Tin Catalyst Removal with Reaxis Tinex
Introduction

This article describes the use and application of Reaxis’s TINEX products. All data and information are based on the experience and results from our own research and development laboratories.

Since its introduction, the TINEX products have found uses for the removal of tin catalysts from esterification processes.

Why Removal of Tin Catalysts?

Whether it is necessary to remove an esterification catalyst from an ester depends on the application of the product and the final use requirements the ester product. Examples where residual tin is not acceptable include:

- In plasticizers, residual tin catalyst content is not beneficial. When used in wire and cable PVC-applications, plasticizers must fulfill certain electrical conductivity limits. Any ionic substance in the plasticizer will increase the conductivity over accepted limits.

- In esters used for cosmetic applications, the total heavy metal content – and tin is regarded as being one – is limited by laws and regulations. Typically the catalyst concentration in the final ester is above the limits.
- Residual tin in esters for lubricant applications will decrease both the thermal and hydrolytic stability.

- In polyester polyols used as raw material for polyurethane formulations, residual tin catalysts can react with the isocyanates causing reactivity at an undesired stage of the formulation process.

Depending on the nature of the ester, inorganic tin catalysts – those of the oxidation state of II – tend to precipitate due to hydrolysis and/or oxidation over a period of time, resulting in turbid esters. Ester producers and their customers certainly do not like this effect.

**Tin Catalysts in Esterification Reactions**
As catalysts for esterification reactions, two types of tin catalysts are used:

**Type 1:** Inorganic Tin catalysts

Examples: Stannous oxalate  
Stannous oxide  
Stannous chloride  
Stannous octoate

**Type 2:** Organic Tin catalysts

Examples: Monobutyltinoxide  
Dibutyltinoxide  
Dibutyltindiacetate  
Dibutyltindilaurate.
All these catalysts have their special benefits depending on the special requirements of the reaction. In general it can be said, that all catalysts of type 1 have a salt like character and therefore can be removed easily from an organic environment.

Those of type 2 show an organophilic character. Their solubility in esters is high and their removal is not always easy. There are applications where type II catalysts are chosen because there is no need to remove them and they guarantee a stable, non-turbid end product.

**Methods for the Removal of Tin Catalysts**

The traditional methods for the removal of tin catalysts from the finished ester involve hydrolytic treatment. The esters are treated with sodium carbonate solutions, calcium hydroxide suspensions, or hydrogen peroxide and alcaline substances. Other methods make use of phosphorous or phosphoric acid and other acids.

The goal is always the same: all reagents should precipitate the tin catalyst in form of its insoluble oxide.

Depending on the type of ester and catalyst used, the traditional methods work quite well. A residual tin content between 1 – 10 ppm in the final ester can be achieved, which is sufficient for most applications.

The key disadvantage is that hydrolytic treatment does not leave the ester unaffected. A slight increase of the acid values often cannot be avoided. Residual water has to be
removed from the ester in order to maintain the stability and performance of the product. And additional drying of the ester is necessary to remove the moisture.

**What can REAXIS TINEX do?**

Reaxis Tinex products have been developed to overcome the disadvantages of the hydrolytic removal of residual tin from esters.

The goal was to find an easy and reliable process that enables the ester manufacturer to remove the tin catalyst simply by adding a substance during the ester work-up procedure. This makes it possible for the ester manufacturer to eliminate a complete work-up step, saving costs and expensive reactor time.

Reaxis Tinex products absorb the tin catalysts without introducing anything into the ester. Very often an improvement of product color can be achieved.

It is important to note, that **REAXIS TINEX products work only with inorganic tin catalysts of type 1.** Reaxis Tinex products are inefficient with organic tin catalysts. It is our ongoing interest to find agents showing the same efficiency towards the organic tin catalysts as the REAXIS Tinex materials show towards the inorganic tin catalysts.
What are REAXIS TINEX Materials?

Reaxis is offering 3 types of REAXIS TINEX materials. The following table shows the important features of each product:

<table>
<thead>
<tr>
<th>Properties</th>
<th>REAXIS TXP</th>
<th>REAXIS TXT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Status of the product</td>
<td>Commercial</td>
<td>Commercial</td>
</tr>
<tr>
<td>Chemical nature</td>
<td>Natural alumosilicate</td>
<td>Synthetic silica</td>
</tr>
<tr>
<td>Surface</td>
<td>Acidic</td>
<td>Acidic</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>70 % &lt; 63 µm</td>
<td>20 µm</td>
</tr>
<tr>
<td>pH-value of suspension in water</td>
<td>2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

REAXIS Tinex TXP is based on natural products that are carefully processed to enhance their surface properties, which give them their unique ability to absorb tin ions.

Reaxis Tinex T is a pure synthetic silicic acid which is surface treated to optimize the absorption properties.

High specific surfaces of all TINEX products support the adsorption abilities.
Mechanism of Tin Removal

A catalyst – by definition -- should be unchanged by the catalysis reaction. This is not completely true for inorganic tin catalysts used in esterification reactions. Catalysts like stannous oxalate (REAXIS C160) or stannous oxide (REAXIS C188) are not the actual catalysts in the esterification reaction but are considered precursors. In the reaction mixture these catalysts are transformed into a catalytic active species. In most cases, the first reaction taking place is a ligand exchange with the organic acid to be esterified.

For example:

Stannous oxide reacts with the acid to form a stannous carboxylate, as follows:

\[
\text{SnO} + 2 \text{R-COOH} \rightarrow \text{Sn(OOC-R)}_2 + \text{H}_2\text{O}
\]

Stannous oxalate may perform a ligand exchange or an addition reaction as the initial step:

\[
\text{SnC}_2\text{O}_4 + \text{R-COOH} \rightarrow \text{HOOC-COO-Sn-OOC-R}
\]

These intermediate species are then furtheron transformed into the actual catalytically active species.
After the reaction is finished, the tin catalysts are not left in their original form. Stannous oxide is present in a form of the carboxylate, which may or may not be soluble in the ester. Experience gained so far allows the prediction that in case of most fatty acids, stannous carboxylate stays soluble.

Stannous oxalate does not completely precipitate at the end esterification. Approximately 50% of the initial catalyst stays in solution in the form of the carboxylate. The other 50% precipitates in the form of the oxalate or oxidized compounds like stannic oxide.

Stannous compounds tend to oxidize to tin(IV) during the esterification. The tin(IV) species is present as stannic oxide, which can be dispersed in colloidal form in the ester. These colloidal particles are difficult to filter and tend to agglomerate and precipitate over a period of time.

Any tin removal agent must then being designed for the removal of these carboxylates.

REAXIS TINEX products have two key properties that enable them to remove tin from esters:

- Acidic character
- High polar surface

The acidic character of the TINEX products allows reaction with the stannous carboxylates (as shown below) because acidity of the TINEX material is higher than the ester.
The second reaction that takes place is simply adsorption. Because of the high specific surface area and polar nature, polar stannous carboxylates are readily adsorbed.

It can be estimated that Van der Waals-Forces are the major attracting forces. These forces are also beneficial for the attraction of colloidal particles in the ester.

Which of those two mechanism is the dominant is unknown, but similar mechanisms are known from refining edible oils, where phosphor containing compounds or nickel residues from hydrogenation catalysts are removed.

Scope and Limitations of TINEX use

In general, TINEX products can be used for nearly all kinds of esters. There is one key factor that involves the efficiency of the TINEX products: the viscosity of the ester.

Since the mechanism of the tin removal is based on reactions between the stannous carboxylate and the surface of the TINEX particle, it is absolutely necessary that the stannous compound contact the TINEX particles. Otherwise no tin removal is possible.

If the viscosity of the ester is now very high (e.g. 1000 mPas and higher) the migration speed in the ester is low – even at the suggested processing temperature – for the stannous compound as well as for the TINEX material.
This has consequences: the removal rate is low and a higher loading of TINEX is necessary.

Which type of TINEX material is the best one for a specific ester is not easy to tell. It is recommended to test all types and take the most efficient one for further optimization.

TINEX materials can be used in combination with inert filter aids like fuller´s earth or diatomaceous earth, decalite and others in order to improve the filtration.

Furtheron it has to be emphasized again, that TINEX products are only efficient for the removal of inorganic tin catalysts. Due to their organophilic nature organic tin catalysts are not effected by the presence of TINEX. Nevertheless the removal of other inorganic metallic species is also possible, because the above mentioned removal mechanism is not specific to inorganic tin but to all similar metallic compounds.

**Achievable Tin Levels**

In general, the final level of residual tin in the ester can be as low as 1 ppm. 1 ppm is the detection limit of the analytical methods applied by the Reaxis´s laboratories.

If higher concentrations of tin are possible, the TINEX concentration that is added to the ester can be varied. The correct dosage for the TINEX products has to be tested in the laboratory.
How to use REAXIS TINEX?

It was one of the major goals for the development of the TINEX products to offer easy to use products which can be adjusted to the process conditions in esterification reactions.

A typical treatment procedure with TINEX can be formulated as follows:

After the esterification reaction is finished, the raw ester is cooled and normally transferred to a post-treatment reactor for final quality adjustment.

At temperatures around 90 – 120°C, TINEX can be added to the ester. Addition of TINEX above 140°C is not recommended because the acidic nature of TINEX increases the acid value of the ester. At temperatures between 90 – 120°C, the acid value insignificantly affected.

The TINEX material has to be dispersed very well in the ester, in order to facilitate contact between the tin soap and the adsorption material. Good agitation is thus required. Contact time between TINEX and ester depends on the viscosity; the lower the viscosity the shorter the required contact times. Low viscosity esters like dioctylphthalate or trimethylolpropaneoleate need about 30 – 90 minutes mixing time. It is preferred, but not absolutely necessary, to keep the ester temperature at 90°C.

After this contact time, the ester can be cooled and filtrated with conventional filtration equipment like a frame filter press. If necessary the filtration times can be increased by
adding inert filtration aids prior to the filtration. The amount of inert filtration aids (like siliceous earth) has to be evaluated in lab trials.

If the TINEX treatment is performed in the esterification reactor, a good cleaning of this reactor is recommended, otherwise residual TINEX may infect the catalyst efficiency of the following esterification batch. Insufficient cleaning will lead to lower reactivity of the REAXIS catalysts.

Other cleaning steps for the ester such as bleaching or stripping of surplus of alcohols should be performed before the TINEX treatment. It is possible to perform those steps after TINEX treatment, but any particle formation may make an additional filtration step necessary. If the bleaching is done with active charcoal this process can be combined with the TINEX process. Active charcoal does not affect the tin adsorption properties of TINEX. On the other hand, certain types of active charcoal also have some ability to absorb metal ions, but – to the best of our knowledge – not as good as the TINEX products.

The clear ester should be tested for its tin content in order to control the efficiency of the removal process.

As alternative, a fixed bed filtration process is under development. For this method, REAXIS TINEX C has been developed. The advantage of such a process is to that contamination of the reaction or post-treatment reactor by TINEX materials is alleviated. TINEX C can be filled into a heated filter column (90°C – 120°C) and the heated ester can be pumped over the column at a certain flow rate. The rate is determined by the tin-uptake of TINEX C. After the adsorption limit of TINEX C is reached, the column must be replaced. Obviously, a dual parallel column set up would minimize down time.
TINEX C works in the traditional mixing process as well, but due to its lower surface (or bigger particle size) higher loadings might be necessary in order to achieve good results. On the other hand, its filtration properties are outstanding.

**Lab Procedure**

Lab trials are recommended in order to determine the best concentration of and type of TINEX required.

A recommended procedure is as follows:

In a 250 ml 1-neck flask, 100 grams of raw ester is added. TINEX material is added at the desired level; a suggested starting concentration 1%. The flask is mounted on a rotary evaporator and rotated at a certain speed in the heated oil bath (90°C suggested). Rotation speed can be adjusted to stirrer speed in the plant reactor. After 60 minutes, rotation is stopped and the mixture filtered over a buchner funnel to determine the filtration properties. Filtration can be performed at temperatures similar to those experiences at plant conditions. Pressure filtration is also possible to test different filter media types.
Possibilities for Optimization

Of course there is always room for optimization. Questions like the following rise:

- How can we reduce the TINEX loading?
- How can we further reduce the Tin content?
- Can we combine the TINEX process with other residual removal processes.

The answers of course depend on the special conditions of each manufacturing process. The following suggestions should be understood as general guidelines, which have to be adapted to the individual process:

Suggestion 1: TINEX materials can be activated by water.

The TINEX process can be modified as such: TINEX is added to the raw ester followed by addition of water. The amount of water should not exceed the amount of TINEX. In lab trials, a ratio of 1 part TINEX and 0.6 parts of water has proven to be adequate. The water activates the surface of the TINEX materials, creating more polar and active sites on the surface. This results in an increase in the adsorption properties of TINEX. It has to be determined whether additional vacuum treatment is necessary to remove residual moisture.
Suggestion 2: TINEX materials can be used in combination with acidic work-up procedures.
A typical procedure would involve either phosphorous or phosphoric acid being added to the ester and stirred, followed by addition of the TINEX. After the normal contact time, the work-up procedure can be done as described above. Implementing this procedure requires that the acid value be carefully monitored. The phosphorous based acids precipitate inorganic tin catalysts to form insoluble tin phosphites or tin phosphates. These particles are adsorbed on the surface of TINEX.

The TINEX procedure in combination with the alcaline method is not recommended, because this would result in a neutralization of the acidic sites of TINEX and a loss of the adsorption ability.

Spent TINEX
When the raw ester is processed, the remaining residue is a filter cake consisting of the TINEX material, residual ester, eventually of additional filter aid. The filter cake contains approximately 1 – 5 % inorganic tin. This filter cake can be treated and disposed of in a manner similar to that of normal filter aids.

Depending on the regulations, options for reuse of the waste filter product include:

- Landfill and soil improvement
- Raw material for bricks
- Raw material for cement production.

Recycling of the waste product is not possible.
TINEX Applications: Case Studies

To show the efficiency and the effects of TINEX materials some case studies are provided below.

Removing Inorganic Tin from Esters: Removal of REAXIS C160 (stannous oxalate) from DOP and TMP-caprylic acid ester

Description of the Process:

The filter aid is added to the raw ester at 80°C. It is possible to add the filter aids at higher or lower temperatures. This is important when solid or high viscous products are involved. The resulting mixture is stirred for about 15 to 30 minutes. After cooling, the ester is filtered using commercially available filter media (for example: Schenk AF 1000).
Results:

Removal from Trimethylolpropanetricaprylate

<table>
<thead>
<tr>
<th>Filter aid 1%</th>
<th>No Filter aid</th>
<th>Charcoal</th>
<th>REAXIS TXT</th>
<th>REAXIS TXP</th>
<th>Bleaching earth Opt. FF</th>
<th>Bleaching earth L80 F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-value (mg KOH/g)</td>
<td>11.6</td>
<td>11.6</td>
<td>11.8</td>
<td>11.8</td>
<td>11.3</td>
<td>11.7</td>
</tr>
<tr>
<td>Turbidity (TE/F)</td>
<td>90</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Sn-Content (ppm)</td>
<td>900</td>
<td>52</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>280</td>
<td>700</td>
</tr>
<tr>
<td>Iodine-color number</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Removal from DOP

<table>
<thead>
<tr>
<th>Filter aid 1 %</th>
<th>no Filter aid</th>
<th>Charcoal</th>
<th>REAXIS TXT</th>
<th>REAXIS TXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-value (mg KOH/g)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Turbidity TE/F</td>
<td>128</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Sn-Content (ppm)</td>
<td>1200</td>
<td>3</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Iodine color number</td>
<td>6</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Application of REAXIS TINEX products for the removal of inorganic tin catalysts from Esters: Glycerol mono/di stearate

With REAXIS TXP, it is possible to reduce the final tin content of the ester to approximately 1 ppm. The efficiency of REAXIS TXP towards different tin catalysts is shown by the attached adsorption isotherm.

Description of the Process:

The TINEX material is added to the final ester product at 90 °C; the ester contains approx. 570 ppm of tin. The mixture is intensively stirred for 30 minutes. A vacuum may
be applied at 20 - 30 mbar. REAXIS TINEX is removed by filtration over a conventional filter plate.

Results:

<table>
<thead>
<tr>
<th>Amount of REAXIS TXP relative to the ester</th>
<th>Final content of tin in the ester after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 %</td>
<td>30 ppm</td>
</tr>
<tr>
<td>0.3 %</td>
<td>12 ppm</td>
</tr>
<tr>
<td>0.5 %</td>
<td>4 ppm</td>
</tr>
<tr>
<td>1.0 %</td>
<td>1.3 ppm</td>
</tr>
<tr>
<td>1.5 %</td>
<td>0.9 ppm</td>
</tr>
</tbody>
</table>

Application of REAXIS TINEX products for the removal of inorganic tin catalysts from Esters: Glycerol mono/di linolate

The adsorptive properties of the REAXIS TINEX products depend on the type of ester involved. For determination of the optimum concentration of TINEX, an adsorption isotherm is an appropriate way to find the lowest concentration of TINEX for maximum adsorption of tin.
In this example, glycerol mono/di linolate is produced with different inorganic tin catalysts and post-treated with REAXIS TINEX products. It can be shown that the amount of tin in the ester can be reduced to 1 ppm.

**Description of the Process:**

The TINEX material is added to the ester at 80 - 90 °C. The ester contains approximately 300 ppm of tin. The mixture is intensively stirred for 30 minutes to 1 hour. A vacuum may be applied at 20 - 30 mbar for half of this time. REAXIS TINEX is removed by filtration over a conventional filter plate.

**Results:**

The table shows the amount of REAXIS TINEX that is necessary to obtain a final tin content of 1ppm.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>REAXIS TXP</th>
<th>REAXIS TXT</th>
</tr>
</thead>
<tbody>
<tr>
<td>REAXIS C129 (stannous octoate)</td>
<td>0.6 %</td>
<td>&gt; 1.5 %</td>
</tr>
<tr>
<td>REAXIS C160 (stannous oxalate)</td>
<td>0.6 %</td>
<td>&gt; 1.5 %</td>
</tr>
<tr>
<td>REAXIS C188 (stannous oxide)</td>
<td>&lt; 0.3 %</td>
<td>0.8 %</td>
</tr>
</tbody>
</table>