BASF and BTC
Supporting the Environment & The Future Of The Rubber Market.

Presented By Allan Dixon
BTC products for the rubber market

- Colouration of Rubber
- Process stabilisation for rubber.
- Light stabilisation
- Other products for the rubber market
<table>
<thead>
<tr>
<th>Polymerisation</th>
<th>Warehousing &amp; storage</th>
<th>Manufacture of finished product</th>
<th>Application &amp; end use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Stabilisation</td>
<td>Whatever was put in during processing</td>
<td>Compound stabilisers</td>
<td>Whatever was put in during compounding</td>
</tr>
</tbody>
</table>

**To survive production:**
- Catalysts
- Heat
- Shear
- Tamol – emulsion process only
- Pluriol etc.
- Antioxidants

**Long term Storage:**
- Gel
- Colour
- Storage
- Viscosity

**Production economies (e.g. recycle stability):**
For adequate production life:
- Antioxidants
- Light stabilisers
- Flame Retardants

**To survive end use:**
- Heat
- Light
- Ozone
- Extraction
- Etc.
Process stabilisation for Rubber
Autocatalytic process

Auto-oxidation
Primary Antioxidants (Free-Radical Scavengers)

- Primary Antioxidants (Free-Radical Scavengers) -- Hindered Phenols
  - Free-radical scavengers react with chain-propagating radicals such as peroxy, alkoxy, and hydroxy radicals in a chain terminating reaction.
  - The most widely used primary antioxidants are sterically hindered phenols. They are very effective radical scavengers during both processing and long term thermal aging, and are generally non-discolouring.
  - Many also have received FDA approval.

IRGANOX 1010

IRGANOX 1076

IRGANOX 245
Primary Antioxidants – BHT type

Pro’s
Low prices in the marketplace.
Multi suppliers in the market.

Concerns
Patch testing performed under lab condition to patient in some cases has indicate that they have a contact allergy to BHT.

Concerns about possible Carcinogenic effects

(Information from the Sciencelab.com)
Secondary Antioxidants (Peroxide Scavengers)

- Peroxide scavengers (secondary antioxidants).
  - Decompose hydroperoxides (ROOH) into nonreactive products.
  - They are often used in combination with free radical scavengers (primary antioxidants) to achieve a synergistic inhibition effect.
  - The most common secondary antioxidants are phosphites types.
  - Another class of secondary antioxidants are thioethers or organic sulfides.
  - Organic sulfides are very effective hydrogen peroxide decomposers.
  - During long term thermal aging and are often used in combination with other antioxidants like hindered phenols.

![Chemical structures of IRGAFOS 168, IRGAFOS 126, and IRGAFOS 38]
Secondary Antioxidants - Phosphite, Thioether

Phosphite

R\_P\_OR'

OR'

R: OR'  R': Ar  R: OR'  R': Alkyl

IRGAFOS 168

IRGAFOS 38

IRGAFOS

Thioether

IRGANOX PS-800: “DLTDP”  R = C\textsubscript{12}H\textsubscript{25}

IRGANOX PS-802: “DSTDP”  R = C\textsubscript{18}H\textsubscript{37}
Irganox 1520L
Dual Anti-oxidant: One Molecule – Two stabilisers

- Primary antioxidant action
- Secondary antioxidant action
- Irganox 1520 L is a multifunctional liquid phenolic antioxidant
- Irganox 1520 L is non-staining, non-discoloring.
- Low involatility, and stable to light and heat.
- Good high temperature performance
- Excellent processing stability
- Good storage stability
Irganox 1520L -- Food Contact Approvals

- Approved for rubber articles in contact with food (BGVV: Empfehlung XXI, FDA: 177.2600)

- Approved for HIPS (BgVV: Empfehlung VI + other European Countries, FDA: 177.1810 + 177.1640)

- Other approvals granted (ex.: adhesives); FDA 175.105; 175.125

- These approvals allow the use of IRGANOX 1520 for both tire grades and HIPS grades rubbers

“Antioxidant consolidation = cost savings”
BTC products for the rubber industry
Process stabilisers by rubber type

- Butadiene Rubber - BR
- Ethylene propylene rubber - EPM/EPDM
- Nitrile Butadiene Rubber – NBR
- Butyl Rubber (isobutyl-co-isoprene) – IIR & CIIR/BIIR (Halobutyl rubber)
- Styrene Butadiene Rubber – SBR
- Polyisoprene – IR
- Neoprene - CR
## Processing Stabilisers for rubber

### Recommendations for Butadiene Rubber (BR)

<table>
<thead>
<tr>
<th>Cure Mechanism</th>
<th>Heat Stabilisation</th>
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<tbody>
<tr>
<td>Sulfur Cure</td>
<td>Irganox 245; 1 phr</td>
</tr>
<tr>
<td></td>
<td>Irganox 1035; 1 - 1.5 phr - best for BR</td>
</tr>
<tr>
<td></td>
<td>Irganox 1520L; 1 phr (Food Contact Approvals)</td>
</tr>
<tr>
<td></td>
<td>Irganox 5057; 1 phr - best for dynamic/anti-fatigue properties</td>
</tr>
<tr>
<td>Peroxide Cure</td>
<td>Non- Discolouring</td>
</tr>
<tr>
<td></td>
<td>Irganox 1010 + PS 800/802 0.5+1 phr - best performance</td>
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<td>Irganox 1010; 0.5 - 1 phr</td>
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Stabilisation of High Cis (co-type) Polybutadiene
Influence of antioxidants

**80° C aging: Gel formation**

- % Gel Formation vs. Weeks aging at 80° C

**Discolouration of 2mm sheets during daylight exposure (weeks)**

- yellowness index vs. Weeks exposure

Legend:
- Red: Unstabilised
- Orange: 0.25% Irganox 1076
- Blue: 0.1% Irganox 1520
- Black: 0.15% Irganox 1520
- Green: 0.1% I-1076 + 0.25% I-B 900 + 0.3% I-PS 800
Stabilisation of low cis Polybutadiene
Influence of AO on accelerated aging & gel sensitivity

![Graph showing gel content over days aged at 80°C](image)
Stabilisation of low cis Polybutadiene
Influence of AO on Brabender processing stability

Longer Induction time indicates improved processing stability
## Processing Stabilisers for Rubber

### Recommendations for Ethylene Propylene Rubber (EPM/EPDM)

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</tr>
<tr>
<td>Non-discolouring anti-oxidants</td>
<td></td>
</tr>
<tr>
<td>Irganox 1010 + Irganox PS 800/802 0.5 -1 +1 - 1.5 phr</td>
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</tr>
<tr>
<td>Irganox 1035; 1 - 2 phr</td>
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</tr>
<tr>
<td><strong>Peroxide Cure</strong></td>
<td></td>
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<tr>
<td>Non-discolouring anti-oxidants</td>
<td></td>
</tr>
<tr>
<td>Irganox 1010 + Irganox PS 800/802 0.3 - 0.7 +0.5 - 1 phr - long term stability</td>
<td></td>
</tr>
<tr>
<td>Irganox 1010 + Irganox PS 800/802 0.5 -1 + 1 - 1.5 phr - high Temperature aging</td>
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Processing Stabilisation of EPDM: Mooney viscosity after 80°C oven aging.

- 0.075% Irganox 1076
- 0.15% Irganox 1076
- 0.05% Irganox 1520
- Unstabilised
Processing Stabilisation of EPDM: Yellowness index after oven aging at 80°C

![Graph showing the change in yellowness index over weeks of aging at 80°C with different stabilizers.](image)

- **0.075% Irganox 1076**
- **0.15% Irganox 1076**
- **0.05% Irganox 1520**
- **Unstabilised**

**Legend:**
- Black line: Unstabilised
- Orange line: 0.075% Irganox 1076
- Blue line: 0.15% Irganox 1076
- Green line: 0.05% Irganox 1520
Processing Stabilisation of EPDM:
(Coagulated at pH 10): Mooney viscosity after 180°C hot mill test

![Graph showing Mooney viscosity ML 1+4 (100) vs. hours hot mill aging at 180°C for different stabilizers: 0.075% Irganox 1076, 0.15% Irganox 1076, 0.05% Irganox 1520, and Unstabilised. The graph illustrates how different stabilizers affect the viscosity over time.]
Light Stabilisation for the rubber industry

- Photo-oxidation is initiated by the action of photons onto the rubber article
- Photo-oxidative degradation results from the combined action of light and oxygen
- The degradation process proceeds analogous to the auto-oxidation cycle

\[ \text{Photo-oxidation} \]

\[ \text{Photo-oxidative degradation} \]

\[ \text{Photodegradation} \]
Light Stabilisation

- Rubbers absorb UV-light due to their intrinsic chemical structure
- If there is no light, there is no photo-degradation
Light Stabilisation – Two main routes

- **UV Absorbers**
  - Absorb harmful UV radiation and dissipation as heat
  - Protect the polymer bulk; in thickness sections >0.1 mm (Lambert-Beer)
  - Not effective at protecting surfaces or thin sections

- **Hindered Amine Light Stabilisers (HALS)**
  - Scavenge radicals
  - Activated during light exposure
  - Protect bulk & surface
  - Independent of article’s thickness
  - Conventional HALS are deactivated by strong acid, NOR HALS are not.

- Combination of HALS & UV absorber gives highest level of protection.
BTC products for the rubber industry
Light Stabilisation by rubber type

- **Diene Rubbers**
  - Butadiene
  - Styrene Butadiene
  - Isoprene
  - Natural rubber

- **Ethylene propylene rubber - EPM/EPDM**

- **Nitrile Butadiene Rubber – NBR**

- **Butyl Rubber (isobutyl-co-isoprene) – IIR & CIIR/BIIR (Halobutyl rubber)**

- **Neoprene – CR, no light stabilisation recommendations**
### Light stabilisers for rubber

#### Recommendations for Diene rubbers (BR, SBR, NR & IR)

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<td>Sulfur Cure</td>
<td>UV absorber 1 - 2 phr</td>
</tr>
<tr>
<td></td>
<td>Tinuvin 234</td>
</tr>
<tr>
<td></td>
<td>Tinuvin 213 (liq)</td>
</tr>
<tr>
<td></td>
<td>HALS 1 - 2 phr</td>
</tr>
<tr>
<td></td>
<td>Flamestab NOR 116 - best performance (2 - 4 phr without UVA)</td>
</tr>
<tr>
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<td>Tinuvin 123</td>
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# Light stabilisers for rubber

## Recommendations for EPDM

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**Light stabilisers for rubber**

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<td>Tinuvin 770 DF</td>
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### Light stabilisers for rubber

**Recommendations for NBR**

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Light stabilisers for rubber
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# Light stabilisers for rubber

## Recommendations for IIR

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BTC products for the rubber industry

Other Products

- Waxes
  - Luwax A
  - Luwax AL 3
    - Luwax AL 61 – reduces tack, especially in chlorinated rubbers.
- NOP – for improving dispersion of Carbon black.
- Koresin – tackifier – available via BASF.
- Formic Acid – for processing of natural rubber.
- Amines – for accelerant manufacture.
- Pluriol – Used as mold release agents, lubricants, dispersant, vulcanisation promoter & foam control. Also as a vulcanisation activator.
  - Modification of vulcanisation rate; modulus of elasticity
  - Reducing scorch time
- Defoamers – waterbased foamaster or foamstar range, solvent based EFKA.
BTC products for the rubber industry

Other Products

- Plastisol – available from BTC in certain regions
- Pluriol A can be used as a plasticiser for rubber, reactive PEG group could be used as a copolymer in rubber formulations. The reactive groups are:
  - Ally - Pluriol A….R & Pluriol CA….211 M 43
  - Vinyl – Pluriol A…..V
  - Iosprenyl – Pluriol A……I
- For the Emulsion production process anionic and non-ionic surfactants.
  - Tamol – Dispersion agent in rubber synthesis using emulsion process, particularly for tire applications
  - Disponil
  - Pluronic
  - Lutensol
- Crosslinking Co-agents: TMPTMA and Laromer TMPTA. Additives to improve the peroxide and radiation crosslinking of rubber.
End of presentation....

Thank You