"Polyester Catalysts: A Critical Analysis of Current Technology and Available Alternatives"

Dr. rer. nat. Ulrich K. Thiele

The European PET Conference

11 – 12 October 2006 Barcelona
Ladies and Gentlemen,

first of all I would like to express my thanks to PETCORE and Frank Koelewijn who gave me the opportunity to present a paper with the title "Polyester Catalysts: A Critical Analysis of Current Technology and Available Alternatives“ at the first Polyester Conference of PETCORE.

May I introduce myself briefly. My name is Ulrich Thiele and I am serving now in the 8th year as technical and scientific consultant for the polyester industry. Those who might be further interested in my activities are warmly invited to visit my homepage

www.polyester-technology.com

Attending numerous polyester conferences during the last 15 years it became obvious that catalyst related issues where provided to public in large numbers and in controversial manner. This is a good inducement to analyze the current situation more in detail.
CONTENT

1. Introduction

2. Antimony today

3. Why and How a Non Antimony Catalyst - NAC?

4. The role of phosphor as stabilizer and catalyst retarder/synergist

5. The currently available NAC based on Ti, Al, Si / Zr and Mg

6. Producer of polyester resin, fiber and film based on NAC

7. Summary
Seemingly encouraged by environmental fears of the public a number of **Non-Antimony-Catalysts (NAC)** has been developed, presented and advertised [1,2,3]. Some times one could get the impression that the conversion from antimony to NAC is fully gaining momentum.

At the other side the producer of antimony catalysts – for example aligned in IOAIA (www.iaoia.org) for antimony oxide - defended their products and tried to convince the polyester industry about their high catalyst quality with success.

### 2. Antimony today

**Market**
When we are looking at the current situation of antimony as catalyst for the production of polyester we are talking about antimony products of the highest purity level offered in the market compared to flame retardant or alloying applications.

Together with special purification treatments or chemical conversion to antimony trioxide, antimony triacetate or antimony tri-glycolate market prices of those catalyst products are widely spread.
But basis of all is the antimony metal price of a purity > 99.65% which was heavily volatile over the last ten years. The data of table 1 demonstrate the volatility during one year and the tremendous price hike during the last years and especially in 2006. In diagram 1 the metal price development graph is shown.

**Sb Metal Price**
Table 1: Antimony metal price development since 1992 in US$/kg, [4]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LOW</td>
<td>1,74</td>
<td>1,05</td>
<td>1,08</td>
<td>1,53</td>
<td>1,15</td>
<td></td>
<td></td>
<td>3,24</td>
<td>5,34</td>
</tr>
<tr>
<td>HIGH</td>
<td>5,02</td>
<td>1,12</td>
<td>1,53</td>
<td>1,63</td>
<td>3,13</td>
<td>2,21</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1:** Antimony metal price development since 1992 in US$/kg, [4]
Diagram 1: Antimony metal price development since 1993 [in US$/kg]
The presently estimated world polyester production of about 42 Mio t/a is more than 97% based on antimony catalysts which represents, presumed about 220 ppm antimony metal is applied in the average, a yearly metal consumption of about 8 970 t/a antimony metal. Until the 1990th antimony acetate was in favor over the oxide. Meanwhile purity of Sb2O3 is improved and increasingly producer changing form acetate to oxide – mainly to reduce cost.

During the last 15 years the total antimony production was cyclic and dependent on mine capacity, consumption growth and even speculation. Since 1990 the production was 90.000 t/a and was grown to 126.000 t/a in 1996 and declined to 117.000 t/a in 2005 [5].

Thus the consumption as catalyst for polyester production reaches about 10% of the world antimony production.

Looking at the history one can assume that there is not much mining capacity left to fuel completely the further increasing need of the industry.

One can predict that the in future consumption growth will proceed, which is even today the trigger of significant price increases and will also hit polyester producers during the coming years.
The antimony catalyst producers
Another development is the still increasing number of antimony catalyst producers, mainly those who offer antimony trioxide (ATO).

This results in growing product diversity accompanied by more uncertainty of catalyst consumers about catalyst quality and quality consistency.

On the one hand low margins out of polyester, high raw material prices and the price fight among the catalyst producers are forcing some polyester makers to try wooed price offers of catalyst producers not seldom with sobering results regarding the polyester quality.

On the other hand mainly driven by the requirement of bottle PET resin producers for lowest lead and arsenic content in their Sb-catalysts the top quality products like offered for example by Arkema, Campine, Chan Long, Honeywell, J&M/Synetix, Mikuni, or Yizheng has been improved in quality remarkably over the last 10 years.
Accepting the dictatorship of economy there is a clear trend to apply antimony trioxide in account of antimony triacetate and antimony triglycolate. The world is somehow divided in this respect because in China antimony acetate is preferred whereas the western world tends more to ATO.

**Optimization of catalyst application and logistic**

As one way of reducing dependency on catalyst pricing and quality differences between different sources the larger polyester producer are fading to the blending of two or three ATO-brands in constant mixing ratios. This procedure reduces the risk of quality inconsistency.

Same principle is since long time practice at polyester direct spinning plants. To balance quality differences between the PTA sources two or three different PTA sources are blended.

Especially large PET producers gaining from catalyst blending improved quality consistency and also equalized purchasing prices despite somehow higher expenditure of human labor and additionally logistic and some investment efforts.
By applying the chemical in-situ conversion of ATO to antimony triglycolate during catalyst preparation by sufficient reaction conditions like solution temperature > 180°C, removal of process water to stabilize the intermediate originated antimony triglycolate and fine filtration of the cooled catalyst solution the so prepared catalyst differs not much from a solution of antimony triglycolate in glycol.

To reduce filter blocking caused by antimony related precipitations (Sb-polyhydroxides) which takes place especially in PTA based processes running at comparable high water contents in the feed and balance glycols the optimization of feeding points and feeding sequences as well as the addition of complexation aids is useful to optimize filter life time.

One often observed problem is the precipitation of SbPO4 which is related to filter blocking and turbidity because despite of separated feeding points phosphor compounds are straying across the glycol circuits and reaching finally this stage of reaction where antimony is fed. Here the right selection of the P-stabilizer and the minimized application concentration will find a remedy.
There is no natural law to use 280 – 350 ppm Sb to produce successfully polyester!

Not the motto “much helps much” BUT “less is more” should be the guideline.

Increasing catalyst concentration and process temperature are of course the simple means to optimize a polyester production process.

Down optimization of catalyst concentration by a bundle of measures even at stable SSP velocity is possible and feasible today to improve product quality, reduce filtration cost and reduced catalyst consumption.
What about food compliance and environment impacts?

One may not neglect the facts and the meanwhile established limits:

In drinking water

<table>
<thead>
<tr>
<th>Antimony</th>
<th>max. 20 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVO Germany</td>
<td>max. 5 ppb</td>
</tr>
<tr>
<td>Germany</td>
<td>&lt;&lt; 1 ppb – 16 ppb</td>
</tr>
<tr>
<td>TAP water</td>
<td>&lt;1 – 5 ppb</td>
</tr>
<tr>
<td>USA drinking water</td>
<td>max. 6 ppb</td>
</tr>
<tr>
<td>Japan</td>
<td>max. 20 ppb*</td>
</tr>
</tbody>
</table>

(* the limit was increased from 2 to 20 ppb recently)

[0.001 ppm = 1 ppb = 1000 ppt = 1 µg/kg]

Scientific leaching tests of different laboratories using water and edible oil reported Sb leaching depending on time and temperature in a range of 0.02 – 0.6 ppb [6,7].
As one can easily see the range of Sb concentration increase by leaching of antimony to liquid foodstuff packed in PET bottles is one order of magnitude less than limits of USA and EU drinking water standards. And for most of the laboratories the detection limit is 1 ppb which classifies such results clearly to the scientific background.

AND: Any reduction of the Sb limits in drinking water by country governments or the EU commission would at first demand for huge investments to enable the public waterworks and drinking water suppliers to maintain such lower levels. The removal of antimony and arsenic from ground and surface water needs high energy and sophisticated and expensive technique.
As interim results one can say

→ Antimony is the still dominating catalyst and covers a share of > 97% of the world polyester production

→ Antimony prices will go up further by increased demand in the future

→ Price volatility remains a large element of uncertainty

→ Number of antimony catalyst producers is increased as well as range of quality specifications

→ Top antimony catalyst producers have improved catalyst quality and consistency continuously

→ Further means to increase the antimony catalyst efficiency are improved catalyst preparation, support of solubility, optimized feeding in sequence and locality, reduction of water impact and leveling of quality and price fluctuations by catalyst blending,

→ Food compliance of antimony catalyst for the time being not in acute danger but reduced limits, high sensitive analysis capabilities and a critical public community should remain in the focus.
3. Why and how a non antimony catalyst - NAC?

The wish list for a new catalyst will be long. A hand full of negative process or product properties caused by antimony is commonly known and therefore a new generation of catalyst should at first and solely sell advantages. Restrained on the main topics there are remaining some key points like:

~ Higher specific activity, lower application concentration – target < 50 ppm
~ No black deposits at pipe and reactor walls
~ Lower or no precipitations, longer filter life time, longer pack life time during spinning
~ No or negligible discoloration by catalyst or its conversion products
~ No metal oligomers, no ore less spinning smoke
~ Universal to use for bottle and textile PET based on PTA and DMT based as well
~ Lower or utmost same catalyst cost per ton polyester
~ Low nucleation and crystallization acceleration
~ Reduced amounts of necessary co-monomers like IPA or CHDM for bottle resins
~ Severely reduced leaching to dying bath, wet skin, packed liquid food
~ Easy to handle, without toxicity and negative public image
~ No toxic ash during waste incineration
~ High SSP acceleration
~ Last but not least providing an alternative to antimony in case food and environmental regulations are becoming more stringent

This list demonstrates a broad improvement potential which should be the driving power to develop and introduce new polyester catalyst technology more committed.
The discrepancy of NAC R&D and practical realization

Tracking frequently the globally released publications in the polyester field by CAS-Selects Polyester [12] since many years and looking for the number of patents related to new catalytic active core-substances the frequency of occurrence is:

\[ \text{Ti} > \text{Ge} > \text{Mg} > \text{Si} / \text{Zr} > \text{Al} > \text{others} \]

Most NAC patents are filed by Japanese companies. These are the resonate of former Japanese germanium catalyst tradition, the pressure to reduce cost and the lowest Sb-limit in drinking water in the world. Alternatively Japan is using Ge-based catalyst compositions still today on industrial scale.

The diagrams 2 and 3 are showing the current situation of Ge. The world production in 2005 was 86 t/a whereof 32 % or 27,52 t/a have been used for polyester production.

Assuming an average Ge metal content of 80 ppm, this presents a polyester production of 344 000 t or about 0,72 % of the world production.
Diagram 2: Market segments of Germanium [8]

Source: Teck Cominco

Source: Metal Bulletin, MetalPages
Because the GeO2-price dropped down continuously during the last decade the application of GeO2 as catalyst for special grades has a good chance to keep or even improve its market position.

Especially the high clarity and low crystallization speed of Ge-based polyesters are of interest for various technical applications like film for TV screens or technical yarn.

GeO2 catalyst grade producer of larger scale are for instance Teckominco [8] and Umicore [9]

**What is the reality of NAC Ti, Mg, Si or Al-based in today's polyester industry?**

Polyester based on NAC is still a small but growing niche product with some lights in the dark like some efforts made in Japan, USA and Europe

It is a matter of fact, despite the market offers a broad variety of NAC substances, the introduction of NAC to the commodity polyester in bottle, film and textile grade is still sitting in the starting blocks. And it is hardly to say that we will experience a real starting shot and a run on it within the very near future.
What are the scientific hurdles introducing NAC?
The homogeneous catalysis where the catalyst substance remains in the polymer matrix has in general the drawback that the catalyst and all its side or conversion products will occur and alter in correlation to process conditions.

More severe are chemical and technical circumstances of esterification and polycondensation where always side- and exchange products are generated.

Another hurdle is that the new catalyst must be active comparable to antimony in melt phase and solid state polycondensation as well.

And as we know polyester processes round the world have a high technology diversity which means the new catalyst substance must be inured and robust fit to large numbers of different process environments.

What are economic, logistic and knowledge hurdles introducing NAC?
The plant capacity is drastically increased and the catalyst replacement in continuous polyester plants of 100 -1200 t/d is possible during start up or maintenance shut down only.
Still growing plant capacities, high quality standards within all downstream processes and narrow correlation between catalyst base and processing properties are increasing enormous the financial risk of any change within the polyester production and processing chains.

Nearly all large continuous polyester production lines are exercising the more or less complete closed MEG loop (total MEG-recycling) where no external MEG-recovery exists and no discharge of side and destruction products takes place.

These MEG circuits where catalyst traces and catalyst destruction and conversion composites are created and accumulated and may or may not react are the real success hurdles to introduce a completely new catalyst system.

All test batches produced on bench scale, pilot scale or even at discontinuous lines are teaching nearly nothing about the real behavior of a new catalyst within precursor and closed split-off product loops of continuous plants.

Diagram 4 is trying to visualize size and complexity of a closed loop steady state plant situation.
Diagram 4 [10]:
PET PLANT AS STEADY STATE AND CLOSED LOOP SYSTEM
The catalyst producers have no or limited access only to such detailed information and if so this information is proprietary to plant owners.

As example: To reestablish the product and concentration equilibrium within the total EG recycling circuits of a 500 t/d PET plant after capacity or additive changes needs from 3 days until 1 week and severe problems by pipe plugging or black specks could even occur after weeks. Especial pipe or valve plugging bear high risks of subsequent plant shut down.

Result is that NAC producers are not in the position to provide the whole production technology including full guarantees to capacity, material consumption, quality and downstream processability. The risk is bearing the plant owner and polyester producer.

The theoretical ways out would be that one NAC producer is simulating such a continuous process on a small scale continuous line containing all features of a closed loop system to collect all possible side and accumulation effects and to optimize at the same time the catalyst technology. But extreme costs of such R&D work are sending those ideas away from our current reality.

The practical consequence out of this situation is the still existing high entrance barrier of NAC to produce bulk polyester products.
4. The role of phosphor as stabilizer and catalyst retarder/synergist

Among all discussion about a new catalyst metal or metal combination one is often not aware that non of those new catalysts based on Ti, Al, Mg, Ti-Si behave like antimony and can be used without a tailored P-stabilizer, reactivity retarder and synergist.

Especially polyester dedicated to SSP and bottle application needs stabilization against thermooxidative degradation and in some cases a special SSP enhancer.

Numerous P-stabilizer are available whereas only those are useful to produce bottle PET which are FDA approved.

Phosphonates, phosphonic acids, phosphinates and phosphinic acids which have the properties to convert the catalyst metal to a more stable catalyst complex and which react with OH- or COOH-groups are useful.

Similar to the need to separate Sb-catalyst and P-stabilizer during the process the NAC especially based on Ti and Al are in general more phosphorous sensitive and the intermingling of catalyst and stabilizer within the closed MEG loop is becoming an even more severe problem.

Therefore the P-stabilizer are an inherent part of new NAC technology [13, 14, 15]
5. The currently available NAC based on Ti, Al, Si/Zr and Mg

Hopes for high profits out of new NAC did not becoming reality till now but there is still a number of companies which offer commercial NAC products (see table 2). Polyester NAC are for those companies a small segment only of their product portfolio. One can estimate that R&D budgets are limited accordingly.

Table 2: Commercial NAC producers

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>CATALYST NAME</th>
<th>METAL BASIS LITERATUR EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARKEMA</td>
<td>S28 ® [16]</td>
<td>Ti-OR [17,18]</td>
</tr>
<tr>
<td>HONEYWELL RIEDEL DE HAEN</td>
<td>K-Ti-oxid-oxalate</td>
<td>Ti [21]</td>
</tr>
<tr>
<td>JOHNSON &amp; MATTHEY SYNETIX</td>
<td>VERTEC ® AC 450 [22]</td>
<td>TiOR + P-stabilizer [23]</td>
</tr>
<tr>
<td></td>
<td>Ti-CATALYST C-94 ®</td>
<td>Ti/Si [26]</td>
</tr>
</tbody>
</table>
Besides the catalyst producing chemical companies of table 2 there is another number of companies which developed their proprietary NAC as polyester manufacturer like Mitsui, Mitsubishi, Toray, Teijin, Toyobo and DuPont / Invista and as process vendors like Uhde-Inventa-Fischer and Zimmer-AG, see also table 3.

The situation about status of industrial introduction is diffuse and only few information about real production is available.

Mitsui Chemical Inc. advertised to produce in Indonesia and Thailand based on NAC technology at a capacity of 175 000 t/a [28]. Figures about amounts of Sb-free PET resin are not available.

Teijin announced the production of fiber, film and bottle resin based on NAC technology of about 22 000 t/a in 2006 out of this about 18 000 t/a bottle grade [31].

Toyobo which is the only company developed Al-base NAC has established similar to Teijin a broad base of applications in bottle, film, fiber and engineering plastics [33]. The commercialization especially via license partnership is ongoing, no information about production capacities of NAC-based polyester available.
Table 3: Companies developing NAC and / or producing PET based on proprietary NAC

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>CATALYST / TECHNOLOGY NAME</th>
<th>METAL BASIS LITERATUR EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>MITSUI</td>
<td>MP Catalyst [28]</td>
<td>Ti / Mg [27]</td>
</tr>
<tr>
<td>MITSUBISHI CHEMICALS</td>
<td>NC2 Catalyst [29]</td>
<td>Ti / Mg [30]</td>
</tr>
<tr>
<td>TEIJIN</td>
<td>PURITY ® [31]</td>
<td>Ti-based [32]</td>
</tr>
<tr>
<td>TOYOBO</td>
<td>GS Catalyst ® [33]</td>
<td>Al-based [34]</td>
</tr>
<tr>
<td>UIF</td>
<td>NN</td>
<td>Ti-complex-cat [35]</td>
</tr>
<tr>
<td>ZIMMER-AG / POLYTRADE</td>
<td>ECOCAT B, ECOCAT T ® [36]</td>
<td>Ti-based [37]</td>
</tr>
</tbody>
</table>
6. Polyester resin, fiber and film products based on NAC

Meanwhile a number of companies is producing – most of them on demand – limited amounts of polyester based on NAC. Because polyester for textiles, technical yarns, film and engineering plastics is less sensitive in terms of oxidative stability and color tuning the NAC application among these products is further developed.

The characteristic of Ti- and Al-catalysts is their hydrolytic sensitivity. For this reason the DMT-based polyester processes are confronted with less hurdles which lowers the introduction barrier of NAC.

Table 4 is showing a collection of PET producer which are offering NAC-PET for different applications.

When all public available production data are summarized one can estimate that NAC-PET based on Ge covers 350 000 t/a and NAC-PET based on Ti, Al, Mg covers about the same amount. This confirmed the former statement: PET based on NAC is still a niche product.
Table 4: PET producer which are involved in producing NAC-PET

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>PRODUCT NAME / METAL BASE</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>WELLMAN</td>
<td>Ti818 ThermaClear ® [38]</td>
<td>Hot fill bottle resin</td>
</tr>
<tr>
<td>INVISTA</td>
<td>Special products</td>
<td>On request</td>
</tr>
<tr>
<td>BRILENE</td>
<td></td>
<td>Eco-friendly fiber</td>
</tr>
<tr>
<td>FUTURA</td>
<td>Special products</td>
<td>On request</td>
</tr>
<tr>
<td>TWD Elana</td>
<td>Special Products</td>
<td>On request for eco-friendly fiber</td>
</tr>
</tbody>
</table>
7. Summary

~ Antimony catalysts are dominating today and will dominate for the foreseeable future the industrial production of polyester.

~ Improvements of the current catalyst technologies based on Sb are bearing further optimization potential.

~ Ge-based polyester is till now seemingly the largest portion of NAC-PET, the price decline of Ge might support its application in future.

~ NACs are offering a broad potential to optimize and improve process and product properties as well as reducing the commonly known drawbacks of antimony.

~ The high cost pressure on PET producers, the meanwhile huge single line capacities and the compared to antimony minor knowledge about the behavior of NAC in closed loop and total MEG-recycling applying continuous production lines are main hurdles for NAC introduction.

~ Japanese companies are at the forefront of research and introduction of NAC thanks to their history applying germanium and the lowest Sb-contamination level in drinking water in Japan.

~ A break through we would see when the first large resin producer is starting up one world scale continuous line based on NAC – but this will take time.
Information Sources:

[1] Are there new catalysts for polyester production in sight?; Thiele U., Nova-Pack ‘97 conference, 4.-5.06.1997, Mainz, Germany


Information Sources:


[12] CODEN: CAPOE9, ISSN: 0734-8703, Chemical Abstracts Service, a division of American Chemical Society, Columbus, OH 43210-0012, USA

[13] USP 6 066 714

[14] USP 6 080 834

[15] USP 5 992 828


Information Sources:

[18] EP0970983 (A3)


[21] USP 6841604, USP 5922828,


[23] PCT WO 97/47675; EP0812818A1


[25] DE19513956

[26] PCT WO 95/18839

[27] USP 6451959, USP 6346070, EP 1270640

Information Sources:

[29] New catalyst resin now – in a large variety of the market”, Fujimori, Y.; Mitsubishi Chemical Corp., 10th Polyester World Congress, Maack, Amsterdam 2005


[31] Advanced catalyst technology for polyester; Tsukamoto, R.; Teijin Fibers Ltd., 10th Polyester World Congress, Maack, Amsterdam 2005


[33] TOYOBO GS Catalyst®: Aluminium ready to challenge antimony, Gyobu, S.; Toyobo Co. Ltd; 10th Polyester World Congress, Maack, Amsterdam 2005


[35] EP0827518


[37] USP 6417320, WO02090419, DE10121542, DE10337522, EP1031590

[38] internal information, courtesy provided by Wellman Inc.