Catalysing PET

Is the wait for a new polyester catalyst finally over?

Dan Weissmann investigates

Non-Antimony PET catalysts (NAC) have been in the market for more than a decade, but have struggled to gain broad market acceptance. Titanium (Ti), Germanium (Ge) and Aluminium (Al) are among the metal-based catalysts that have been demonstrated, to various degrees, to be viable alternatives to Antimony (Sb)-based catalysts.

Along with the natural reluctance to change and the enormity of the task, there was a concern about the impact that these catalysts might have on PET resin colour, line yield and quality. Antimony-based catalysts are the mostly used in present-day PET production. Of the Antimony-based production facilities about 70 per cent use Antimony Trioxide, while Antimony Triacetate is used in the others, with a higher occurrence in fibre plants.

Texas, US-based Dorf Ketal Specialty Catalysts has made a commitment to commercially develop a Titanate-based catalyst (which is based on inorganic compounds composed of titanium chelates) called Tyzor ACtivate for use in the polymerisation of PET. This commitment is supported by extensive laboratory work, a pilot and production line, both batch and CP (continuous polymerisation), and evaluations to provide the knowledge and confidence needed to move forward.

The work provided the answers needed, especially regarding processing conditions and mitigating the colour issues. The testing was not limited just to pellet production, but extended all the way to the final product performance, from bottle blowing and sheet extrusion to thermoforming.

The use of a certain catalyst implies changes in some of the additives used for resin production such as stabilisers and colourants. With the base-colour concerns, both the traditionally-used cobalt and alternative dyes were compared in the masking of basic yellowness of the resin. Not only was the effectiveness of the colourants checked but also any possible effects it may have in any step of production. It was found that an equivalent rate of solid state polymerisation (SSP), a major part in PET production that takes several hours, can be achieved when dyes replaced cobalt. The possibility to change to the use of dyes is in line with the general industry trend to move away from cobalt as from any other heavy metal.

Combined, the catalyst and the additives used induce subtle differences in the manufacturing of the resin and are claimed to produce favourable results in bottle production, material performance and cost.

The main contributor for the differences is the high level of activity of the Titanate catalysts in comparison with the Antimony-based ones. ACtivate catalysts have a typical loading level of about 8-10ppm of Ti, compared to 200-300ppm of Sb. The lower inorganic level results in less potential nucleating sites within the polymer, which significantly impacts the crystallinity and the crystallisation process of the resin.

Activate-catalysed resins typically have a higher crystallisation temperature on heat up compared to Antimony-catalysed resins. This difference in crystallinity allows for a potential reduction in IPA content used to retard crystallisation of up to 40 per cent, which would lower the PET production costs. Additional benefits of the ACtivate catalyst system are reduced acetaldehyde (AA), oligomers and haze.

Alternatively, the crystallinity differences can be exploited to develop new resins with superior performance that make it possible to light-weight all bottles and increase the fill temperatures of hot-fill bottles, further contributing to cost savings in the end product.

Another benefit is derived from moulding at a lower melt temperature, as much as 10 Celsius degrees lower, which translates to a reduction in cycle time by as much as 8 per cent, leading to higher productivity. Lower melt temperatures also translate to energy savings and to reduced

Maintaining colour and quality is a key concern during PET production

Cost saving comparisons

	Antimony Standard formulation*	**Tyzor ACtivate 422** Standard formulation*	40 per cent reduced IPA	Formulations to exploit crystallinity (Reduced moulding temp/light-weighting/higher fill temps)	
Target market segment	All	CSD/water	CSD/water	CSD/water	Hot-fill
Cost impact CP producer ($/MT PET)	0	$0 to $1	(-)$3 to (-)$4	$0 to $1	$0 to $1
Cost impact ($/MT PET - preforms)	0	0	0	(-)$20 to (-)$24	(-)$7 to (-)$8
Total cost impact ($/MT PET)	0	$0 to $1	(-)$3 to (-)$4	(-)$20 to (-)$24	(-)$7 to (-)$8

* Includes all dyes and other additives

manufacturing costs. A summary including potential cost savings of the various steps is shown in the table.

Of interest is the point that the largest part of the estimated saving comes at the convertor's end in bottle manufacturing, rather than in the resin production.

While the commitment to a catalyst and a certain polymerisation process when designing a new manufacturing line may be easy, converting an existing line presents a technical and operational challenges resulting in a high entrance barrier. This becomes even more daunting as line productivity increases.

Converters stand to make the best gains from catalyst developments

The amount of material involved in such a move is huge, not to mention the time and production loss. Nevertheless, several PET manufacturing plants using the Dorf Ketal technology are already in operation in North America and the South East Asia.

Dorf Ketal is the leading producer of organo-titanate and organo-zirconate catalysts in the world, serving a broad base of markets from inks and coatings to oil-field stimulation and polymer production. The company has established a global supply and service infrastructure with the ability to support any development through applications testing and to demonstrate the performance and benefits of the catalysts it supplies.

In a polyester catalyst review article written in 2001 (*J Polymeric Materials, Vol 50*), Dr Ulrich Thiele wrote: "The risk to change the catalyst of a large continuously running polyester plant is high because of the very close connection between the kind of catalyst and the downstream processing performance in textile and bottle processing. Therefore, we may see a prolonged development phase until one could say that a new polyester catalyst was successfully introduced to the industry."

It looks like the waiting period may be over.

More information from Dorf Ketal Speciality Catalysts, LLC, 11200 Westheimer Road, Suite 400, Houston, TX 77042, USA. Tel: 1 832 361 9400. www.dorfketal.com