#### Advanced offerings of antimony trioxide

# Positioning ATO versus the pallet of synergists

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# Agenda

- Intro to Campine
- The pallet of synergists for halogenated flame retardants
- Study of synergists in PVC

Ø LOI

- Cone calorimeter
- Study of synergists in PE
  - 🖉 LOI,UL 94
  - Cone calorimeter
- Study of synergists in PA
  - 0 UL 94
  - Cone Calorimeter
- Conclusion

# **Campine history**

- 1912 Foundation Campine
- 1924 Start-up of antimony oxide production
- 1965 Focus on fire retardancy for antimony trioxide
- 1987 Launch of dust-free ATO masterbatches
- 1991 ISO 9001-certification
- 1998 Launch of first halogen-free masterbatches : Mastertek
- 2000 Campine founding member of i2a & lead REACH-registrant for ATO
- 2004 ISO 14001-environmental certification
- 2011 Investment in Sb-metal recovery
- 2012 100 years of Campine
- 2013 New exploitation permit for next 20 years
- 2015 Doubling capacity of Metal recovery
- 2016 Campine participating in bio-diversification project



# Sustainable antimony trioxide

#### Availability of Antimony

- Sufficient presence in earth crust, urban mining and metal recovery
- Growing number of operational mines in multiple continents
- Roasting activities concentrated in limited territory which creates monopoly
  - ⇒ Breakthrough in Sb-reduction technology: European project submitted to support innovative process & Metal recovery technologies
  - ⇒Campine leading company in Metal recovery and sustainable antimony

# Sustainable antimony trioxide

Antimony Association

International

Health & Safety



- Hazard : Particle effect (Hansen study):
  - **Fine dust inhalation** leads to lung overload and lung toxicity, which has triggered a carcinogenic response in certain test animals through inflammation and hypoxia (NTP)
- Risk = Hazard \* Exposure avoid exposure : Zero risk !
  - => Campine leading company in advanced **dust-free solutions**.
  - => Campine eliminates the risks : wetted ATO, dispersion, monobatches, sealed dosable bags

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## Sustainable antimony trioxide



# The pallet of synergists

- Campine MT (ATO) is functional as synergist in the gas phase for halogenated FR-additives. It functions as a radical stabiliser and delays the ignition
- Ø Alternative mineral & organic additives claim equivalent functionality
- Research is focused on question whether these alternative products are functional replacements
- Ø 4 groups of additives are studied:
  - Ø Borates
  - Ø Organic additives
  - Stannates
  - Silicones

# Tests in PVC plastisol

Ø Formulation:

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- Ø 95 % PVC + Plasticiser
- 5% Synergist
- Coating of PVC Plastisol :
  - 🖉 LOI-test : 500µm

Oxygen Index : ISO 4589-2, ASTM D2863

Cone calorimeter test : 35kW Standard : ISO 5660





#### Evaluation of synergists in PVC LOI (oxygen index)

Plasticised PVC: 500µm sheets with 5% synergetic additive



Campine MT has highest LOI = better fire retardant properties => fire stops even in 27% oxygen enriched air

## Evaluation of synergists in PVC LOI (oxygen index)

Plasticised PVC: 500µm sheets with 5% synergetic additive: 50/50



#### Evaluation of synergists in PVC Cone calorimeter: helicopter view



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Campine MT is outperforming alternatives in all fire retardant properties

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# Summary of PVC formulations

Campine MT <u>outperforming</u> all alternative synergysts.

- When combining Campine MT with other additives the LOI values lift up again to the generic level of the ATO : the additives are <u>not</u> <u>disturbing the radical stabilising</u> function of Campine MT in the gas phase.
- Complementary functions : Stannate as stand- alone has a weak performance. In combination with Campine MT <u>complementary</u> <u>smoke reduction</u> is obtained.

# Tests in polyethylene formulation

- Ø Formulation :
  - Ø 80 % PE
  - Ø 15% BR
  - 5% synergist



- Injection molded parts :
  - C LOI –test : 2mm
  - Cone calorimeter test : 35KW/ 2mm
  - O UL94 -test : 2 mm

## Evaluation of synergists in PE LOI (oxygen index)

PE bars 2mm: formulation PE/BR/Synergist: 80/15/5



Campine MT has higher LOI => better "extinguishing" properties => fire stops even when 30% oxygen enriched air is available

#### Evaluation of synergists in PE UL 94 testing

PE bars 2mm: formulation PE/BR/Synergist: 80/15/5



## Evaluation of synergists in PE cone calorimeter (35kW): heat release

PE sheets 2mm: formulation PE/BR/Synergist: 80/15/5

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Campine MT showing lowest max Heat Release Rates & Total Heat Release

### Evaluation of synergists in PE Cone calorimeter: max rate of HR & total HR

PE bars 2mm: formulation PE/BR/Synergist : 80/15/5-> 80/15/2,5 & 2,5



When Campine MT is 50/50 added to alternatives , max HRH & THR reduces.

### Evaluation of synergists in PE Cone calorimeter: time to ignition (by spark)

PE bars 2mm: formulation PE/BR/Synergist: 80/15/5



Longer time to ignition of borates with ceramic forming of intumescent layer. This can be a valuable complementary effect.

#### Evaluation of synergists in PE Cone calorimeter : helicopter view

#### PE sheets 2mm: formulation PE/BR/Synergist: 80/15/5



## Summary of PE formulations

Campine MT <u>outperforming</u> all other synergysts in fire extingishing & fire retardant properties in LOI, UL 94 and Cone Calorimeter tests.

Icol LOI tests show that Campine MT can be combined with proposed alternatives: they <u>do not disturb</u> the functionality of ATO.

Alternative synergists as stand–alone have weak performance. When added to Campine MT, <u>complementary</u> functions are obtained: intumescence & smoke reduction.

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# Tests in polyamide formulation

- Ø Formulation:
  - Ø 80 % PA
  - Ø 15% BR
  - 5% synergist
- Injection molded parts:
  - UL94 -test :1,6 & 3,2mm
  - Cone calorimeter test: 35 kW/2mm

#### Evaluation of synergists in PA UL94 testing

PA bars 3,2mm: formulation PA/BR/Synergist: 80/15/5



#### Evaluation of synergists in PA UL94 testing

PA bars 1,6mm: formulation PA/BR/Synergist: 80/15/5





#### Evaluation of synergists in PA Cone calorimeter: time to ignition (by spark)



Campine MT has longest time to ignition. The charring effects of borates not visible in PA.

#### Evaluation of synergists in PA Cone calorimeter: heat release

PA sheets 2mm: formulation PA/BR/Synergist: 80/15/5



Alternative additives are showing higher max Heat Release Rates and higher Total Heat Release .

#### Evaluation of synergists in PA Cone Calorimeter : MAHRE

PA bars 2mm: formulation PA/BR/Synergist: 80/15/5 --> 80/15/2,5/2,5



When 50/50 replaced by ATO, MAHRE reduces for most formulations

#### Evaluation of synergists in PA Cone Calorimeter: helicopter view

PA sheets 2mm: formulation PA/BR/Synergist: 80/15/5



# Summary of PA formulations

The UL test is the ruling norm for electric & electronic equipment.

- The <u>UL94 test</u> show that Campine MT reaches the V0 level with minimal addition levels. None of the tested alternatives approaches this performance. Doubling addition levels of alternatives only works with the organic additive.
- Cone Calorimeter data MAHRE, THR and max RHR confirm and quantify these findings: Campine MT has best in class heat reduction performance
- Best results are obtained when the tested additives are used as a supplement /not as substitution to the regular Campine MT levels. They bring <u>Smoke reduction</u> function.





- The definition of <u>co-synergists</u> is capturing best the value of the tested products. The proposed alternatives cannot replace Campine MT as synergist, but show interesting <u>complementary properties</u> like smoke reduction, retraction and charring.
- Campine has all these products in the range, offered as highly <u>concentrated monobatch</u> in thermoplastic matrix.
- Campine offers fully formulated FR-masterbatches with Campine MT and co-synergists.

Thanks for your attention !