

Compatibility of Reaxis Catalysts with Antioxidants in Selected Case Studies

In esterification and transesterification processes the color of the final ester is often an important issue. The color of the final product is influenced by a number of factors, including:

- presence of oxygen
- quality of raw materials
- type of catalyst
- reaction conditions like temperature and vacuum
- reaction time.

The development of color during an ester formation process is chemically caused by different side reactions, including:

- dehydration
- formation of olefins, aldehydes or ethers
- elimination reactions with formation of conjugated double bonds
- polymerization reactions.

Tin catalysts normally have a positive influence on the development of color in an ester formation process. This is due to the fact that the catalysts either shorten the reaction time or lower reaction temperatures. Tin catalysts are - with a few exceptions (Reaxis C 250) - non-corrosive materials, which minimize acid catalyzed side reactions.

Nevertheless, color development still can reach an undesirable level and some additional precautions have to be taken. The addition of antioxidants to the reaction mixture is one of the options that can be considered.

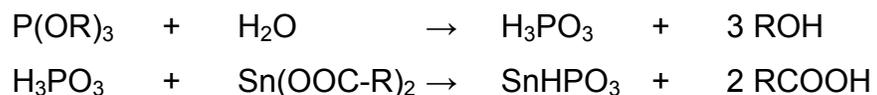
There are many different types of antioxidants available in the market and this paper presents the results of interactions between various different types of antioxidants and our catalysts.

Interaction of Antioxidants With Inorganic Tin Catalysts (100-series)

Commonly used antioxidants in esterification reactions include:

- Phosphites (for example triphenylphosphite)
- hypophosphorous acid
- sterically hindered alkylphenols
- sterically hindered amines (HALS)

Experiments have shown that the combination of inorganic tin catalysts with phosphorous-based products is not ideal. If the phosphorous containing material is not hydrolytically stable the following reactions will take place:



The reaction water hydrolyzes the phosphorous chemical to an acid, which then rapidly reacts with the tin(II) component to form an insoluble product. Tin-Phosphorous components have in general terms a very low solubility in an organic matrix. They result in a turbid ester product and in a decrease in catalytic activity. Esters produced with the use of tin(II) catalysts are usually filtered and thus the precipitation problem caused by the antioxidants can be remedied, leaving the loss of catalytic activity as the main problem.

In order to avoid catalyst deactivation and precipitation, it is a must to use hydrolytically stable phosphorous components or to switch to other antioxidants.

The use of HALS-antioxidants is not recommended because there is the possibility of complex formation between the catalyst and antioxidant that will also lead to turbidity and loss of catalyst activity. This experience is probably not true in general terms, but it is based on our lab experiments with some typical representatives of HAL-type oxidants.

Good results have been obtained by combining tin(II) catalysts with sterically hindered phenols as exemplified in the following test results.

Synthesis of Dioctyladipate with Reaxis C160 and Antioxidants

Formulation:	Adipic Acid	146.14 g	0.5 mol
	2-Ethylhexanol	130.23 g	1.2 mol
	REAXIS C 160	0.23 g	0.1 %
	Antioxidant	0.23 g	0.1 %

Procedure: reaction temperature: 220°C max.
remove water by distillation and excess of alcohol by vacuum distillation
add inert gas
filter after reaction is complete

Results:

Catalyst	Antioxidant	Final Acid Value	Hazen Color Number
REAXIS C 160	-	1.0	85
REAXIS C 160	Irganox 1076	0.6	< 15
REAXIS C 160	Irganox 1098	0.8	15
REAXIS C 188	-	0.5	30
REAXIS C 188	H ₃ PO ₃	1.5	< 10

Use of the sterically hindered phenol antioxidants (Irganox supplied by Ciba Geigy) increased the catalytic activity while at the same time reduced the color. The results also show that the catalytic activity is decreased when phosphorous acid is used.

Interaction of Organic Tin Catalysts (200-series) With Antioxidants

In general, the arguments given for the inorganic tin catalysts are also valid for the organic tin types: phosphorous hydrolysis will lead to the increased turbidity of the ester product and a decrease in catalytic activity.

Organic tin catalysts are designed to stay in the final product. The esters produced are clear and storage stable. The tin catalysts themselves are very soluble in the esters. Addition of phosphorous-based antioxidants causes turbidity of the final product, which can not be remedied as readily as with inorganic tin catalysts because the ester products are often difficult to filter due to their high viscosity. In applications using organic tin catalysts it is necessary that the catalyst and antioxidant harmonize to not only limit loss of catalytic activity but also limit the generation of turbidity. An example of such an application is provided below.

Synthesis Of Long Oil And Medium Oil Alkyd Resins Based On Soya Oil

Formulation: proprietary

Procedure: transesterification reaction: 240°C

esterification reaction: 220 -240°C

nitrogen as inert gas

azeotrop distillation with xylene in a dean-stark trap

Results:

The table below shows clearly the positive affect of different antioxidants on the color prevention in the prepared alkyd resins. Depending on the type of antioxidant used, the Gardner Color Number can be lowered by two units. All tested antioxidants had an influence on the catalytic activity. The antioxidants Irgafos P-EPQ and Chimasorb 119 had the most deleterious affect on catalytic activity.

The best results were achieved with Ralox 630 (Raschig AG, Ludwigshafen), and with Irganox 245 (Ciba Geigy). The ratio of catalyst to antioxidant seems to be optimum when between 1 : 0.5 - 1 : 0.8.

Further work is necessary to evaluate the effects more clearly.

Catalyst	Amount	Antioxidant	Chemical Description	Amount	Total Reaction Time ¹	Final Acid Value	Gardner Color Number	Turbidity
REAXIS C 248	0.1 %	-	-	-	90 min.	9.4	5.5	clear
REAXIS C 233	0.1 %	TNPP	Trisnonylphenylphosphit	0.25 %	-	-	-	hazy
REAXIS C 233	0.1 %	TBP	Trisbutylphosphit	0.25 %	-	-	-	hazy
REAXIS C 248	0.1 %	Ralox 630	Pentaerythrit-tetra(3,5-di- t.butyl-4-hydroxyhydrocinnamat	0.06 %	140 min.	10.6	3.4	clear
REAXIS C 248	0.1 %	"	"	0.03 %	140 min.	10.4	4.4	clear
REAXIS C 248	0.1 %	"	"	0.07 %	125 min.	9.8	3.6	clear
REAXIS C 248	0.1 %	Irgafos 168	Tris(2,4-di-t.butylphenyl)phosphit	0.06 %	120 min.	9.0	4.7	clear
REAXIS C 248	0.1 %	Irgafos P- EPQ	PCl ₃ -reaction product with 1,1-biphenyl and 2,4-bis-1,1-dimethylethyl)phenol)	0.06 %	> 125 min.	catalyst inhibition	-	-
REAXIS C 248	0.1 %	Irganox 1098	N,N'- Hexamethylen-bis- (3,5-di-tert.butyl-4-hydroxyhydrocinnamat)	0.06 %	75 min.	15.7	6.9	slightly hazy
REAXIS C 248	0.1 %	Irganox 245	Triethylenglycol-bis[3-(5-tert.butyl-4-hydroxy-m-tolyl)-propionate]	0.06 %	145 min.	10.5	4.6	clear
REAXIS C 248	0.1 %	Chimasorb 119	HALS-based mixture	0.06 %	> 50 min.	catalyst inhibition	-	-

1- Reaction time given for transesterification stage