Esterification vs. transesterification

– comparison of DEHT production methods

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European markets of plasticizers are continuously evolving. The catalyst for the changes is high competitive and regulatory pressure resulting in the replacement of the traditional plasticizers with the new, alternative solutions. An example of such an impact is the replacement of phthalate DEHP with its non-orthophtalate alternative – DEHT – which is produced on the basis of the same OXO alcohol. DEHT systematically gains the market share on the European market of PVC plasticizers. In this paper, we will look into DEHT production methods and indicate significant differences that may influence on the DEHT quality.

Two primary methods for the production of di-esters used as plasticizers are the following: esterification (employed by Grupa Azoty ZAK S.A. for production of Oxoviflex®) and transesterification (employed by some other manufacturers). The composition and properties of plasticizers may differ based on the production technology.

**Production process**

Oxoviflex® is produced in a continuous process, based on a direct reaction of terephthalic acid with 2-ethylhexanol. It enables continuous monitoring of the process and maintaining stable quality parameters of the product. In DEHT transesterification, the batch production method is dominant, which may result in the inconsistencies in the product batches, especially if the production is carried out in swing mode at the same production line with another plasticizer.

**Raw materials**

Another property that differentiates both processes are raw materials. The esterification process is carried out directly in the reaction of terephthalic acid with 2-ethylhexanol (PTA + 2EH). Therefore, the risk of undesirable impurities affecting the quality of the final product is substantially lower. Additionally, conducting the process solely with PTA and 2EH reduces the risk of forming more volatile – methyl octyl esters.

In case of transesterification, the basic raw material, apart from 2-ethylhexanol, is dimethyl terephthalate (DMT). DMT may be obtained from terephthalic acid (PTA) or by alcoholysis of polyethylene terephthalate with methanol (recycling of PET products), which may result in the introduction of impurities into the raw material.

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**The quantity of volatile elements (150ºC/2h) in DEHT plasticiser depending on the production method**

<table>
<thead>
<tr>
<th>Method</th>
<th>Quantity of Volatile Elements (0.00% - 0.14%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxoviflex® - DEHT produced with esterification method</td>
<td>0.03%</td>
</tr>
<tr>
<td>DEHT - produced with transesterification method</td>
<td>0.13%</td>
</tr>
</tbody>
</table>

Source: GA ZAK S.A. estimation
**Reaction catalyst**

The esterification process employed in Oxoviflex® production is carried out in the presence of titanium compounds, mainly TnBT as catalyst. Titanium catalyst is an amphoteric catalyst that decomposes in water to TiO₂, this facilitates its separation from the product during distillation, and reduces the quantity of media required to neutralise raw DEHT. Metalorganic catalysts are more selective, their use results in the production of fewer by-products, and they highly facilitate the separation of the catalyst residue by its precipitation.

Transesterification uses an acidic catalyst (sulphuric acid, methanesulfonic acid, p-Toluenesulfonic acid) or a Sn, Ti, Zr-based catalyst. In this case larger quantities of by-products are obtained and may affect the quality of the final product, in particular, the colour.

**Process conditions**

Oxoviflex® esterification is carried out at 180–200 °C and under reduced pressure. The process is carried in the terephthalic acid suspension in an excessive quantities of 2-ethylhexanol. It improves the separation of unreacted terephthalic acid from ester through adequate filters. The transesterification process requires increased pressure and higher temperature of 180–260 °C. Moreover, it is carried in a homogeneous mixture of reactants, which contributes to the occurrence of undesired by-products.

<table>
<thead>
<tr>
<th>DEHT manufacturing method</th>
<th>Transesterification</th>
<th>Esterification (Oxoviflex® as an example)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production process</td>
<td>In batches</td>
<td>Continuous</td>
</tr>
<tr>
<td></td>
<td>Inconsistencies possible across the production batches</td>
<td>Direct reaction, lower risk of introducing impurities, lower risk of forming more volatile esters</td>
</tr>
<tr>
<td>Substrates</td>
<td>DMT + 2EH</td>
<td>PTA + 2EH</td>
</tr>
<tr>
<td></td>
<td>DMT obtained from PTA or recycled PET, higher risk of impurities occurring in DEHT, higher volume of volatile esters</td>
<td>Direct reaction, lower risk of introducing impurities, lower risk of forming more volatile esters</td>
</tr>
<tr>
<td>Reaction catalyst</td>
<td>Acidic catalyst or catalyst based on Sn, Ti, Zr</td>
<td>Titanium derivatives, mainly TnBT</td>
</tr>
<tr>
<td></td>
<td>Larger quantity of by-products that may negatively affect the quality of the final product, in particular the colour</td>
<td>Easier filtration, no acidic catalyst residue</td>
</tr>
<tr>
<td>Process conditions</td>
<td>180-260 °C, increased pressure</td>
<td>180-200 °C, decreased pressure</td>
</tr>
<tr>
<td></td>
<td>Undesired by-products</td>
<td>Improved separation</td>
</tr>
<tr>
<td>The content of other esters in the final product</td>
<td>minimum 3%</td>
<td>No other esters</td>
</tr>
<tr>
<td>The content of pure bis (2-ethylhexyl) terephthalate in the final product</td>
<td>minimum 96%</td>
<td>minimum 98%</td>
</tr>
</tbody>
</table>
Summary

All of the above differences affect the final product quality. Oxoviflex® is produced employing esterification method and is chemically pure because of its manufacturing conditions that prevent occurrence of excessive by-products while DEHT manufactured in the transesterification method may contain even 3% of by-products. Furthermore, Oxoviflex® contains, among others, min. 98% of bis (2-ethylhexyl) terephthalate while the products obtained in transesterification process – 96%.

In the process of selective esterification, employing terephthalic acid and 2-ethylhexanol only, DEHT produced is of good qualitative parameters, pure and with low content of by-products.

Oxoviflex® is a safe product that does not contain acidic catalyst residue, residual methanol or phthalates. As for the metal content, it is comparable to a plasticizer produced for medical purposes for medical purposes and meets top qualitative criteria, including those specified in the European Pharmacopoeia.

DEHT produced according to esterification method is characterised by much higher homogeneity of subsequent batches with respect to transparency (colour). It can turn out especially important in the production of coloured elements as the risk of colour inconsistencies of the products is minimised, thus, contributing to lower volume of pigments used in PVC processing. It particularly pertains to bright colours (white through beige to light brown tones), where the changes in the plasticizer’s transparency significantly affect the perception of the final product.

Bibliography:
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• WO 2010/071171 “Polymer compositions comprising terephthalates”
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