# Importance of high purity antioxidants seen from a polyolefin producer

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Innovation through Insight

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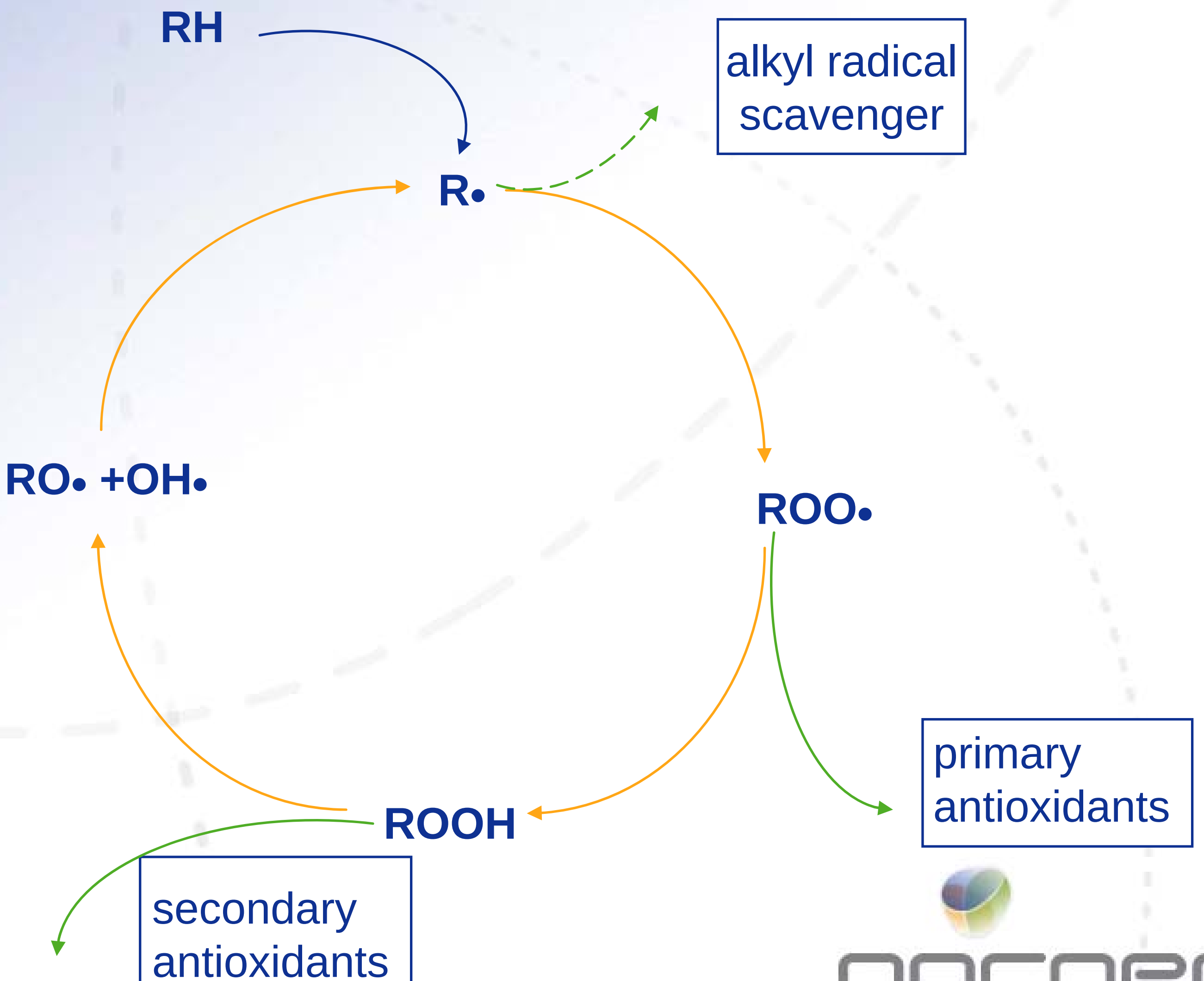
- Short review of polyolefin degradation and stabilisation
- Main mechanisms of phenolic AOs and phosphites
- Process stabilisation of PE and PP

- PART 2:
- Production processes and specifications of commercial core AO
- GCMS investigation of water extracts of lab. produced PE
- Unexpected reaction in HDPE with silica supported Cr-catalysts

- Conclusion

# Degradation and Stabilisation of polymers

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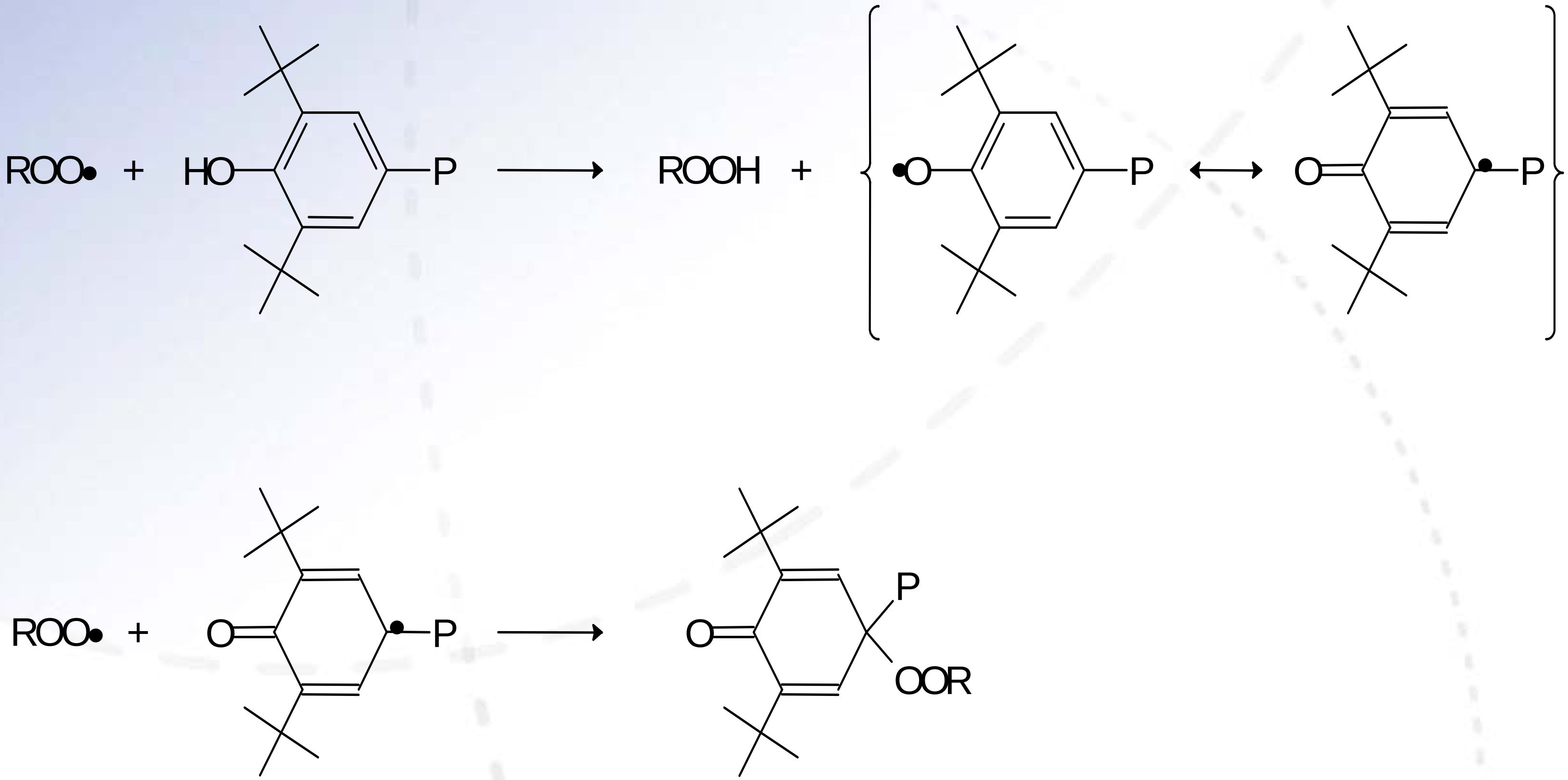
# Reaction mechanism of phenolic AO



# Reaction mechanism of phosphites

Main reaction

| | | |
|---|---|---|
| **$(RO)_3$-P + R'-OOH** | $\rightarrow$ | **$(RO)_3$-P=O + R'-OH** |
| phosphite | | phosphate |

Hydrolysis (possible side reaction)

| | | |
|---|---|---|
| **$(RO)_3$-P + $H_2O$** | $\rightarrow$ | **$(RO)_2$-P-(O)H + ROH** |
| **$(RO)_2$-P-(O)H + $H_2O$** | $\rightarrow$ | **RO-P-$(O)_2(H)_2$ + ROH** |
| **RO-P-$(O)_2(H)_2$ + $H_2O$** | $\rightarrow$ | **$H_3PO_3$ + ROH** |

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# Testing of process stability

Compounding

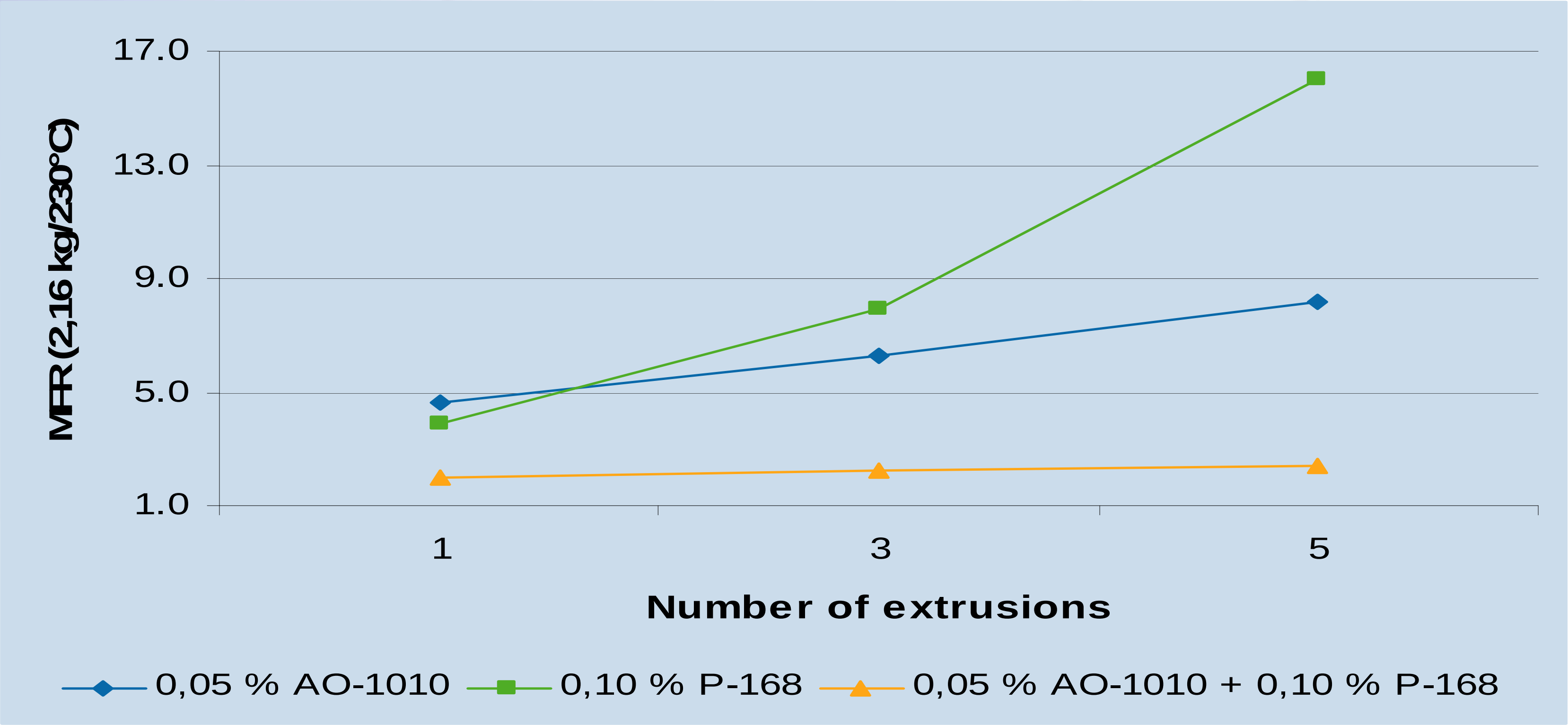
- Unstabilised polymer powder and additives are premixed
- Compounding is done on a twin-screw extruder
- Nitrogen flush is used to simulate inert conditions used in the plants

Converting process

- Process stability is checked with multiple extrusions in air atmosphere
- This is simulating the conditions used at converters
- Influence on MFR and YI (yellowness index) is checked

# Figure 1: PP homopolymer - multiple extrusions at 260°C

Recipes contain 0,05 % Ca-stearate



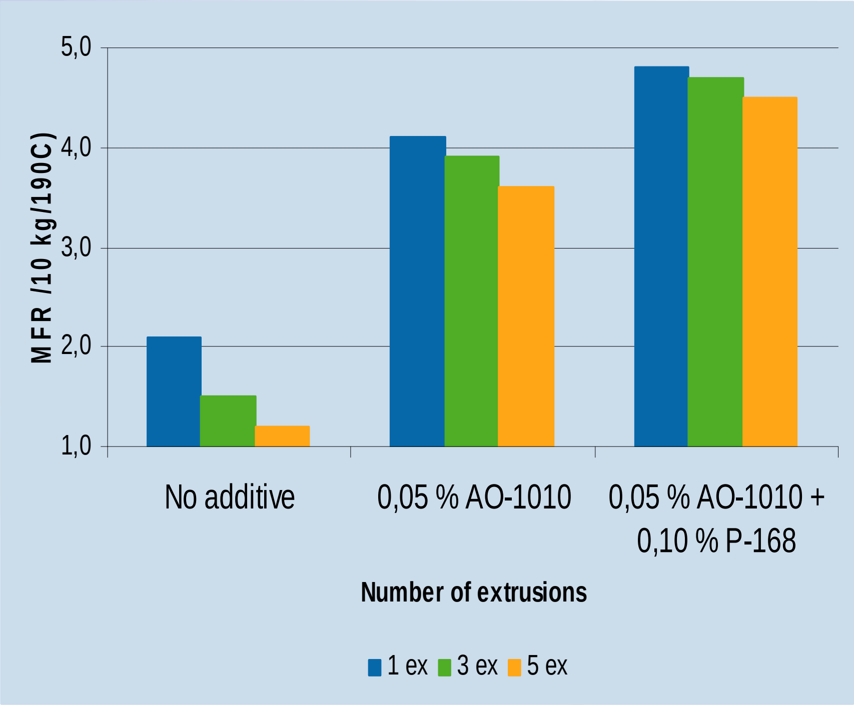
# Synergistic effect by combining AO-1010 and P-168 as in Figure 1

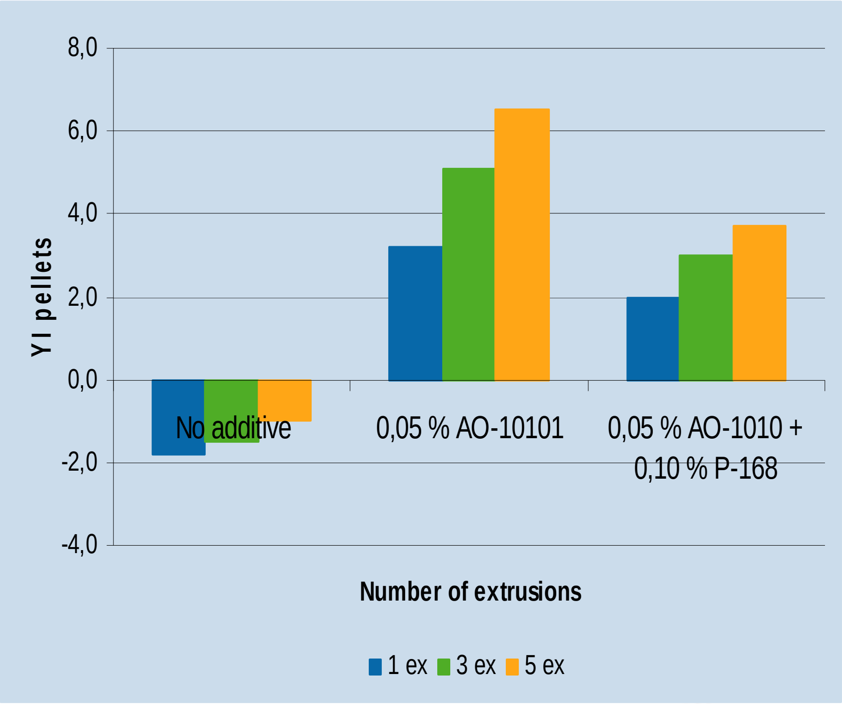
$R'OO\bullet + Ph\text{-}OH \rightarrow R'OOH + Ph\text{-}O\bullet$

$(RO)_3\text{-}P + R'OOH \rightarrow (RO)_3\text{-}P{=}O + R'OH$

A combination of phenolic AO and phosphite takes care of both ROO• and ROOH

# Figure 2: HDPE (silica supported Cr-cat) multiple extrusions at 260°C



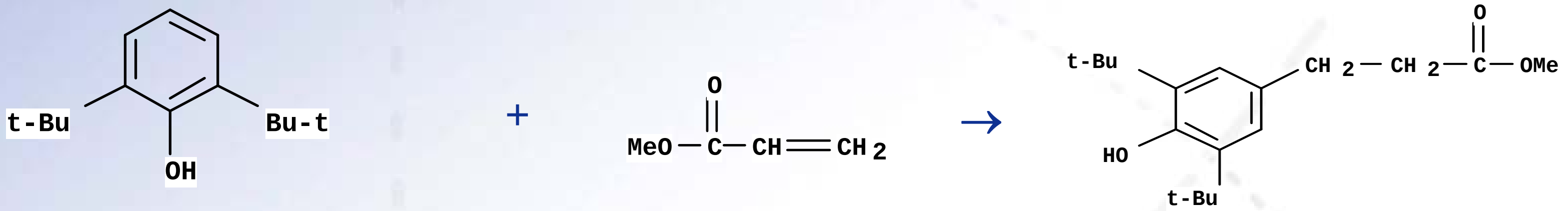



# Conclusion part 1 – general part

- Combination of phenolic AO and phosphite gives a synergistic system
- Phenolic AO contributes to yellowing
- Addition of P-based AO improves initial colour and colour stability

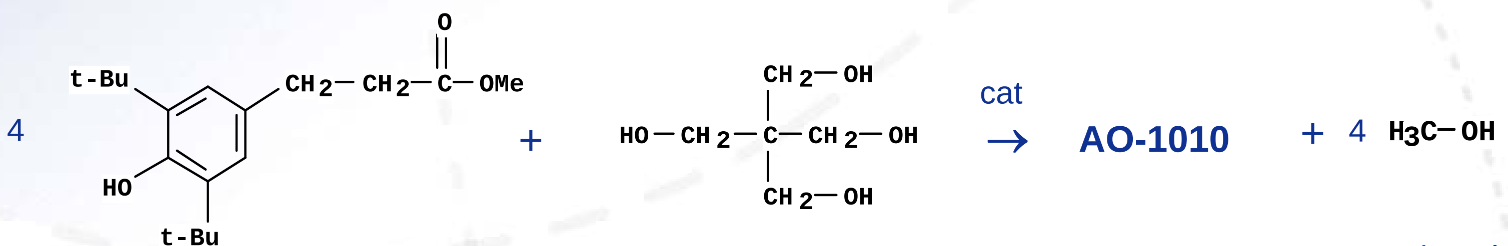
# Production process of AO-1010

1st Step



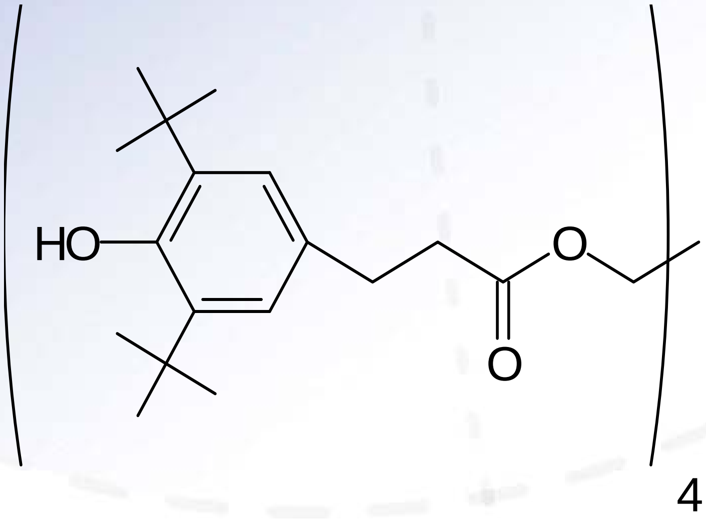
2,6-DTBP | Methyl acrylate | Intermediate

2nd Step



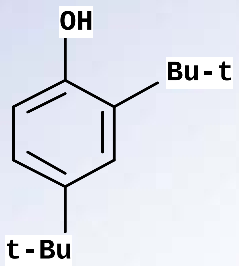

Pentaerythritol | Methanol

# AO-1010: Main component (a tetra-ester)




| Specification | (wt-%) |
|---|---|
| Assay | min. 98,0 |
| (Main component | min. 95,0) |
| Intermediate | not specified |
| Volatiles | max. 0,5 |
| Ash | max. 0,1 |

# Production process of P-168

3 

+ $PCl_3$ → **P-168** + 3 HCl

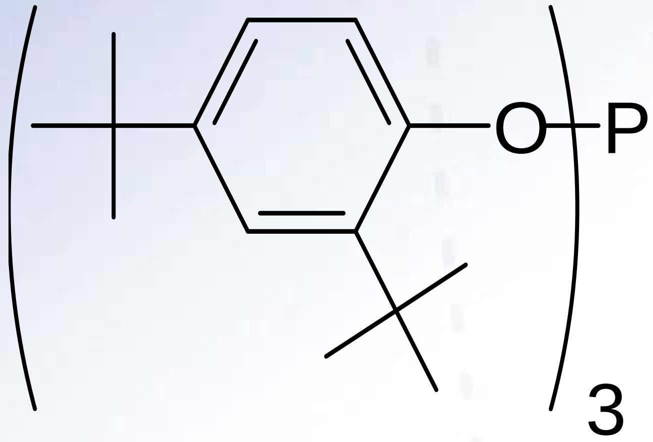
2,4-DTBP

Phosphorus trichloride

Hydrogen chloride

# P-168: Main product (a phosphite)

## Specification




| Specification | (wt-%) |
| --- | --- |
| Assay | min. 99,0 |
| 2,4-DTBP | max. 0,5 |
| Volatiles | max. 0,5 |
| Ash | max. 0,1 |

# Purity - Trends and background

- Increased focus on purity and tougher hygienic requirements in EU, but change of European Approval System (EAS) approach
- The new test method prEN 15768 “The GC-MS identification of water leachable organic substances from materials in contact with water intended for human consumption” will be sent for national enquiry 2008
- The test method is included to ensure that ‘unsuspected substances’, i.e. not specified in the formulation of the material, do not migrate into drinking water in significant amounts
- This ‘unsuspected substances’ may also originate from intermediates, by-products from e.g. additives

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# Plastic materials in contact with food

- The packaging producer has to fulfil article 3 of the Framework Regulation 1935/2004/EC
- This "general safety requirement" requires a risk assessment for food contact materials as such
- This includes all substances which are able to migrate from the food contact material into the food and that can influence the organoleptic properties of the packed food or endanger the health of the consumer
- For monomers and additives we can rely in that respect on the restrictions from the plastics directive (2002/72/EC + amendments)
- We can expect some future guidelines in EU on how to monitor that levels of NIAS (Non Intentionally Added Substances) are within acceptable limits

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# Model test of PE in contact with cold water

- Samples were compounded in lab.

| Sample | AO-1010 | P-168 |
|---|---|---|
| MDPE 1 | A | A |
| MDPE 2 | 4A | A |
| HDPE | A | A |

- Dosing level A is a typical dosing level used in PE
- 3 mm thick PE samples were made in lab.
- Samples were sent to an external institute for EAS GCMS analyses

# Migration and EAS-GCMS

- Samples were leached with unchlorinated water according to EN-12873-1 at a temperature of 23±2°C
- The third migration water was analysed for content of organic compounds according to prEN 15768
- The concentrations were then calculated according to

$$[D] = AD/AI * [I]$$

where

[D] is the concentration of a compound D (in µg/Liter);

AD is the peak area of a compound D;

AI is the peak area of the internal standard;

[I] is the concentration of the internal standard (in µg/Liter)

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# EAS GCMS results for PE samples in contact with cold unchlorinated water (µg/l)

| Compound | Substance no. | MDPE 1 | MDPE 2 | HDPE |
|---|---|---|---|---|
| Phenol, 4-ethyl- | I | 0 | 0 | 0 |
| Phenol, 4-tert-butyl- | II | 0 | 0 | 0 |
| 2,6-Di-tert-butyl Benzoquinone | III | 0 | 0 | 0 |
| **Phenol, 2,4-di-tert-butyl** | **IV** | **2,4** | **2,1** | **2,2** |
| 3,5-di-tert-butyl-4-hydroxy Styrene | V | 0 | 0 | 0 |
| 3,5-di-tert-butyl-4-hydroxy Benzaldehyde | VI | 0,6 | 0,7 | 0 |
| 3,5-di-tert-butyl-4-hydroxy Acetophenone | VII | 0,4 | 0,6 | 0,1 |
| 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione | VIII | 0,8 | 1,1 | 0,6 |
| **Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate** | **IX** | **1,3** | **4,2** | **0,4** |

**Factor 3.2 vs. MDPE 1**

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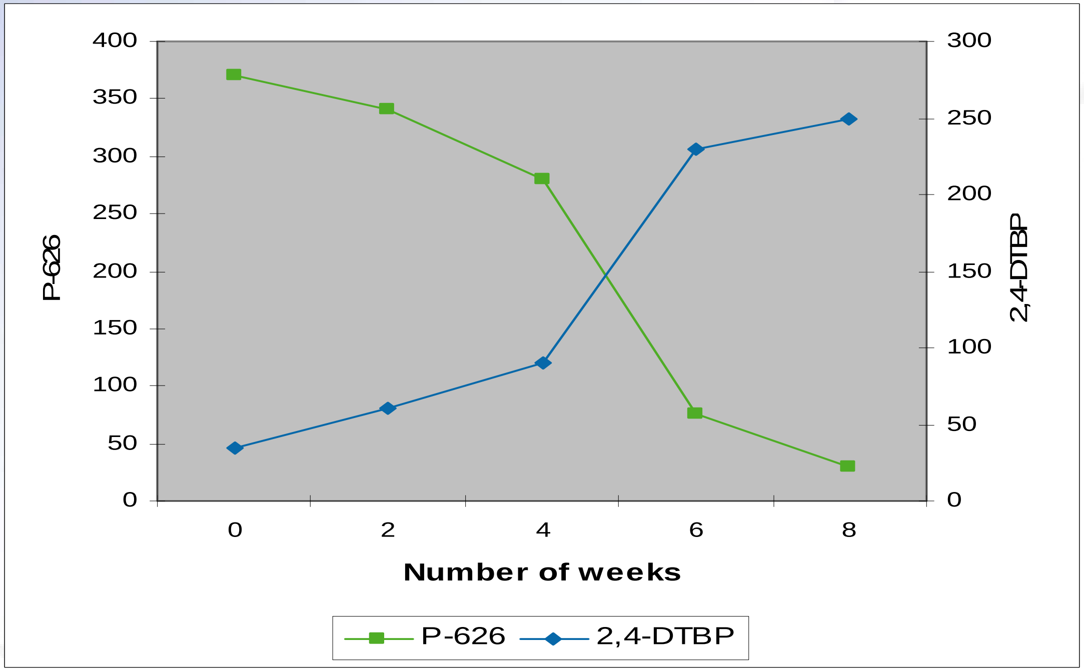
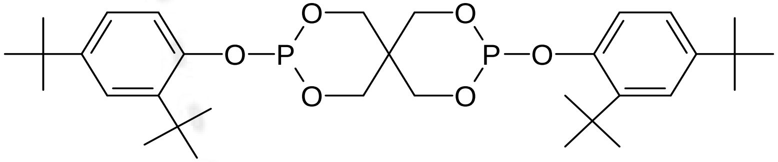
# Loss of P-626 during room temperature storage of HDPE with silica supported Cr- catalyst

S.H. Jamtvedt, H. Øysæd: Addcon 2005



# Conclusion

- Antioxidants are needed to secure proper process- and end use stabilisation of polyolefins
- GC MS data when using classical AO-systems indicate very low level of leached out impurities.
- Polyolefin industry feels that the future requirements of EAS will be fulfilled without problems although very strict.
- The found impurities seem to be mainly due to by-products present in the core AO
- Unexpected hydrolysis reactions (e.g. example with P-626) could lead to too high level of NIAS for future requirements
- **Additive suppliers should focus on minimising impurity level in AO and develop AO less sensitive to hydrolysis and thermal degradation to meet tougher future requirements**

# Thank you for listening!