An evaluation of the sustainable use of halogenated/antimony trioxide flame retardant systems.

Karen Janssens, Campine

AMI Fire Resistance in Plastics

Köln, Dec 2019

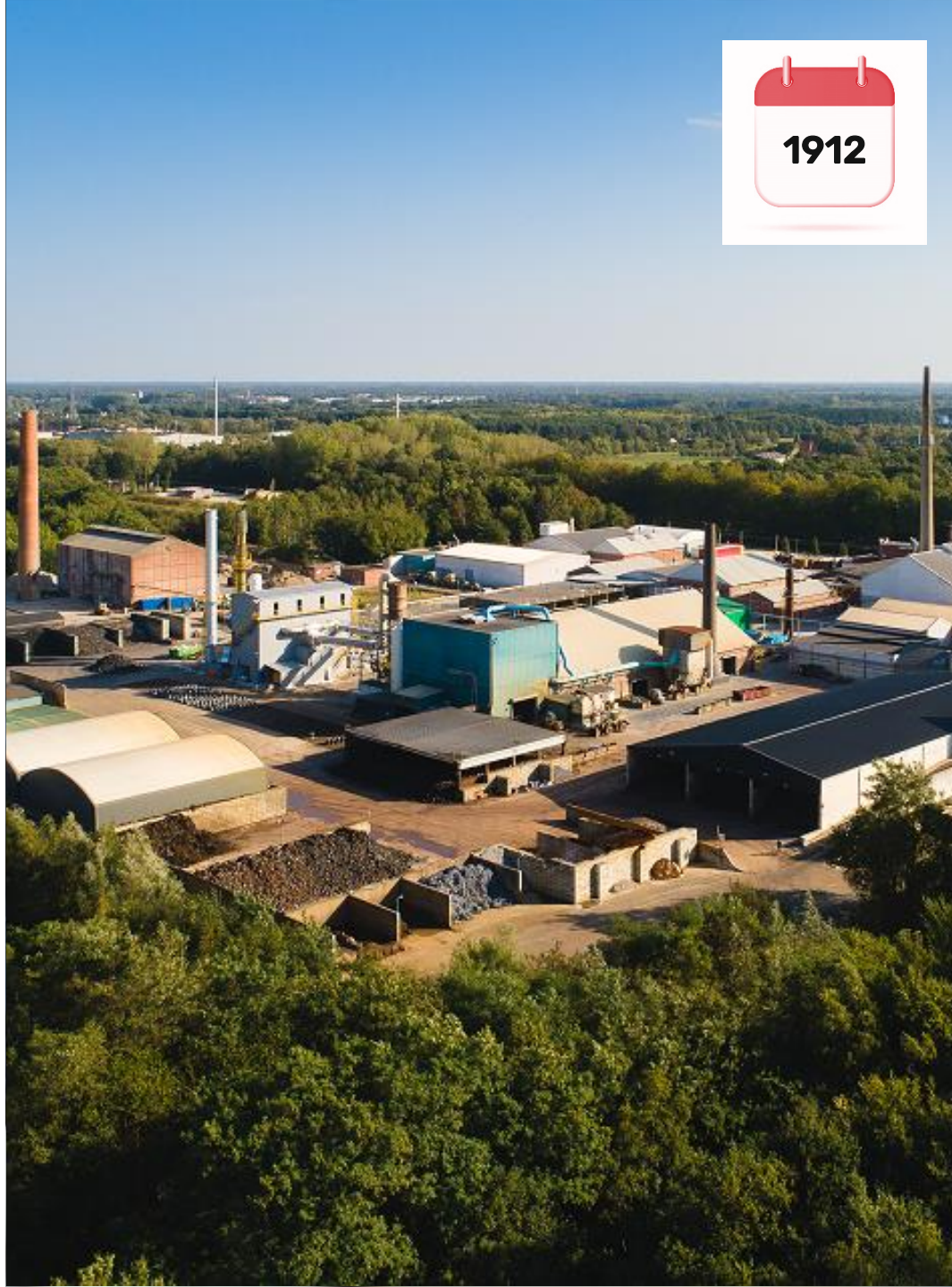
About Campine

Metals recycling

- 60.000 tons recycled Pb
- 1.500 tons recycled Sn, Sb, Ag, Au

Specialty Chemicals

- 12.000 tons Sb_2O_3
- 6.500 tons FR masterbatches



Use of Flame Retardants in Plastics

Conventional flame retardant formulations are based on halogenated substances.

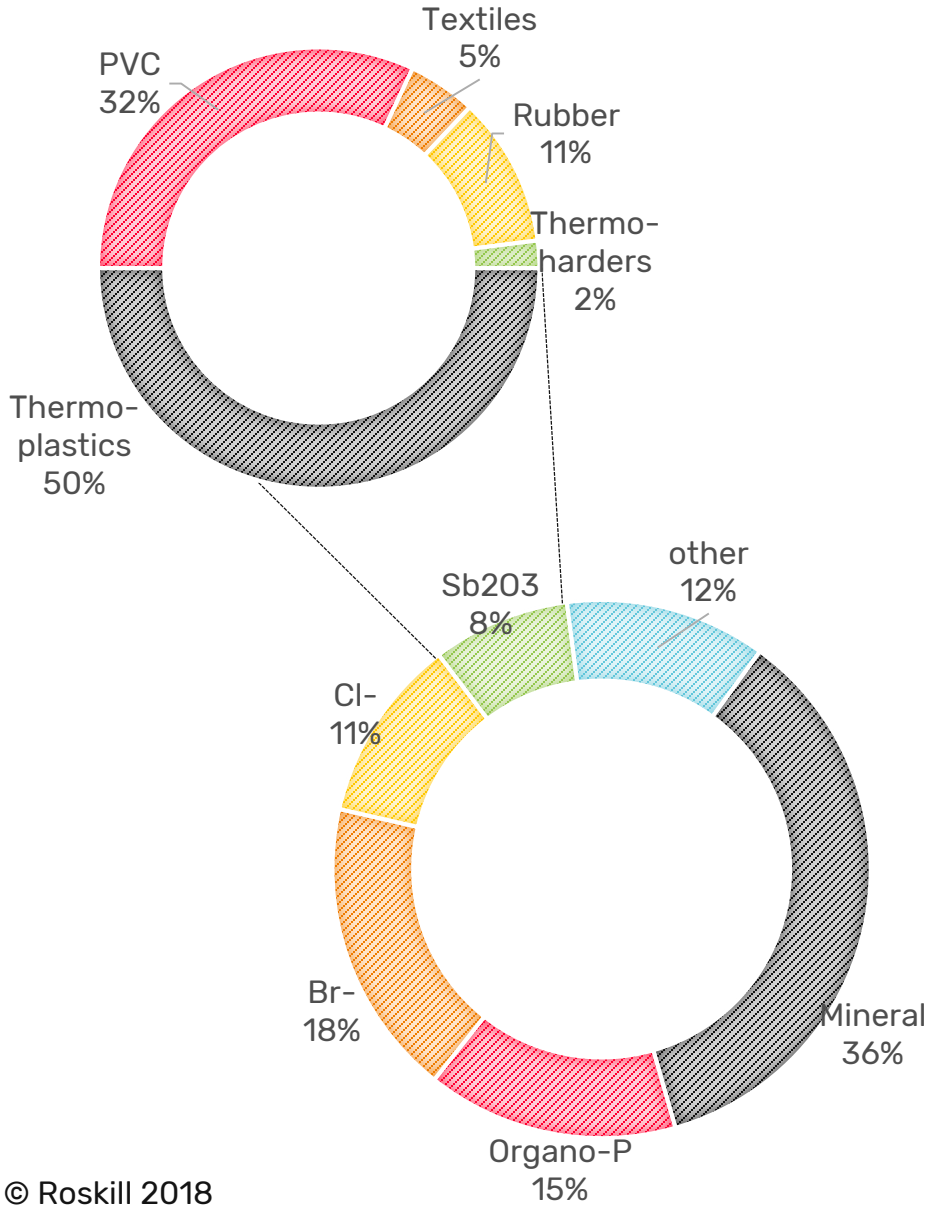
- effective in low doses
- minimal impact on the physical properties of the polymer
- have a good price / performance ratio.

Flame retardancy of halogens can be boosted by the use of different synergists

- Sb_2O_3 is by far the most frequently used synergist

Use of Flame Retardants in Plastics

- 29% of the flame retardants used are halogenated
- Sb_2O_3 is the most used synergist in combination with halogenated flame retardants
- Most of the Sb_2O_3 is used in thermoplastics



Selection of Flame Retardants

Selection of flame retardants comprise different aspects

- Flame retardant norm to be reached
- Other properties beside the FR
- Cost of the solution
- Health & Environmental awareness
- Sustainability

In order to make such a selection, appropriate risk-management is necessary

SAFR® methodology

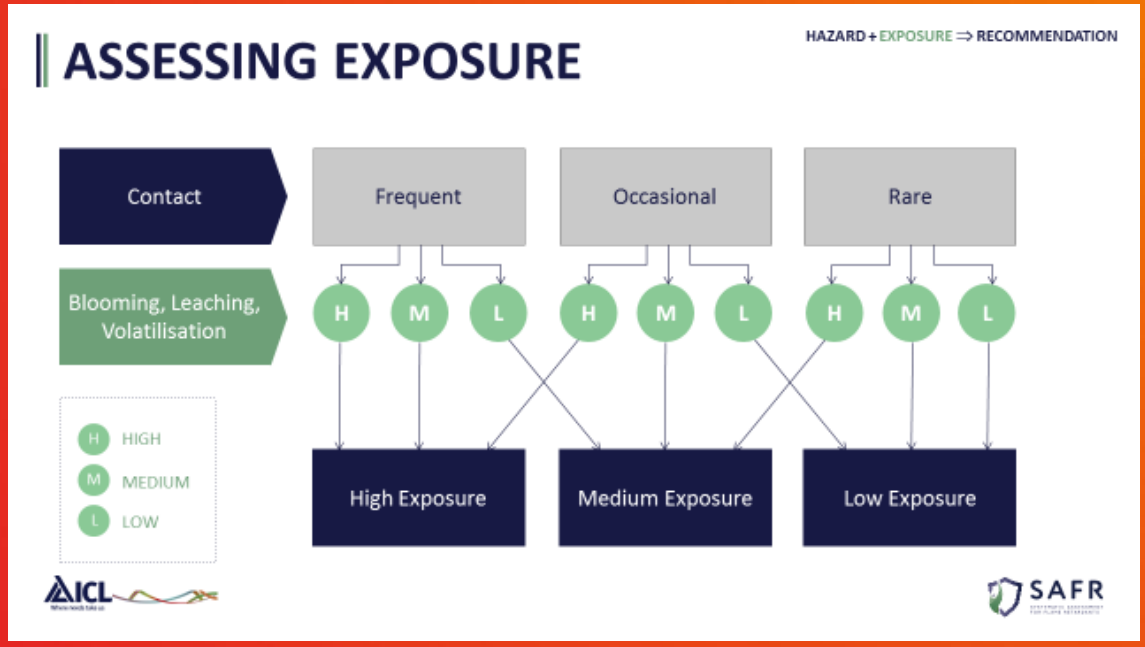
ICL, a leading producer of brominated and organophosphorus-based Flame Retardants (FRs)

- SAFR® = Systematic Assessment of Flame Retardants
- Sb_2O_3 is not part of the SAFR® evaluation

Our study

The aim of our study is to make a similar assessment of the use of Sb_2O_3 in different halogenated flame retardant formulations

SAFR®



SAFR® the way to more sustainable fire safety solutions,
ICL, Animony day Nov 2018

HAZARD + EXPOSURE ⇒ RECOMMENDATION

HAZARD / EXPOSURE	LOW	MEDIUM	HIGH	UNACCEPTABLE
LOW POTENTIAL	RECOMMENDED	RECOMMENDED	ACCEPTABLE	TO BE PHASED OUT
MEDIUM POTENTIAL	RECOMMENDED	ACCEPTABLE	NOT RECOMMENDED	
HIGH POTENTIAL	ACCEPTABLE	NOT RECOMMENDED	NOT RECOMMENDED	

BLOOMING

- Preparation of **plastic samples** according to known formulation
- **Ageing** of samples at 70°C for 35 days
- **Sweeping** of samples
- **Analysis** of filters for bromine

Blooming levels $\mu g Br^-/cm^2$: **Low/No: $Br^- \leq 1$, Medium: $1 < Br^- \leq 10$, High: $Br^- > 10$**

Sb_2O_3 Hazards

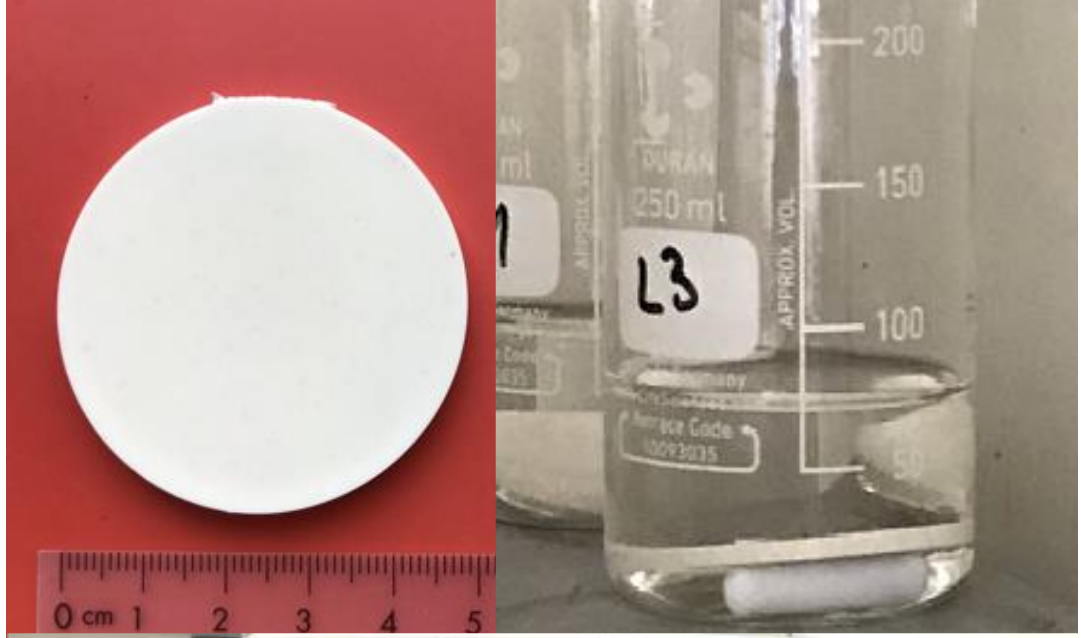
- GHS Classification (29 CFR 1910.1200)
  - H351 pot.carc class 2
  - H373 STOT RE lung (voluntary listing)
- GHS Label Elements

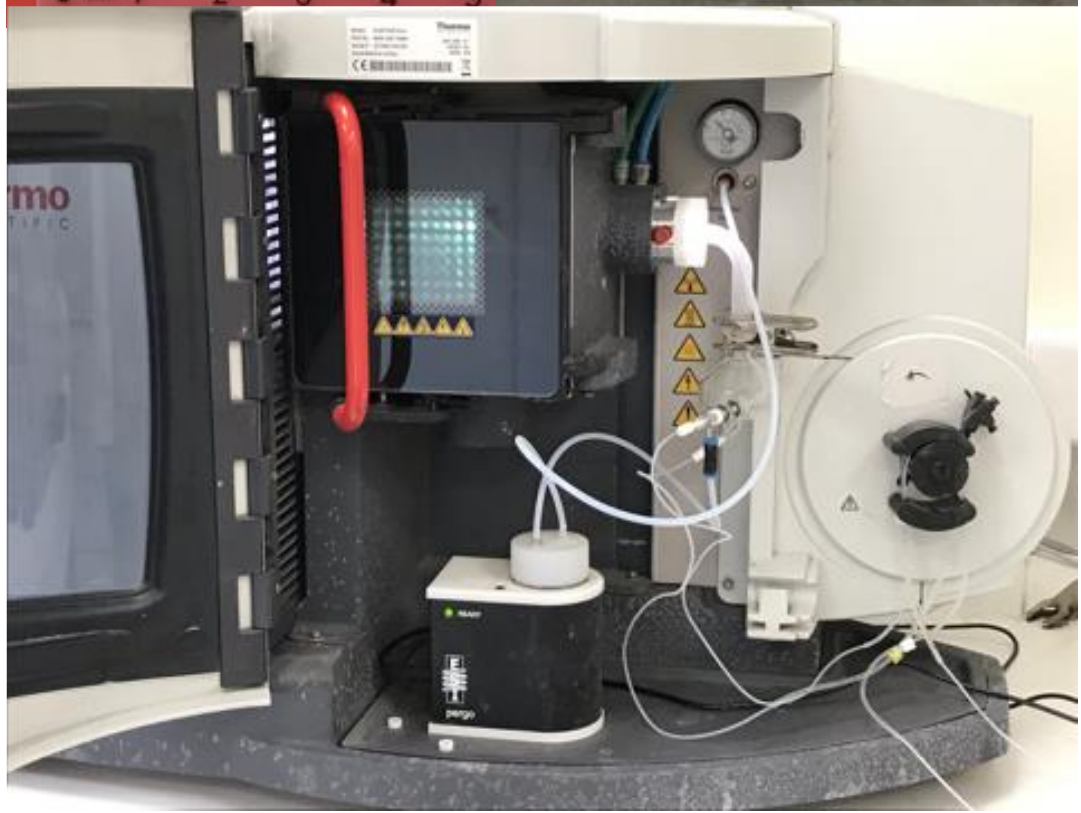
- Sb_2O_3 has no environmental classification

Blooming of Sb_2O_3

- Preparation of plastic samples
- Ageing at 70°C
- Samples are immersed and stirred in Ultrapure H_2O @ 38°C for 1h
- Addition of HBr
- Solution is analysed with ICP-OES

Measurements Sb_2O_3 ($\mu g/cm^{2)}$
at 0, 14 and 30 days





Formulations

Polymer	Flame retardant*	Synergist
LDPE	DBDPE	Sb_2O_3
LDPE	DBDPE	
PPco	BDDP of TBBA	Sb_2O_3
PPco	BDDP of TBBA	
HIPS	BDDP of TBBA	Sb_2O_3
HIPS	BDDP of TBBA	
PA6	Br Polystyrene	Sb_2O_3
PA6	Br Polystyrene	
PBT	Br Polyacrylate	Sb_2O_3
PBT	Br Polyacrylate	

*Flame retardant		ICL Productname
DBDPE	Decabromodiphenyl ethane	FR1410
BDDP of TBBA	Tetrabromobisphenol A of dibromopropylether	FR720
Br Polystyrene	Brominated Polystyrene	FR803
Br Polyacrylate	Brominated Polyacrylate	FR1025

Blooming of Br

Results are kindly generated by ICL

Blooming levels μBr/cm^2: no/low ≤ 1, 1 < medium ≤ 10, high > 10

Formulation	t_0 μg Br/cm^2	14 days μg Br/cm^2	35 days μg Br/cm^2
LDPE/DBDPE/Sb_2O_3	No/Low	No/Low	No/Low
LDPE/DBDPE	No/Low	No/Low	No/Low
PPco/ BDDP of TBBA /Sb_2O_3	No/Low	No/Low	Medium
PPco/ BDDP of TBBA	No/Low	No/Low	Medium
HIPS/ BDDP of TBBA /Sb_2O_3	No/Low	No/Low	No/Low
HIPS/ BDDP of TBBA	No/Low	No/Low	No/Low
PA6/Br Polystrene/Sb_2O_3	No/Low	No/Low	No/Low
PA6/Br Polystyrene	No/Low	No/Low	No/Low
PBT/Br Polyacrylate/Sb_2O_3	No/Low	No/Low	No/Low
PBT/Br Polyacrylate	No/Low	No/Low	No/Low

Conclusions
Br Blooming

- Presence of Sb_2O_3 has no effect on the Br blooming out of the investigated samples

- No/Low blooming for
  - HIPS/FR720/Sb_2O_3
  - PA6/FR803/Sb_2O_3
  - PBT/FR1025/Sb_2O_3
  - LDPE/FR 1410/Sb_2O_3

- Medium blooming for
  - PPco/FR 720/Sb_2O_3 (despite low addition levels)

Blooming of Sb_2O_3

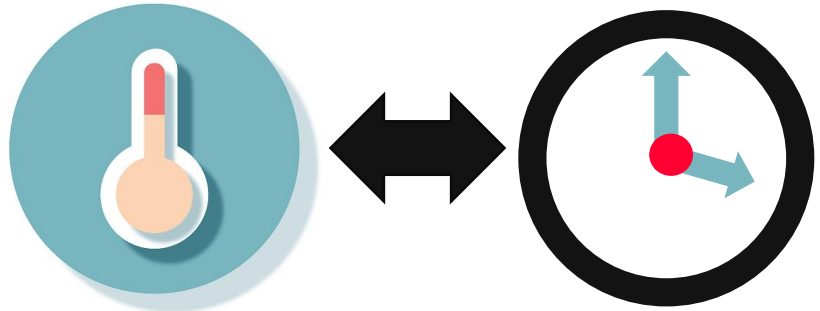
Formulation	t_0 µg Sb_2O_3/cm^2	14 days µg Sb_2O_3/cm^2	35 days µg Sb_2O_3/cm^2
LDPE/DBDPE/Sb_2O_3	< 2	< 2	<1
LDPE/DBDPE	< 1	< 1	< 1
PPco/ BDDP of TBBA /Sb_2O_3	< 1	< 1	< 1
PPco/ BDDP of TBBA	< 1	< 1	< 1
HIPS/ BDDP of TBBA /Sb_2O_3	< 1	< 1	< 1
HIPS/ BDDP of TBBA	< 1	< 1	< 1
PA6/Br Polystrene/Sb_2O_3	< 2	< 2,5	< 2
PA6/Br Polystyrene	< 1	< 1	< 1
PBT/Br Polyacrylate/Sb_2O_3	< 1	< 1	< 1
PBT/Br Polyacrylate	< 1	< 1	< 1

Conclusions
Sb_2O_3

- Max Sb_2O_3 blooming for all tested samples is < 2,5 µg/cm²
- Blooming < 1µg/cm² of Sb_2O_3 out of
  - PPco/FR720/Sb_2O_3
  - HIPS/FR720/Sb_2O_3
  - PBT/FR1025/Sb_2O_3
- Blooming < 2,5µg/cm² of Sb_2O_3 out of
  - LDPE/FR1410/Sb_2O_3
  - PA6/FR803/Sb_2O_3
  - No extra blooming after ageing

Sb_2O_3 blooming

In perspective

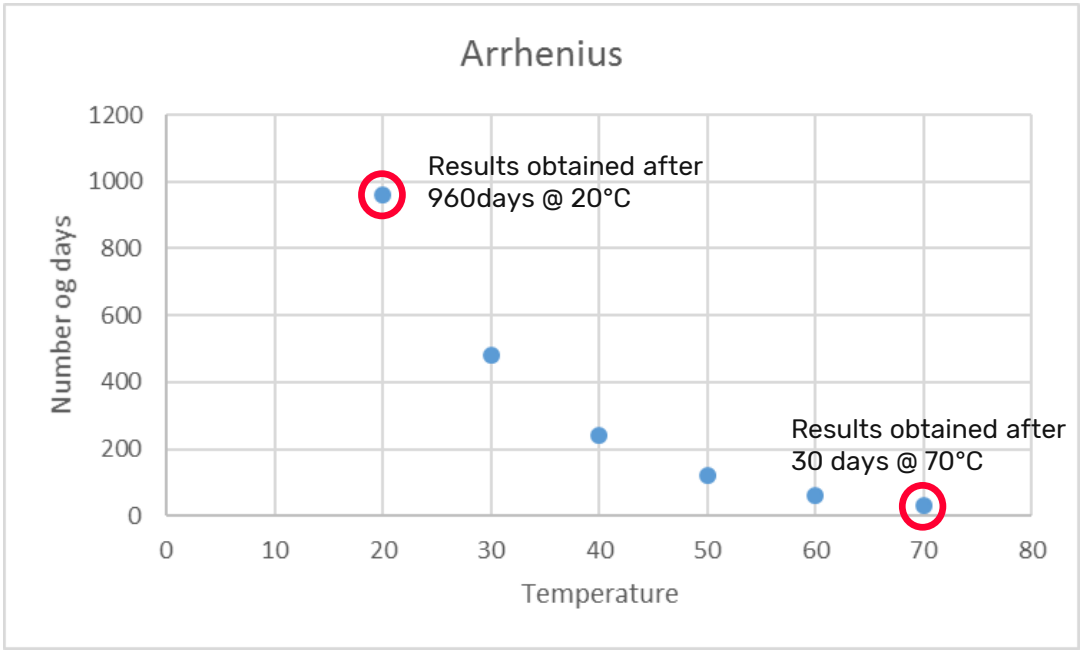


The dependence of migration processes in polymers on the temperature are described by Arrhenius.

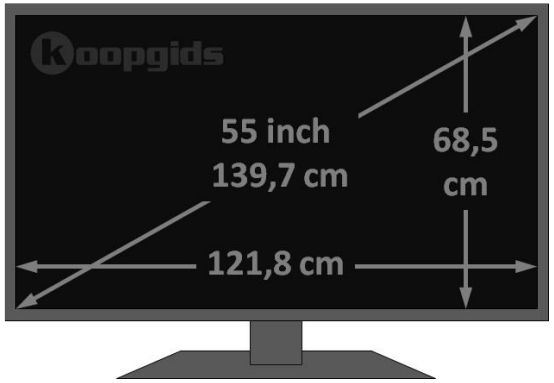
Results obtained
after 30 days @ 70°C

≈

Results obtained
after 960 days (2,6 years) @ 20°C



Sb_2O_3 Blooming
In perspective



Regulation on dust

- Germany OEL/TLV: 0,005 mg/m3 respirable fraction
- Rest of Europe OEL/TLV: 0,5mg/m3 inhalable fraction

The bloomed amount Sb_2O_3 out of the back panel of a 55 inch television is 500 / 50.000 times smaller

- assumed room size: 10m x 6m x 3m
- over 2,6 years

Conclusions

- Real life formulations have been used to determine potential risk of halogenated FR and Sb_2O_3 exposure in different applications
- Presence of Sb_2O_3 has no effect on the Br blooming
- Sb_2O_3 blooming after 30days for all tested samples is < 2.5 µg/cm^2
  - Which is far below any workplace or product limits in the EU and beyond

Next steps

Product stewardship

- Continuous responsibility for all producers
- Promote safe use of Sb_2O_3 (small bags, wetted, masterbatches)

Convey the message to ROHS, REACH, …

Thank you

Rien Repriels, Campine
Gitte Snoeys, Campine

Marc Leifer, ICL-IP
Smadar Admon, ICL-IP

ICL
Where needs take us

SAFR
SYSTEMATIC ASSESSMENT
FOR FLAME RETARDANTS


Thank you for your
kind attention
Campine