Johnson Matthey Catalysts

VERTEC™ – Direct Esterification Technology

VERTEC™

Contents

1. Introduction

1.1 Esters and Esterification

VERTEC titanates are used to catalyse three main classes of esterification reaction: direct esterification, transesterification (or alcoholysis) and polyesterification.

Direct esterification is the reaction between a carboxylic acid and an alcohol to produce an ester plus water:

$$\underset{\displaystyle R-\overset{\displaystyle \overset{O}{\|}}{C}-OH}{} + R'OH \longrightarrow \underset{\displaystyle R-\overset{\displaystyle \overset{O}{\|}}{C}-OR'}{} + H_2O$$
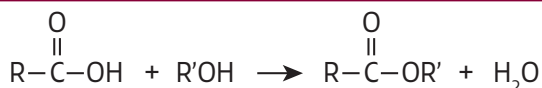
In a transesterification reaction a preformed ester exchanges an alkoxy group with an alcohol to produce a new ester:

$$\underset{\displaystyle R-\overset{\displaystyle \overset{O}{\|}}{C}-OR}{} + R'OH \longrightarrow \underset{\displaystyle R-\overset{\displaystyle \overset{O}{\|}}{C}-OR'}{} + ROH$$

Polyesterification is an extension of either or both of the above reactions. Polyesters are produced by the interaction of a dibasic acid or its lower alkyl ester with a glycol or polyol, i.e. by direct or transesterification reactions.

1.2 Titanates

Organic titanates, such as tetraisopropyl titanate, $Ti(OC_3H_7)_4$, are themselves esters of the hypothetical orthotitanic acid, $Ti(OH)_4$. As such they readily undergo transesterification as described above when mixed with higher alcohols. Thus tetra 2–ethylhexyl titanate is formed from tetra isopropyl titanate and 2–ethylhexanol:

$$Ti(O^iC_3H_7)_4 \;+\; 4\,C_8H_{17}OH \;\longrightarrow\; Ti(OC_8H_{17})_4 \;+\; 4\,{}^iC_3H_7OH$$

This type of transesterification is rapid and occurs as soon as a titanate catalyst is added to a reaction mixture containing free alcohol or glycol and is the first step in the catalysis of ester formation. The lower molecular weight titanates are sensitive to hydrolysis by atmospheric moisture and should be handled with care.

1.3 Advantages of Titanate Catalysts

Because they are esters, titanates are neutral compounds and it is this neutrality that gives titanates many of their advantages over acidic and basic catalysts. Acids and bases cause side reactions and degradation of the reactants. This leads to poor colour and contamination of both the product ester and any excess reactant. **VERTEC** titanates minimise these side reactions. It is therefore possible to use larger excesses of reactant alcohols, which can be recycled without intermediate purification. This in turn leads to higher conversions and yields of purer products. Effluent treatment is minimised or eliminated.

Other metallo–organic catalysts are available, for example, certain derivatives of tin, magnesium and aluminium. However, it is usually found that these are either more prone than titanates to cause side reactions or are less cost–effective. The above advantages will be further illustrated in the following section where each of the three classes of esterification reaction is separately discussed.

2. Direct Esterification

The use of titanates as esterification catalysts has been widely patented, the first claim being made in 1955 in the USA. Since then the demand for titanates for this application has grown steadily and now accounts for a significant proportion of the total market for these compounds. The biggest use is in the large tonnage plasticiser industry for producing such esters as dioctyl phthalate from phthalic anhydride:

For the first stage of the reaction to produce the monoester no catalyst is required.
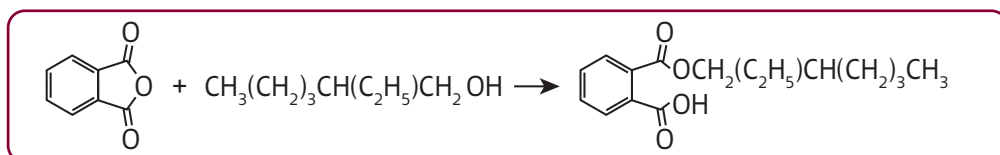
A catalyst is needed for the second stage, which is a reversible reaction.
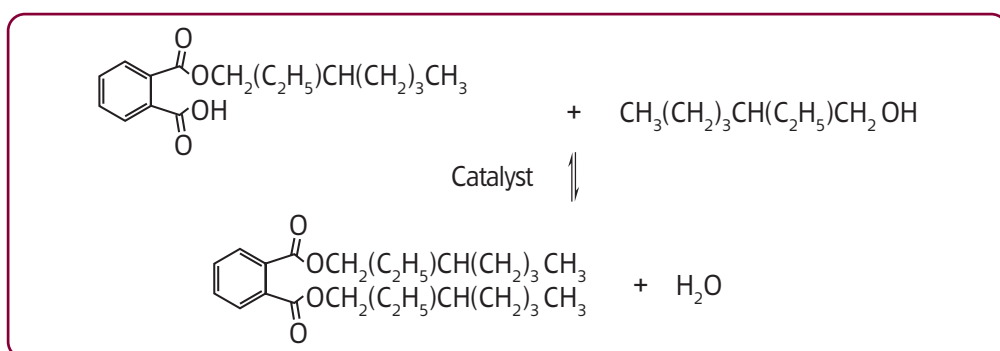
Titanates are very effective at temperatures of 180–220°C. Although this is higher than the temperatures needed with former catalysts, such as sulphuric acid or substituted sulphonic acids, the advantages conferred by using titanates more than compensate for the extra energy input. Titanates minimise side reactions, and do not degrade the alcohol, which can be readily recycled without purification. This means that a large excess of alcohol (e.g. 25%) can be used economically, which gives a higher conversion to good quality diester. Furthermore, with titanate catalysts, the product colour is almost independent of reaction time and no "end–effect" colour is produced. This lack of degradation is particularly important with secondary alcohols, which degrade more readily, yet react more slowly to produce esters.

Perhaps the greatest advantage of using titanates, however, is in the elimination of the product washing stage with its attendant effluent problems. This is a consequence of the very high conversion achieved with titanates and the purity of the product. Titanate–catalysed esterification has been called a 'dry process', virtually the only water going to effluent being that liberated in the esterification reaction. The removal of the washing stage results in a significant reduction in the capital outlay necessary to erect an ester manufacturing plant.

2.1 Titanate Selection

Whichever titanate is used, a transesterification reaction of the type described in Section 1.2 occurs as soon as it is added to the reaction. The choice of which titanate to add is therefore normally influenced more by commercial than by technical factors. For most purposes the requirement is for the highest titanium content per unit price, which means **VERTEC** TIPT. As **VERTEC** TIPT may freeze during outdoor storage **VERTEC** BIP or TNBT are sometimes preferred. **VERTEC** BIP is a modified version of **VERTEC** TIPT developed to avoid freezing problems and is slightly more cost–effective than **VERTEC** TNBT. The physical properties of these three products are shown in Table 1 .

These products liberate either isopropanol or n–butanol when they are added to the reaction mixture. Although these are likely to be removed with the water, which is formed and distilled out of the reaction medium, they may give rise to very slight traces of isopropyl or butyl ester in the product. This is not normally important because of the low concentration of catalyst used (approximately 0.1% by weight on product ester). When such trace contamination of the product ester (or water effluent) cannot be tolerated the titanate derived from the reactant alcohol should be used, e.g. **VERTEC** EHT in the production of bis (2–ethyl–hexyl) phthalate. However, because of its lower titanium content (see Table 1) **VERTEC** EHT must be used at a higher concentration than the lower molecular weight titanates.

Product	Appearance	Ti content %	Density g/ml 25°C	Boiling Point °C/mmHg	Viscosity cp 25°C	Flash Point °C (cc)	Melting Point
VERTEC TIPT	Colourless/pale yellow liquid freezing at 18°C	16.9	0.970	240/760	3	46	approx 17.5°C
VERTEC BIP	Pale yellow liquid	16.5	0.980	236/70	8	49	<–30°C
VERTEC TNBT	Pale yellow liquid	14.1	0.995	312/760	70	40	<–30°C
VERTEC EHT	Very pale yellow liquid	8.5	0.935	205/1	140	45	<–30°C

Table 1: Physical Properties of some **VERTEC** Organic Titanates

It is believed that about 50% of the liberated alcohol from the catalyst reacts to form ester, the other 50% is lost in reaction.

2.2 Process Conditions

The reactor is usually made of stainless steel and designed with a low height to diameter ratio. This gives a high surface area to volume ratio in the reaction medium, which encourages the rapid and complete removal of the water produced. The reactor is fitted with a condenser, which drains into a separator/receiver fitted with a return line to the reactor. This arrangement allows the alcohol distilled off with the water of reaction to be separated from the water and returned to the reactor.

Total reaction time is reduced if both the reactant alcohol and acid can be preheated before being added to the reactor. Phthalic anhydride can be pre–melted in a storage vessel or supplied in molten form. The alcohol is usually added in a 20 to 25% excess which further reduces the reaction time.

The **VERTEC** catalyst is added when the reaction temperature reaches 160°C. This prevents premature hydrolysis of the titanate and also ensures that any solid reactants that are used are melted or dissolved. If desired, the titanate can be pre–diluted with a small amount of reactant alcohol.

VERTEC TIPT, BIP and TNBT are used at about 0.05 to 0.10% by weight based on final product ester. For reactions with secondary alcohols or other less reactive ingredients this may have to be increased to 0.15 to 0.20%.

To obtain very high conversions it is important that the water produced should be removed as quickly as possible, especially towards the end of the reaction. By controlling the heat input and the pressure, the reactants are kept at a brisk boil and the water is distilled out as an azeotrope with the reactant alcohol. The distillate collects in the receiver where it separates into two layers. With higher alcohols, such as 2-ethylhexanol, the upper, alcohol layer contains very little water and can be returned directly to the pot. Lower alcohols such as butanol, however, should be further dried by redistillation before being so returned. To prevent the returning alcohol from carrying the escaping water vapour back into the reaction mixture it should preferably be returned via a dip pipe below the surface of the reactants.

The progress of the reaction can be monitored by, following the decrease in acid value of the reaction mixture. Once plant operating conditions have been established, the reaction time can be predicted and normally only a single determination is needed to confirm that the reaction is complete.

2.3 Catalyst Removal

When a conversion of about 99.7% (0.4 mg KOH/g) has been achieved, the residual mono ester in the reactor product is neutralised. The neutralisation state also serves to convert the titanate catalyst into a form, which is removable by filtration.

There are 2 neutralisation options:

a Hot Neutralisation

In this process aqueous sodium carbonate is added to the hot reactor product. This is followed by steam stripping of the excess alcohol from the reactor product. (Stream or recycled water of 180˚C reactor can be used). The resulting reactor product is dry and contains a precipitate consisting of the sodium salt of the monomer plus the titanate residue.

b Cold Neutralisation

In this process the reactor product is cooled to approximately 100˚C and transferred to an agitated neutralised vessel. Aqueous sodium hydroxide is added and in the vessel the aqueous and organic layers are separated by settling. The aqueous layer is run off taking some of the sodium salt of the mono ester and the titanate catalyst residues. Additional water washing is optional. The excess alcohol is steam stripped to give a dry ester product containing less sodium salt of mono ester and titanate residue, than process a above.

Following both the above processes the phthalate end product needs to be filtered. Because of the very small particle size of the residues in the ester, a precoated filter (Funda type or plate and frame type) must be used.

Because of the non aggressive nature of titanate catalyst, as compare with sulphuric acid or PTSA catalyst, the ester product does not require decolourisation. In addition, the recovered excess alcohol stripped from the reaction product can be recycled directly to the next batch.

The only effluent is the water of the reaction and the water used in neutralisation/washing. It is possible to recycle the reaction water for stripping/neutralisation/washing.

NOTE: That in process b the amount of washing to achieve the same sodium salt of mono ester removal as with say PTSA is relatively small. The conversion with titanate catalyst is at least 99.7% as compare with 98-99% with PTSA.

2.4 Laboratory Evaluation

Johnson Matthey has carried out the following laboratory work to compare the efficiency of titanates with other catalysts. Although the preparation of bis (2-ethylhexyl) phthalate was chosen for the experiments, the use of titanates as esterification catalysts is by no means restricted to phthalate ester production. Any direct esterification reaction that is capable of being carried out at temperatures at or above about 180°C can be catalysed with organic titanates.

2.4.1 Apparatus

The apparatus was a 1-litre, 3-necked flask fitted with a thermometer, a tube dipping below the surface of the reactants and a Dean and Stark apparatus. The equipment was operated under reduced pressure by using on all pump connected to two water condensers fitted above the Dean & Stark apparatus. The flask was equipped with a rubber septum cap ("Suba-Seal") and nitrogen was passed into it via syringe needle. This provided a nitrogen bleed and also prevented hot vapours reacting with the Suba-Seal to give rise to product discolouration.

2.4.2 Method

0.5 moles (74g) phthalic anhydride were added to 1.25 moles (162.5g, 25% excess) 2-ethylhexanol. The mixture was heated to dissolve the phthalic anhydride and the nitrogen flow started.

When the temperature had reached that selected for the experiment a weighed amount of catalyst was added via the Suba-Seal with a syringe. For solid catalysts a small amount of 2-ethylhexanol was retained and used to slurry the solid before injection. The reaction mixture was maintained at a vigorous reflux at the selected temperature by suitable adjustment of the heating rate and vacuum. The water produced was removed substantially as quickly as it was formed and collected in the Dean and Stark apparatus.

The progress of the reaction was followed by withdrawing samples at intervals by means of a syringe. Each sample was added to a known weigh of cold alcohol to quench the reaction, weighed and titrated against standard potassium hydroxide solution in ethanol using bromophenol blue as indicator. The results were used to calculate the amount of unreacted half ester present and a graph was plotted of conversion against time from injection of catalyst.

2.5 Results and Discussion

Figure 1 shows the influence on reaction rate of various catalysts at 200°C. Sulphuric acid is the most active, but at this temperature it causes significant charring of the reaction mixture. Methane sulphonic and p-toluene sulphonic acids also give a faster rate than titanates initially, but they are overtaken by the titanates later in the reaction and take much longer to reach 99% conversion. The tin compounds, stannous octoate and dibutyltin oxide, are considerably less cost-effective than any of the other catalysts.

Figure 1. Preparation of Bis(2–ethylhexyl)phthalate various catalysts at 200˚C
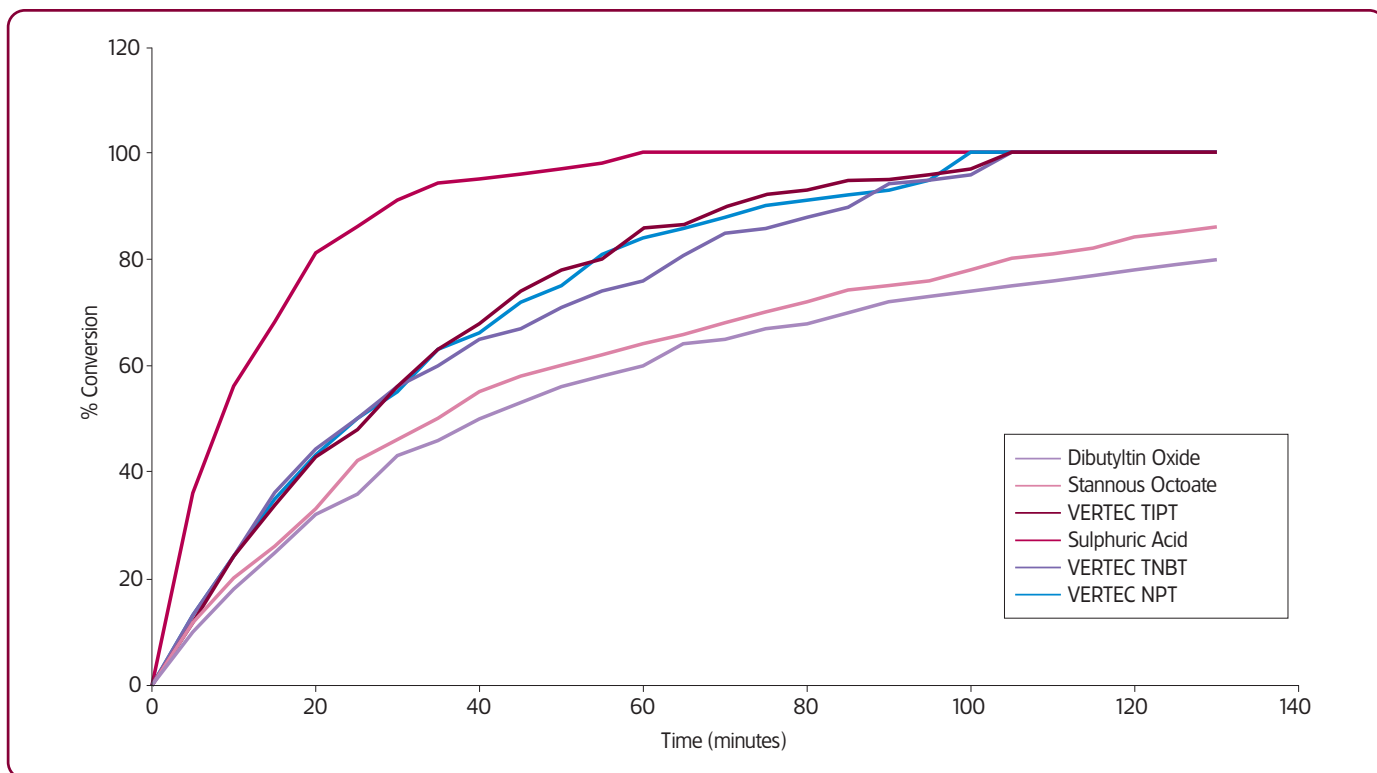
Raising the reaction temperature to 220˚C increases the effectiveness of the titanates more than that of the acid catalysts. Figure 2 shows that the "cross-over point" for **VERTEC** TIPT and methane sulphonic and p–toluene sulphonic acids is at 40-65% conversion compared with 83-93% at 200˚C.

Figure 2. Preparation of Bis(2–ethylhexyl)phthalate various catalysts at 220˚C
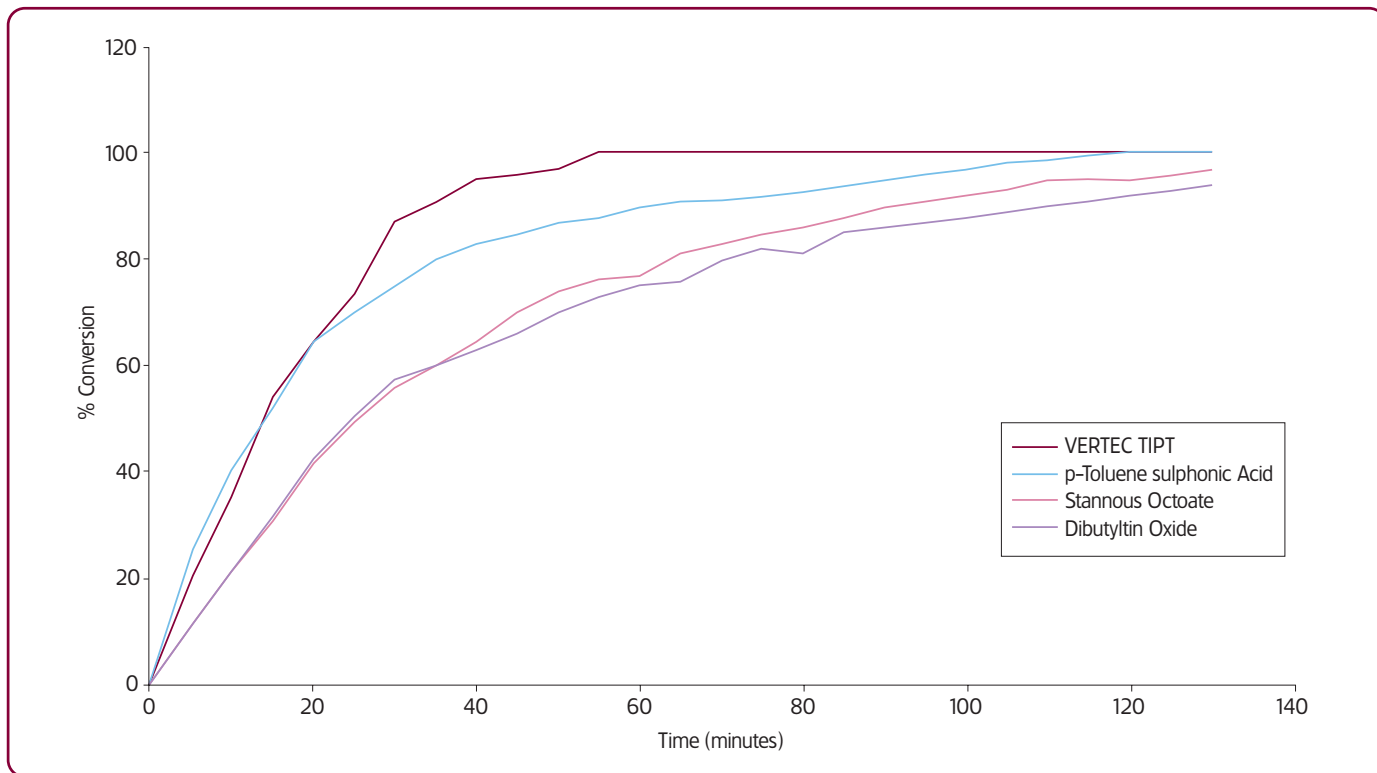
The effect of temperature on the performance of **VERTEC** TIPT is demonstrated more fully in Figure 3. Increasing the temperature from 180°C to 200°C gives a 50% decrease in the time required to reach 99.5% conversion. On raising the temperature from 200°C to 220°C there is again a 50% reduction in reaction time up to about 90% conversion, but at 99.5% conversion the time saving is only about 35%.

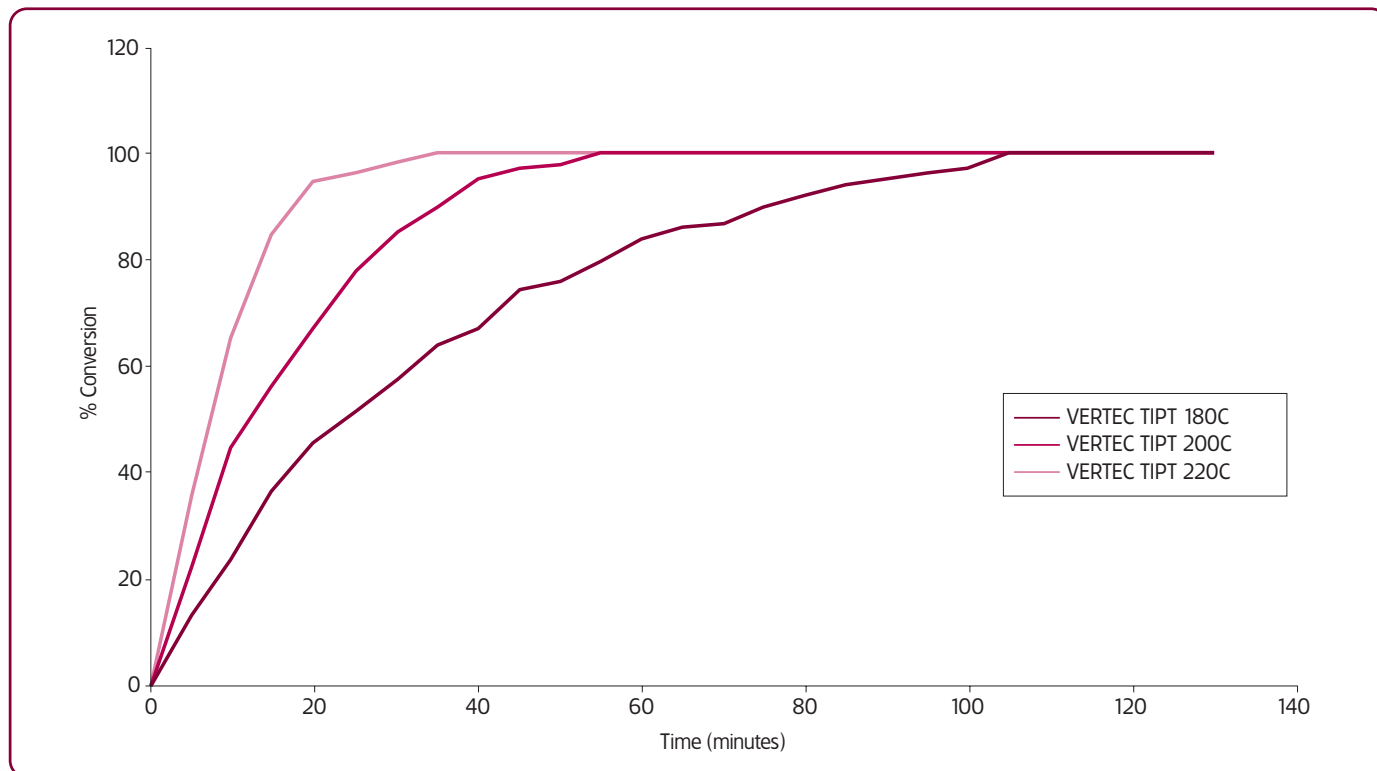**Figure 3.** Preparation of Bis(2-ethylhexyl)phthalate. Effect of temperature on **VERTEC** TIPT activity

Figure 4 shows how the reaction time varies with the quantity of **VERTEC** TIPT used. As would be expected, increasing the catalyst concentration decreases the reaction time, but at high conversions the difference between 0.2% and 0.4% **VERTEC** TIPT is quite small. The optimum catalyst concentration is 0.1–0.2% under these experimental conditions.

Figure 4. Preparation of Bis(2–ethylhexyl)phthalate. Various concentrations of **VERTEC** TIPT
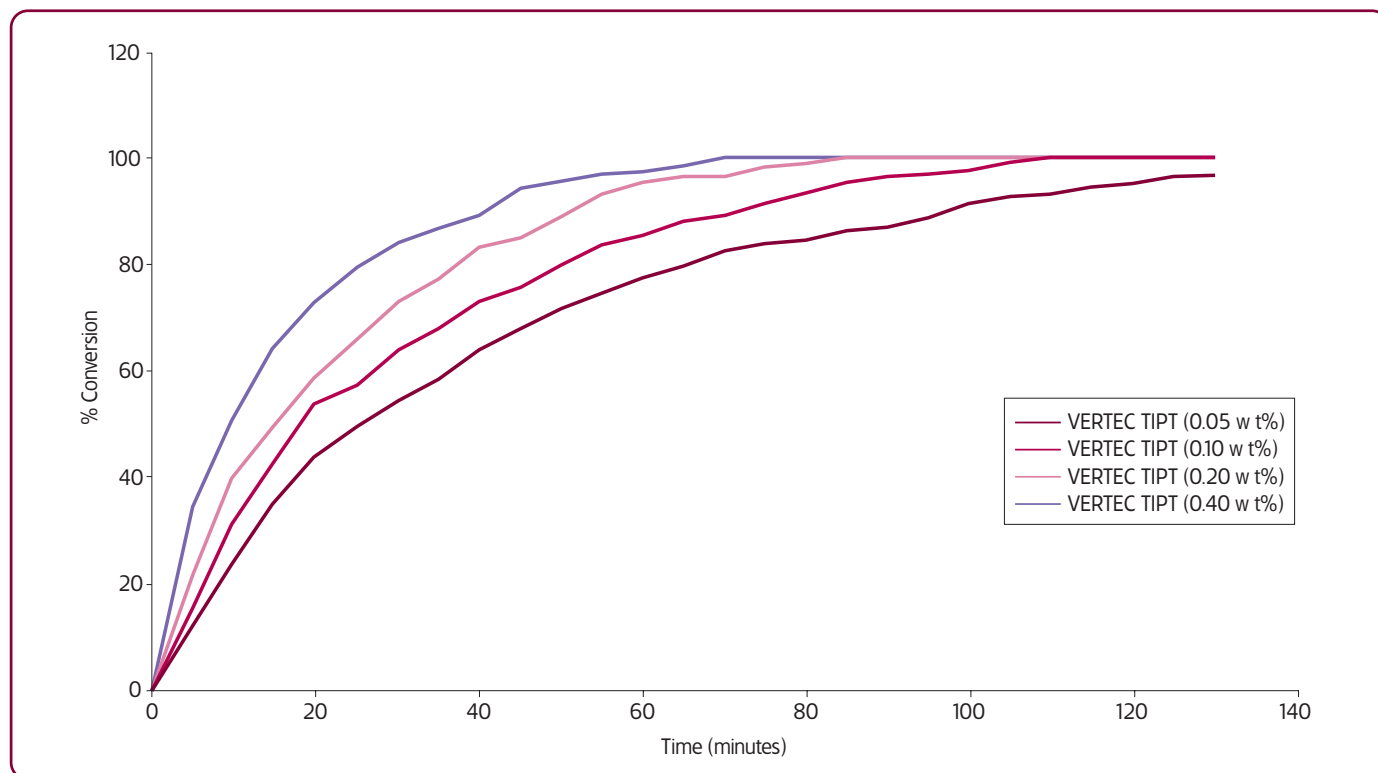
All the above experiments were carried out with a 25% excess of 2–ethylhexanol, which can safely be done when using titanate catalysts. The advantage of being able to use such a large excess is demonstrated in Figure 5 which compares the reaction rate at 25% excess alcohol with that obtained with only 10% excess.

Figure 5. Preparation of Bis(2–ethylhexyl)phthalate. Effect of alcohol concentration
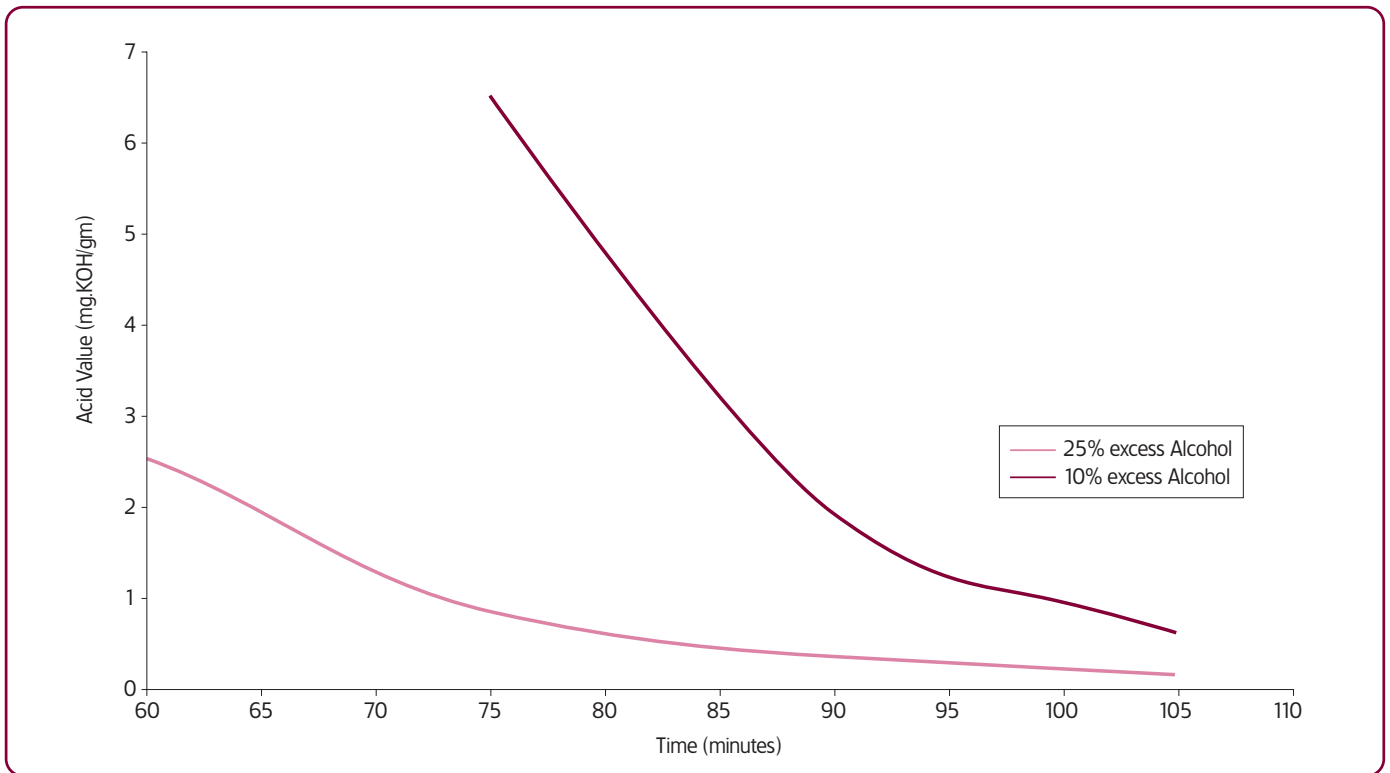
Figure 6 and 7 shows the relative rates of **VERTEC** TNBT at 200°C and acid catalysts at 150°C in the preparation of Diisononyl phthalate.

Figure 6. Preparation of Diisononyl phthalate comprising acids at 150°C and **VERTEC** TNBT at 200°C

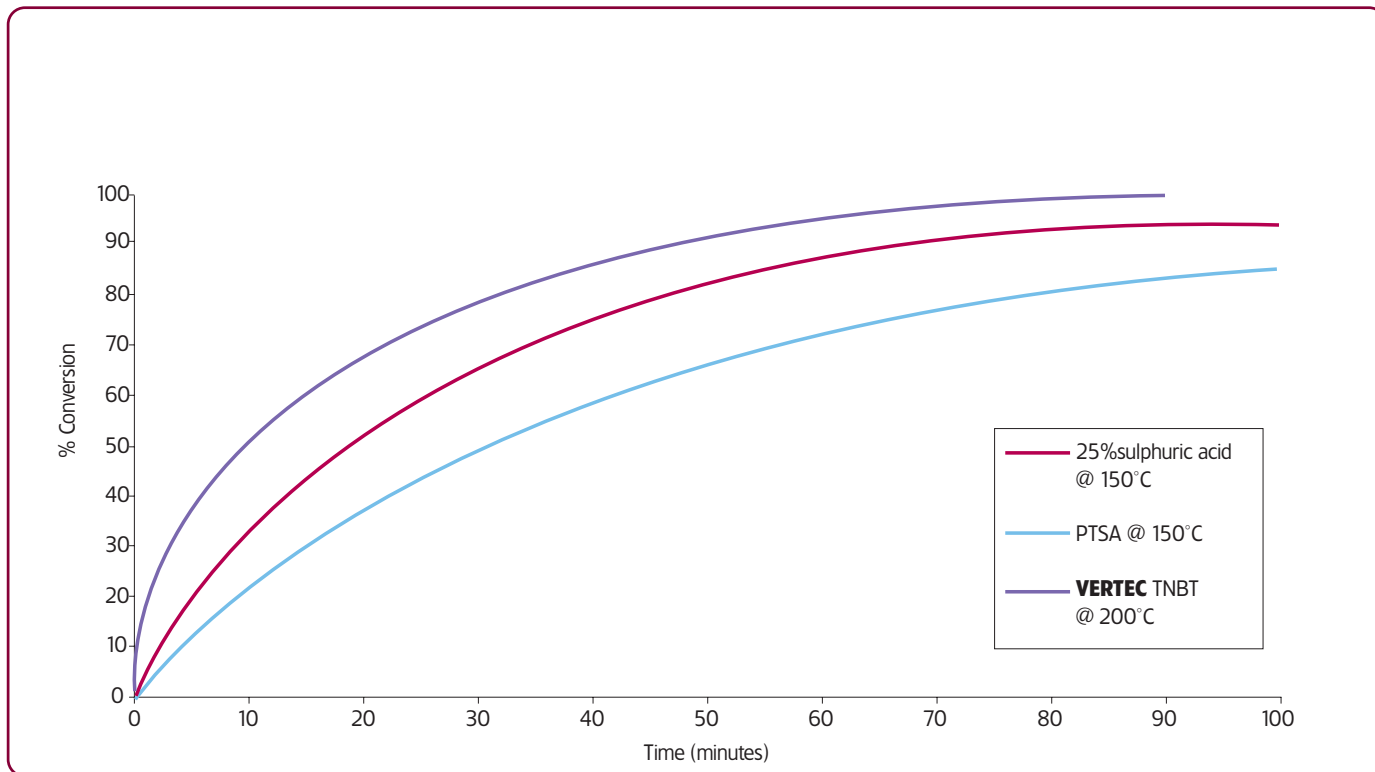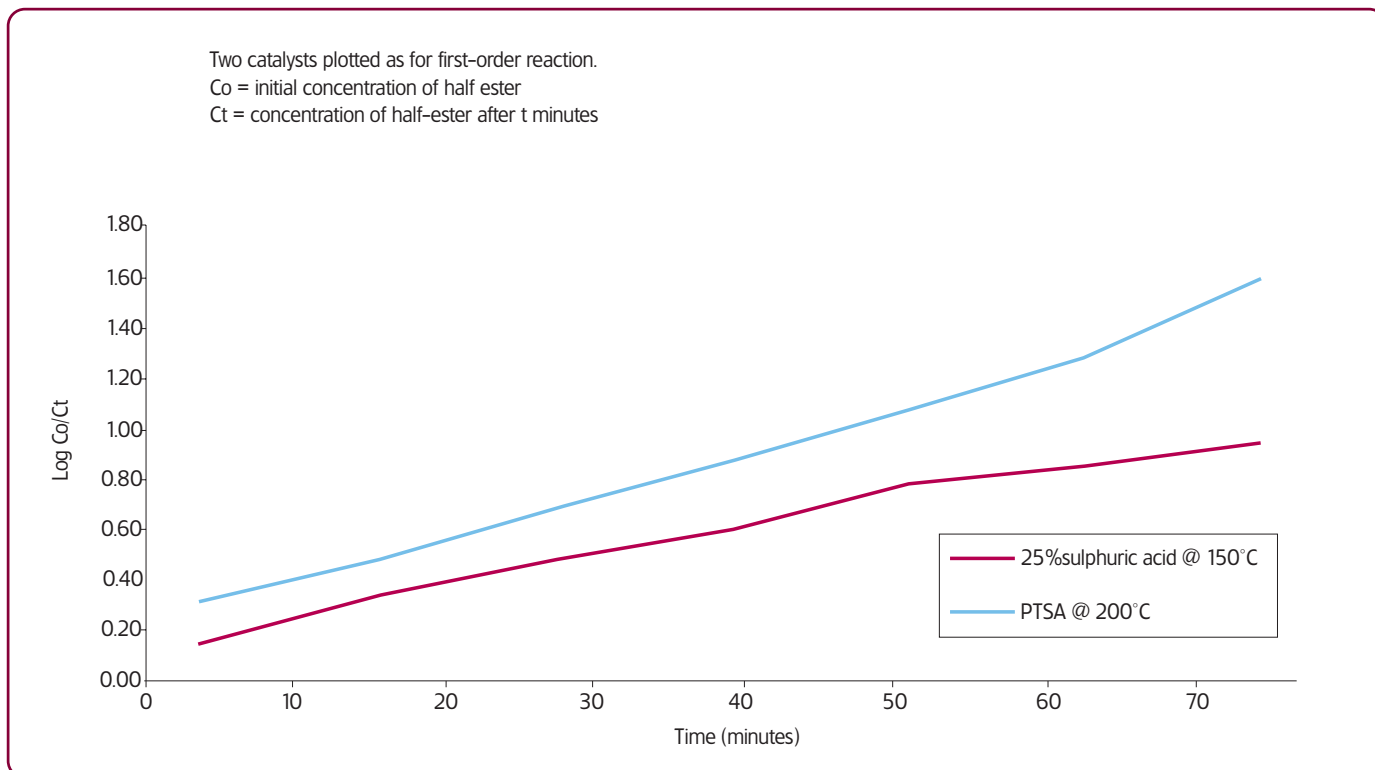All catalyst at 1.0 molar % concentration based on pthalic anlydride

Figure 7. Preparation of Diisononyl phthalate comparing sulphuric acid at 150°C and **VERTEC** TNBT at 200°C.

VERTEC TINT – Tetra Isononyl Titanate Esterification Catalyst

Johnson Matthey Catalysts have developed a new catalyst, which can be used in the manufacture of DINP. The manufacture of DINP addresses some of the issues associated with phthalate ester manufacture.

Currently most ester manufacturers use tetra isopropyl titanate (**VERTEC** TIPT) or tetra n-butyl titanate (**VERTEC** TNBT), as catalyst in the manufacture of DINP.

The use of **VERTEC** TINT has 3 major advantages.

1   Waste Water Chemical Oxygen Demand

When **VERTEC** TIPT or **VERTEC** TNBT is introduced to the reactor the catalyst undergoes a transesterification reaction, this releases isopropyl or normal butyl alcohol. The free isopropyl (or butyl alcohol) is very soluble in the water of the reaction, and is moved almost quantitatively from the process in the waste water. Because of this process the waste water has a significant chemical oxygen demand. Depending on local effluent regulations clean-up of the waste water can be expensive.

In contrast, the **VERTEC** TINT catalyst releases isononanol, which is almost insoluble in the reaction water, the isononanol is then returned to the reactor, where it reacts to form DINP.

Any contamination of the waste water is eliminated almost completely by the use of **VERTEC** TINT in place of **VERTEC** TIPT (or TNBT) and in addition the alcohol produced from the catalyst is recovered as part of the phthalate ester product.

2 Phthalate Ester Product Quality

Any alcohol released by catalyst, during its initial transesterification, will to a small extent take part in the main esterification reaction.

Because the **VERTEC** TINT releases isononanol, the alcohol that is released will not cause any contamination to the DINP.

By using **VERTEC** TINT, any DINP produced this way is pure C9 alcohol based product, providing a key competitive advantage when marketing the DINP made using **VERTEC** TINT catalyst.

3 Potential Financial Benefits

With waste water chemical oxygen demand, there are savings resulting from much reduced cost of waste-water treatment. These savings are site specific and will vary.

As a guide, it has been estimated that the reduction in chemical oxygen demand for a 50 kte/yr DINP plant using **VERTEC** TINT will be about 113 te/yr of oxygen, compared with the use of **VERTEC** TIPT.

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