Quo vadis polyester catalyst?

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It is nearly a decade ago now since Akzo researchers introduced new antimony free titanium based catalyst called "C94" to the public. Especially large polyester producers feared too much attention on an imaginary environmental problem attributed to the old and docile antimony catalyst. At that time, the impact of politically green ideas was still on the ascending star and many people, especially from the food container industry, were worried about a possible sudden scandal caused by a "may be" impact of antimony to public health. For the polyester chemists this signal came at the time where most of the important secrets of the polyester synthesis where unveiled and research money flowed to life science and e-business developments. Interestingly, these unfounded environmental and health fears of the public started a significant research movement towards of antimony free catalysts around the world, and polyester chemists received the last chance for the time being to step down to the mysteries of metal complexes and π-systems.

The disenchantment came to all who started under the flag of earning lots of money immediately with a new catalyst and today still more than 90 % of the world polyester production is made by adding 150-300 ppm antimony whether as antimony oxide, antimony acetate or antimony glycolate. All the same, the move is to finally establish a new catalyst. The emphasis is on a better catalyst which means firstly a more economical one and secondly a catalyst, which smooths out the smaller and larger inconveniences of antimony, which the industry has become accustomed to over the last half century of industrial polyester production.

It should be taken into account that our industrial environment has drastically changed and only most easy handling instant or "plug and play" catalysts will make the race. Plant management does not like to buy a whole new production technology which might cause more headaches than cure them, even in light of the fact that continuous plants up to 800 tons/day capacity and a completely closed loop of internal glycol recycling are running nowadays, and the change over to a new catalyst is bearing high capital risks. The new catalyst should provide generic advantages over the state of the art antimony catalysis.

In Table 1 the most important and known quality and process problems caused by antimony are shown.

These points will enable us to define the main requirements for an acceptable new polyester catalyst, which are as follows:

- less or at least same catalyst cost per ton of polyester compared to antimony
- easy to handle, instant application, plug and play
- no FDA and EU hurdles, no poisons, no heavy metals
- all registrations such as Einecs and Tosca available
- same or better polymer color and clarity
- chemically defined, pure substance, consistent composition
- no precipitation in the polymer
- no shells, deposits or black spots on reactor walls or melt tubes
- no remarkable volatility or losses during polymer production
- no negative impact to the closed loop EG recovery in CPU
- no sublimation during processing like spinning, performing and bottle blowing
- same or better behavior in all downstream operations.

All together these needs are a real challenge for all work in this field, and also a substantial driving force to improve polyester technology.

Publications, conference papers and patents together with the knowledge and networking around the polyester industry are the sources for the following status analysis about important and developed new polycondensation catalysts. A first summary was made in 2001 [1] where most of the new developments where premature and Japanese companies had not published their major offensive on the catalyst topic. Meanwhile, there are a variety of companies which already offer the new catalysts as commercial products to the industry. There is another handful of companies which are active in this field but which do not offer their new catalyst to the public, whereas some of them are cooperating with selected customers based on license agreements. In Table 2 the commercialized catalysts are summarized.

In Table 3 catalysts are listed which are known to be under internal development. Chemical base and the status of development are extracted from publicly accessable literature and patent informa-

Table 1 Quality, process and handling problems of currently used antimony catalysts

Property	Effect or current situation
A: catalyst purity	wide range of Sb_2O_3 sources with a broad span of impurity levels and impurity compositions, main impurities are As, Pb, Se, Bi, Fe, Ni, Cu, SO_4^{2-}, Cl-, Sb_2O_5, Sb-metal, inconsistent levels not seldom
B: chemical uniformity	
Sb_2O_3	Sb_2O_5 and Sb^{metal} by disproportion, amount depending on production route and purification low, good and excellent qualities in the market
$Sb(CH_3\text{-}COO)_3$	good - excellent quality
$Sb[O(CH_2)2OH]_3$	good - excellent quality
C: catalytic efficiency	
polycondensation melt phase	150-300 ppm Sb necessary to increase IV during polycondensation by 0.15-0.25 dl/g and hour
SSP	150-300 ppm Sb necessary to increase IV by 0.012-0.025 dl/g and hour
D: precipitation	depending on the process stage and other additives main antimony precipitation is antimony metal, antimony phosphate and antimony poly-oxid-hydrates → all precipitated matter acts as crystal nuclei and is causing haze → fine Sb precipitations can act as flocculation accelerator to TiO_2
E: volatility	all EG condense circuits during melt phase production containing substantial amounts of antimony, antimony losses in a range of 10%, in closed loop EG recycling reuse of the catalyst and zero losses
F: discoloration	especially at high Sb-concentrations > 250 ppm Sb metal polymer gets the typically greenish to greyish-green hue
G: deposits	black shells and layers at all inner walls of melt guiding tubes, vessels, valves, dies and others → black spots in products / filter plugging
H: Sb-oligomers	spinning smoke contains high content of Sb-oligomers → deposits around spinnerets, egg shells containing high amounts of antimony
I: leaching out during processing and usage	wastewater of wet dyeing processes might contain higher amounts of antimony BUT: water stored in PET bottles will contain 1 ppb or less Sb, EEC limit/Japanese recommendation is < 20 ppb Sb in drinking water, many natural water sources contain more than 1 ppb Sb
J: incineration	off-gas contains Sb-oxide residues and needs to be purified

tion, as well as company information submitted to file for the purpose of this publication.

The chemical base of internal catalyst developments contains, besides the dominating titanium, also aluminum, magnesium and phosphorus compositions.

According to the public access and company information, the most advanced stage of non antimony catalysts introduction to the industrial scale is made in Japan. This is the consequential result of the strong cost pressure to replace germanium based catalysts and the preservation of high brilliancy and transparency. The color tone of the new titanium or aluminum based catalysts is similar to the germanium catalyst based polyester, and in the same way corrected by adding cobalt or blue toner.

The challenge to apply Ti-based catalysts to bottle PET applications is the balance of catalyst concentration necessary for melt phase polycondensation and for solid state polycondensation at a low degree of yellowing. In most cases, Ti-concentrations in the range of 5-20 ppm are sufficient for the melt phase polycondensation and low enough to provide reasonable b-color results between 0 and 3 units. However, this low concentration of Titanium is rather slow during solid state polycondensation compared to 200 ppm Antimony. Here, the introduction of magnesium, aluminum or the presence of special p-chemicals at higher amounts of titanium might be a possible way out.

All together, the status of introduction of new commercialized non antimony catalysts to the industrial production of polyester for textile, bottle and film application is at an early stage dispite a broad base of interest, scientific support and development work. Enough technical and commercial solutions are seemingly available today, yet the industrial progress is still sluggish. Significant acceleration will occur as soon as large European and US-based polyester producers follow the initiative of the Japanese polyester producers. Similar to other new polyester process developments like, for instance, the spherically shaped pellets made by underwater cutters or new compact tower reactors, the introduction of a new catalyst is most convenient during the start up of a new polyester plant producing a new polyester brand. Among the new CPUs coming on stream in the near future some of them will hopefully be starting up with new catalyst technology.

References

[1] Thiele, U.K.: The Current Status of Catalysis and Catalyst Development for the Industrial Process of Poly(ethylene terephthalate) Polycondensation, International Journal Polymeric Materials 50 (2001) 387-394

[2] http://ep.espacenet.com/search97cgi/s97_cgi.exe?Action=FormGen&Template=ep/EN/home.hts

Table 3 Internally driven new antimony free catalyst developments

Company	Chemical base	Patent examples	Status of introduction	Sources
Atofina Chemicals	titanyl-oxalate, Li-enhancer	US6,372,879	n.n.	esp@cenet patent research [2]
Dow Chemical	hydrotalcite	WO2004014982 WO03004547 CA2395051	n.n.	esp@cenet patent research
Inventa-Fischer	Ti , Co	EP 0827518 (A1)	pilot	Inventa-Fischer
Mitsubishi	Ti / P / Mg	US6,500,915 JP2003119269 JP2003040992 EP1099720	type N2C commercial CPU	Maack conference, Zurich 2003; esp@cenet patent research
Mitsui	Ti / Mg /alkali	US 6,346,070 WO03072633 JP2003082084 EP1270640	PET resin made of Ti-catalyst commercially available, production on commercial scale CPU	Mitsui Maack conference Zurich 2002 esp@cenet patent research
Teijin	Ti / P	US6593447 WO03008479 JP2002293909	industrial use discontinuous and CPU bottle, textile, film	Teijin Maack conference Zurich 2002 esp@cenet patent research
Toyobo	Al compound	JP2002 220,447 JP2002 220,448 JP2002 220,449 JP2002 220,451 JP2002 220,452 JP2002 220,443	trial phase in commercial CPU finished in 2003; commercial production planned in 2004	Maack conference Zurich 2002;2003 CAS patent service

Table 2 Commercialized new catalysts

Company	Trade name	Chemical base	Patent examples	Status of introduction for PET
Acordis	C94	Ti/Si	PCT WO 95/18839	catalyst is commercially available; commercial application for the time being more on discontinuous processes
Invista / DuPont	Tyzor (R) examples: TPT TnBT further types available	 tetra-isopropyl-titanate tetra-n-butyl-titanate	broad patent history of DuPont examples: WO02/068497 US5,981,690	catalysts are commercially available discontinuous and CPU further progress under way
Johnson & Matthey formerly Synetix	Vertec - C400 AC905 AC310	Ti-complexes Ti-P-complexes	PCT WO97/47675 EP0812818A1	catalysts and catalyst technology are commercially available 4 CPU applications and several discontinuous applications
Sachtleben Chemie	Hombifast	alkali-titanates	DE59610811D DE19513056	catalyst is commercially available discontinuous and CPU
Teck Cominco former Meld Form	TG/19	Ge based stable aqueous solutions	JP2001019753	catalyst is commercially available (on order), license contract based pilot + batch scale positively finished CPU application expected first half 2004
Zimmer AG Polytrade	Ecocat-T Ecocat-B	Ti + substrate + P-enhancer	US6,417,320 WO02090419 DE10121542A1	catalyst is commercially available pilot phase finished, industrial sized trails ongoing discontinuous and CPU