- Signal word Warning
- Hazard-determining components of labelling:  
Antimony trioxide

## MSDS DETAIL

- Other hazards
- Results of PBT and vPvB assessment

- PBT:

1163-19-5 | bis(pentabromophenyl) ether

(Contd. of page 1)

- vPvB:

1163-19-5 | bis(pentabromophenyl) ether





## MSDS DETAIL

**3 Composition/information on ingredients**

- Chemical characterization: Mixtures
- Description: Aqueous dispersion of antimony trioxide and halogenated compounds

## - Dangerous components:

CAS: 1163-19-5 EINECS: 214-604-9 Reg.nr.: 01-2119472302-47	bis(pentabromophenyl) ether	Non-classified vPvB substance. Non-classified PBT substance.	25-50%
CAS: 1309-64-4 EINECS: 215-175-0 Reg.nr.: 01-2119475613-35	Antimony trioxide	 Xn R40 Carc. Cat. 3  Carc. 2, H351	10-25%

## - SVHC

1163-19-5	bis(pentabromophenyl) ether
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- additional information For the wording of the listed risk phrases refer to section 16.

## Let someone else have the last word(s)

- Beginning October 28, furniture and other products in California containing the flame retardant TDCPP or chlorinated Tris or must have a Prop 65 warning label stating, "This product contains a chemical known to the state of California to cause cancer." Chlorinated Tris, which my research with Bruce Ames help remove from baby pajamas (sic) in 1977, has been a commonly used flame retardant in furniture and baby product foam. Sadly enough, chlorinated Tris and Firemaster 550, as used in furniture do not provide a fire safety benefit. Thanks to California's outdated flammability standard, we appear to be going from a carcinogen to an obesogen in our furniture.

## Epic fail! (not my title!)

- Arlene Blum, a visiting scholar in chemistry at the *University of California, Berkeley*, and executive director of the *Green Science Policy Institute* says: "U.S. manufacturers treat furniture with... either tris (2,3,-dibromopropyl) phosphate, a known cancer-causing agent, or a trademarked mix of four chemicals called Firemaster 500"... "In the U.S., we the have highest levels of flame retardants in our dust and in our bodies." But there's little evidence that these chemicals are making a difference in the number of fires that take place. In fact, Blum says, "[chemical] flame retardants aren't very useful in reducing fire hazards because they slow fires by just a few seconds."

INPUT TO THE  
BIS FFR REVIEW  
2015

## Why the concern?

- Long term impacts of BFRs
- Some meet the criteria for Persistent Organic Pollutants (POPs)
  - **Persistent**: widespread environmental contamination
  - **Bioaccumulative**: found in fatty tissue & human milk
  - **Toxic**: range of adverse health effects in experimental animals
- They delay, not stop fires. May make them more dangerous
  - More smoke, more CO, more toxic chemicals (including dioxins)
- Regulatory activities
  - **PBB** use and manufacture banned in the 1970s
  - PBDE manufacture banned in mid-2000s
  - PBDEs listed under the Stockholm Convention in 2011
  - **Deca-BDE** assessed as SVHC under REACH
  - HBCDDs now listed in Stockholm , with some exempt uses

## Are BFRs the new dioxins?

- Some BFRs are POPs
- BFRs major part ( $\frac{1}{3}$ - $\frac{1}{2}$ ) of annual Dioxin Symposium (plus their own biennial symposium)
- Widespread in the environment
- BFRs are present in the food chain
- Exposure through household dust
- Found in human blood and breast milk
- Levels in food are generally low, but
- Toxicological concerns have been raised
- Also, a new generation of BFRs is emerging
- Further monitoring is needed
- The Commission *MAY* consider limits in food

## MY EXPERIENCE

- Production of textiles in the UK for the FFR has been largely based on the use of ATO and BFR
- HBCDD was more effective than DecaBDE but is going/has gone POP
- Use of DMPPA declined rapidly but phosphorylation techniques are still used – particularly in schedule 3 interliners
- Use of microencapsulated P systems are seen as a “cheat” in some quarters
- TDCPP systems have grown since SVHC listing for DecaBDE
- Plasticisers used are a grey area?

## WHAT CAN WE DO?

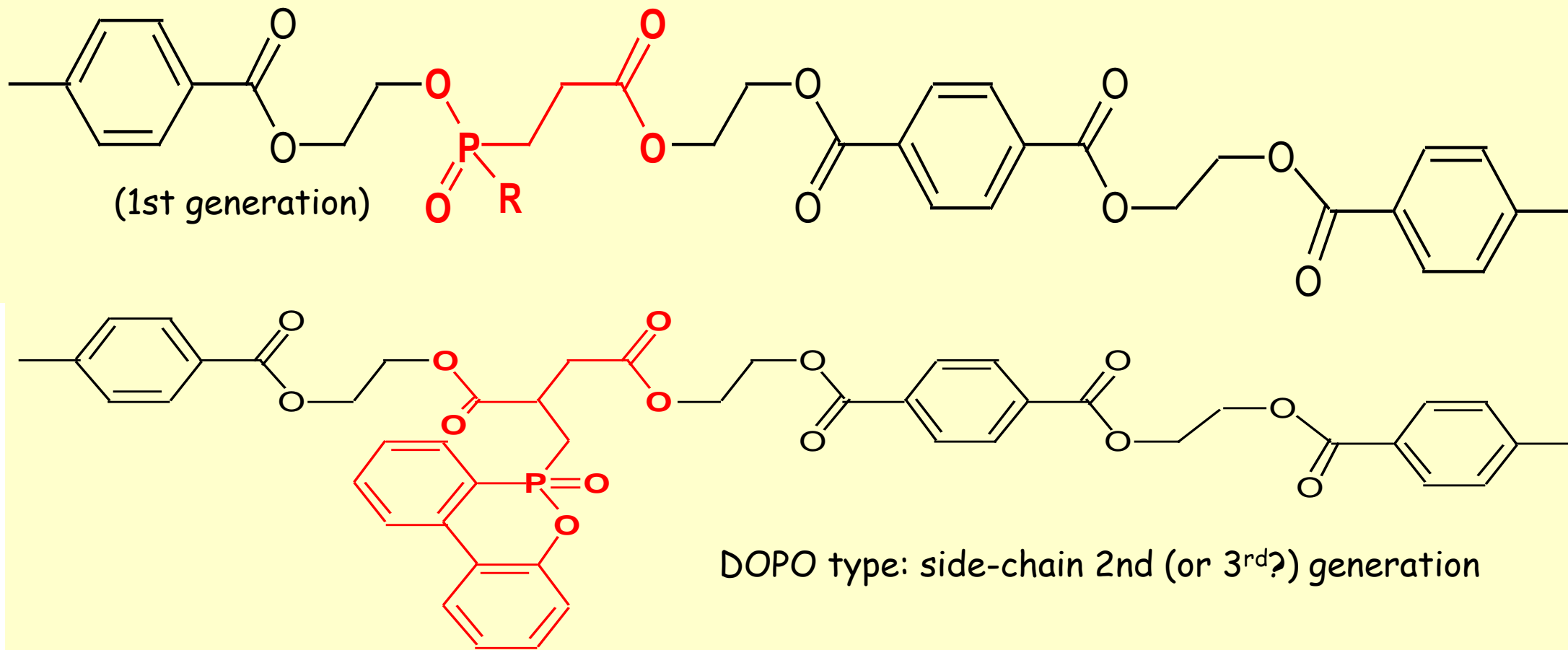
- CAN WE DIFFERENTIATE BETWEEN DISCOVERY LEVELS AND EFFECT LEVELS FOR ENV AND HH?
- PERCEPTION IS NOT THE SAME AS SCIENCE BASED ASSESSMENT
- REACH IS NOT A DEFINITIVE PROCESS IN THESE CIRCUMSTANCES
- WHEN THEY SAY FR's WHICH ONES DO THEY MEAN?
  - ANSWER: IT DEPENDS WHAT THEY ARE TALKING ABOUT

## A TECHNICAL SOLUTION?

- At present it is normal to choose a textile comprising more than 4 fibres including PP and cellulosic which require the use of very strong FR systems and gas phase activity is essential
- Based on what I have described it is important to understand that it is possible to choose fibres and/or combinations that are easier to treat
- This approach has not yet figured in the BIS FFR Review process
- HAS ANYONE A REALLY INSOLUBLE PHOSPHORUS SYSTEM?



## 9,10-DIHYDRO-9-OXA-10-PHOSPHENANTHRENE-10-OXIDE a.k.a. DOPO



fretwork

Thank you for listening

fretwork

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