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TS&D Manager
Summary

- Introduction

- Improvements achieved with the new catalyst system

- Development of new grades
  - Very high ENB (ethyliden-norbornene) grade for automotive sponge application
  - Ultra high molecular weight grade for TPV application
  - Tailored structure for solid profiles application (branching technologies)

- Conclusions
Introduction: Versalis at a glance

With an integrated industrial platform, Versalis – the Italian leading chemical company – offers to the market an extensive portfolio of around 400 product grades and a new range of bio-based chemical products.
Elastomers: product mix

**High performance tyres for passenger cars (SSBR)**

- **Europrene® SBR**
  - Styrene Butadiene Rubber (SBR)

**Technical goods**

- **Europrene® SOL T, TH**
  - Thermoplastic Rubber (SBS,SIS,SEBS)
  - **Adhesives**

- **Europrene® N**
  - Acrylonitrile-Butadiene Rubber (NBR)

**Car/truck Tyres, Styrenics modif.**

- **Europrene® Neocis/Intene**
  - Butadiene Rubber (BR)
  - **Moulded foam and masking tapes**

- **Dutral®**
  - Ethylene-Propylene Rubber (EP(D)M)
  - **Automotive and Building**

- **Europrene® Latex**
  - Synthetic Latexes (HS, CBX)
IMPROVEMENTS ACHIEVED WITH THE NEW CATALYST SYSTEM
The new catalyst system

- **Advantages in terms of:**
  - Polymerization yield
  - Gel control
  - Co-monomers addition
EP(D)M DUTRAL® elastomers polymerizations

**Ethylene**

\[ \begin{align*}
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} \equiv \text{C} \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*} \]

**Propylene**

\[ \begin{align*}
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} \equiv \text{C} \quad \text{CH}_3 \\
\text{H} & \quad \text{H}
\end{align*} \]

**Ziegler Natta catalyst system**

**Catalyst**

**Activator**

**Co-Catalyst**

DUTRAL® CO (EPM)

DUTRAL® TER (EPDM)

(ENB content : 3 - 9 % wt)
DUTRAL®: development of a **new catalyst system**

After years of internal development **Versalis** is **scaling up** an improved **Z-N catalyst**

The **New Catalyst System** keeps the versatility of the traditional one, significantly increases the polymerization yield, improves co-monomers addition to obtain better distribution inside the polymer chain, reduces undesired side reactions.

**Traditional Catalyst System:** very versatile, able to produce from very low to very high Molecular Weight, from low to high Ethylene and ENB content.
DUTRAL®: development of a new catalyst system

- Higher polymerization yield
  - Cleaner products
  - Better monomer distribution and side reactions control
  - Lower up to no gel
  - Better consistency
  - Better curing efficiency

Widening the polymer design

- New polymer structures
- Improved processability

This new catalyst is currently used on industrial scale to produce all the new developed grades
DUTRAL®: new catalyst system ➔ Cleaner Product

Residual catalyst (V and Al)

<table>
<thead>
<tr>
<th></th>
<th>Traditional ZN</th>
<th>Improved ZN</th>
<th>Traditional ZN</th>
<th>Improved ZN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>100%</td>
<td>69%</td>
<td>100%</td>
<td>71%</td>
</tr>
<tr>
<td>Aluminum</td>
<td>100%</td>
<td>44%</td>
<td>100%</td>
<td>45%</td>
</tr>
</tbody>
</table>

-31%, -56%, -29%, -55%
DUTRAL®: new catalyst system ➔ lower gel

Polymer dispersion in std rubber compound

Defects counted in std rubber compound strip

Acceptance limit

Traditional ZN

Improved ZN

Very low gel level
DUTRAL®: new catalyst system ➔ better co-monomer C2 C3 addition

Traditional ZN vs Improved ZN

Crystallinity

ΔH (joule/g)

Semi-crystalline grade (identical composition)
DUTRAL®:
new catalyst system ➔ better ENB addition better ENB addition

Dutral TER

- High MW  ML(1+4)125°C ➔ 65 MU
- Moderate Oil Extension ➔ 15%
- Amorphous grade  C3 ➔ 40%
- High ENB content ➔ 7%

ASTM D3568 Compound Vulcanization @ 180 °C

- Traditional ZN Catalyst
- Improved ZN Catalyst
NEW CATALYST SYSTEM ➔

DEVELOPMENT OF NEW GRADES
The ability to minimize the side reactions can be used to develop a new grade with very high third monomer (ENB) content and high molecular weight, suitable for automotive sponge profiles applications, finally filling the gap of the slurry technology versus the solution technology for such application.

**Sponge profile** is probably the most demanding automotive body sealing application. It requires:

- low Mooney compound to allow proper expansion,
- good collapse resistance,
- high cure rate and
- perfect surface.

Different polymer structures are suitable for the application including the one below reported.
DUTRAL®:
new grades development → Automotive Sponge Grade

Dutra TX reference composition for sponge application

- High MW ML(1+4)125°C → 68 MU
- Moderate Oil Extension → 17.5%
- Amorphous grade C3 → 39%
- Very High ENB content → 8.5%

Gel Count in a reference compound

![Gel Count Chart]
As known the slurry process has advantages versus the solution process in the production of very high molecular weight grades. These grades are typically oil extended to facilitate their processability. The new catalyst system allows to reach molecular weights not possible with the traditional one. A growing application were these type of grades are desirable is the TPV application.

TPV (Thermoplastic Vulcanized)

TPV greatly contributed to the grow of the Thermoplastic Elastomer Family (TPE) at which belongs together with (H)SBC, TPO etc. The reason of this success is its superior elasticity combined with the recyclability.
**TPV (Thermoplastic Vulcanizate)** is a rubber/thermoplastic blend (plus fillers/plasticizers/other additives) where the rubber phase is cross-linked (dynamic vulcanization) and finely dispersed in the continuous matrix of the thermoplastic (typically PP).

Being a blend of a rubber in a plastic, in order to reach the desired hardness, a high amount of oil is required. To emphasize the elastic and mechanical properties ultra-high molecular weight EP(D)M are preferred.
DUTRAL®: new grades development → TPV Grade

Dutral TX reference composition for TPV application

- Very High MW - ML(1+4)125°C ➞ 47 MU
- Extension with White Oil ➞ 50%
- Amorphous grade C3 ➞ 36%
- Medium ENB content ➞ 4,5%

Injection moulding comp.

- C.S. 22h 100 °C
- TR 10
BRANCHING TECHNOLOGY
DUTRAL®: new catalyst system ➔ branching technology

The new catalyst system is particularly suitable to introduce branching technology in a slurry process, to get easy processable grades and to keep a negligible gel content. To evaluate the effect of branching technology another grade was designed starting from a standard reference grade. The two grades are characterized by a high molecular weight, medium third monomer content, amorphous composition. Being the only difference the presence of branching, it is possible to focus just on that characteristic. The induced branching present is evaluated by Mooney slope and Mooney relaxation area. The higher elasticity obtained allows improving the workability in internal mixing without sacrificing the final properties of the vulcanizates.

<table>
<thead>
<tr>
<th></th>
<th>TER</th>
<th>BTR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High MW</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML (1+4) 125°C</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td><strong>Amorphous grade</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene Content</td>
<td>40%</td>
<td>40%</td>
</tr>
<tr>
<td><strong>Medium ENB</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ENB Content</td>
<td>4,5%</td>
<td>4,5%</td>
</tr>
<tr>
<td>Molecular Structure</td>
<td>Linear</td>
<td>Tailored</td>
</tr>
</tbody>
</table>
### New and standard amorphous grades comparison - basic data

<table>
<thead>
<tr>
<th>MAIN PROPERTIES</th>
<th>linear</th>
<th>tailored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene cont. / ENB cont.</td>
<td>%wt</td>
<td>40 / 4,5</td>
</tr>
<tr>
<td>Polymer Mooney - ML (1+4) a 125 °C</td>
<td>MU</td>
<td>78</td>
</tr>
<tr>
<td>Slope</td>
<td>lg M/lg s</td>
<td>-0,942</td>
</tr>
<tr>
<td>Area</td>
<td></td>
<td>175,3</td>
</tr>
<tr>
<td>Area/ML</td>
<td></td>
<td>2,3</td>
</tr>
</tbody>
</table>

### Performance evaluation in compact profile (Composition in phr - total: 379,1)

| Polymer | 100 | 100 |
| C.B. N550 | 140 | 140 |
| Paraffinic Oil | 90 | 90 |
| CaCO3 | 30 | 30 |
| ZnO: 5; Stearic Acid: 1; PEG 4000: 5; Structol WB 16: 3; Sulphur 80: 1,5; MBTS 1; ZBOP/S 1,2; ZBEC 0,7; TBzTD 0,5; Vulcalent E80: 0,2 |

| Compound Mooney - ML (1+4) a 100 °C | MU | 61 | 51 |
| Δ ML (1+4)125°C - ML(1+4)100 °C | | 16 | 27 |
DUTRAL®: new catalyst system ➔ branching technology

**Extrusion properties: Garvey rate vs. mixing time/extr. speed**  
(ASTM D 3568 – cpd)
DUTRAL®: new catalyst system ➔ branching technology

Mooney compounds vs mixing time

Cured compounds T.S. vs mixing time

Mooney compound and Tensile Strength vs. mixing time  (ASTM D 3568 – cpd)
Conclusions

With the adoption of an improved ZN catalyst, in a slurry process, it is possible to obtain EP(D)M grades with low catalyst residual and very low gel content. The new ZN catalyst is also able to improve the co-monomers addition and minimize undesired side reactions to allow the adoption of technics for obtaining tailored polymer structures with improved processability. Consequently it is now possible to overcome the limits of the traditional catalyst used in a slurry process and to obtain new EP(D)M grades suitable for a wider range of applications.
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