



Advanced synthesis of dioctyl phthalate (DOP) and dibutyl phthalate (DBP) plasticizers: I. Comparison between aluminum oxide (Al_2O_3) and tetra-n-butyltitanate (TnBT) as esterification catalysts, II. Successful scaling up the bench scale to a semi-pilot scale

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ABSTRACT

Esterification of phthalic anhydride with 2-ethylhexanol and 1-butanol has been investigated using aluminum oxide/sodium hydroxide catalyst system and tetra-n-butyltitanate (TnBT) catalyst for comparison. TnBT catalyst shows higher activity in esterification. A complete conversion of phthalic anhydride to dioctyl phthalate and dibutyl phthalate are achieved in 2 hrs in presence of TnBT. While in case of using aluminum oxide/sodium hydroxide catalyst system, it requires at least 3 hrs. In addition, at the end of the reaction, TnBT is easily hydrolysable to a polymeric titanium dioxide; an easily filtered solid. An addition of filter aid can help achieve a good, rapid filtration of this polymeric titanium dioxide. An improved purification method has been performed to the synthesized DBP plasticizer, which is then identified by FT-IR, ¹H-NMR and GC. Details of a laboratory scale pilot plant in standard steel components have been designed to produce 50 litres of ester product. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Plasticizer;
Dibutyl phthalate;
Dioctyl phthalate;
Tetra-n-butyltitanate;
Esterification.

INTRODUCTION

In 1951, the International Union of Pure and Applied Chemistry (IUPAC) developed a universally accepted definition for a plasticizer as a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability, or distensibility^[1]. A plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product.

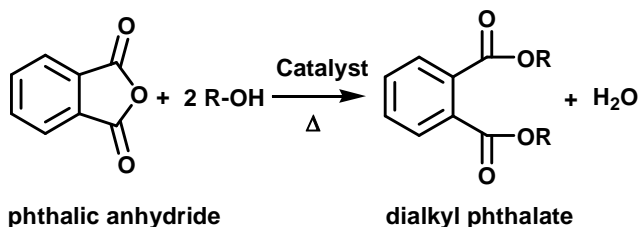
Many thermoplastic resins such as polyvinyl chloride (PVC) are modified for specific use, either with a plasticizer or by restructuring the polymer to make it more flexible, soft, or resilient and then frequently add-

ing a little plasticizer^[2]. Phthalic acid esters are commonly used as plasticizers in various kinds of polymeric materials such as PVC and polyethylene^[3]. They are used in virtually every major product category (construction, automotive, household products, apparel, toys, packaging and medical products). Plasticizers are interfused with high polymers to increase flexibility, extensibility, and workability. This is achieved by lowering the glass transition temperature (T_g) to below room temperature. Consequently, a hard glass-like solid polymer is changed to a flexible, tough elastomer^[4]. In general, ester type plasticizers are extensively used in conjunction with vinyl resins in order to impart to end products made from such resins requisite properties of flex-

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ibility, heat stability, color, and toughness. In this way the usefulness of vinyl resins has been expanded to a point where they have found wide application in a variety of commercial products, including, for example, protective coating, floor tile, calendared sheeting, electrical insulation coatings for wire, toys, shoe, machine parts, decorative finishes, and many other applications.

Phthalate esters are synthesized by the condensation reaction between phthalic anhydride and the appropriate alcohol according to the following reaction:



The ester productivity and quality depend essentially on the applied catalyst and reaction conditions. Up to now, the synthesis processes of carboxylic ester in industry are still catalyzed by sulfuric acid. The disadvantages of this method are: long reaction period, low conversion rate, formation of byproducts, after-treatment difficulties, corrosion of reaction vessels, etc^[5]. Thus, the study of novel esterification catalyst with high catalytic activity to substitute sulfuric acid has long been paid considerable worldwide attentions.

The study of non-homogeneous solid catalyst for esterification has started since 1960s^[6]. Several effective esterification catalysts such as ZnO and SnO have long been used in industrial production^[7]. Recently, more and more studies have been devoted to the novel solid catalysts for ester formation and many new kinds of catalysts are examined and used continuously. The activity and behavior of these catalysts such as rare earth oxides, rare earth salts and transition metal salts have been studied^[8]. Catalyst system composed of metal oxide in combination with sodium hydroxide has shown more advanced results^[9]; others such as Tetra-*n*-Butyl Titanate (TnBT) have proven their way in phthalic anhydride esterifications^[10]. Although these last two groups of catalysts have shown improved catalytic activities and better ester quality, however, some drawbacks associated with each of these systems still require more research.

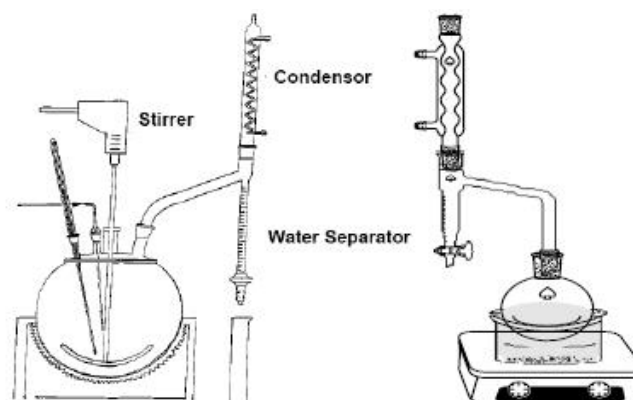
In the present work, phthalic anhydride has been

esterified with *n*-butanol and 2-ethylhexanol using each of these catalysts. The drawbacks of each catalyst system have been clarified and a novel procedure for synthesis and working-up has been adapted to achieve the highest activity and the best color quality. In addition, the reaction size has been scaled up successfully from bench scale to a semi-pilot of 50 kg size.

MATERIALS AND EXPERIMENTAL DETAILS

Phthalic anhydride (PA), *n*-butanol, aluminium oxide, tetra-*n*-butyl titanate (TnBT), sodium hydroxide, potassium hydroxide, hydrogen peroxide, sodium chlorate, bromthymol blue indicator, ethanol, xylene are all of pure grads and used as received.

The core elements of laboratory equipment are a glass flask with stirrer, thermometer, gas inlet, connection to a water separator, water separator with condenser and heating system (oil bath). Esterification reaction was performed in a round bottom flask, which was equipped with a Dean–Stark trap and a condenser and immersed in an oil bath.



The flask is purged with nitrogen before and during the reaction. PA is added to the alcohol (mol ratio 1 : 2). Heating to ca. 150 °C is ideally followed by adding the catalyst as a solution in the alcohol. Then, reflux distillation of the alcohol /water azeotrope and separation of the water in the separator begins at ca. 180 °C; end temperature 220 °C and the reaction was controlled by acid titration.

In a typical reaction, 49.4 g (0.3 mol) of phthalic anhydride, 44.4 g (0.6 mol) of *n*-butanol or 78 g (0.6 mol) of 2-ethylhexanol and catalyst mixture was refluxed. Based on previous literatures^[11], the amount of titanate as catalyst is very low - typically in the range

of 0.05 to 0.5 %. In case of aluminum (amphoteric) oxide/sodium hydroxide, and relative to phthalic anhydride, Al_2O_3 is 10% and NaOH is 0.1%. The progress of reaction was monitored by collected water in the Dean–Stark trap. Using this apparatus, esterification of phthalic anhydride with the appropriate amount of alcohol (n-butanol or 2-ethylhexanol) and in the presence of the calculated amount of catalyst, has been performed. Water is trapped at the bottom of the Dean-Stark trap and by continuous water trapping; the equilibrium is shifted toward the products and conversions were calculated from the amount of collected water. After esterification, the catalyst was extracted from reaction mixture by aqueous solution of sodium carbonate and the ester was washed for decolourisation.

DBP was characterized by IR, ^1H NMR and GC as the sole product. In case of gas chromatography analysis a GC equipped with an FID was used via the following conditions^[12]. Column: HP-1 (5 m, 0.53-mm i.d., 2.65- μm film) zone temp: column 1 min at 75°C, ramp to 270°C at 15°C/min, 1 min at 270°C, injector 270°C, detector 275°C, gas flow: column (He) 5.53 mL/min, auxiliary (N_2) 30 mL/min, hydrogen 32 mL/min, air 395 mL/min, split vent 53 mL/min (split ratio 10:1), injection volume: 2 μL .

Acid number determination^[13]

In a 125-ml Erlenmeyer flask, 25g of the sample was dissolved in 50 ml of ethanol followed by adding a few drops of bromthymol blue indicator solution. Then the titration was performed with 0.01 N KOH solution (0.1 N KOH for high acid number value). In addition, a blank titration on 50 ml of solvent used to dissolve the sample was also performed. The acid number was calculated, expressed as mg of KOH per gram of sample as follows:

$$\text{Acid number} = [(A-B)N \times 56.1]/C$$

Where A = ml of KOH solution used for titration of the sample, B = ml of KOH solution used for titration of the blank, N = normality of KOH solution, C = sample used, g.

De-coloration of the product was done by using activated carbon^[14] where 2-5 % was added and the mixture was stirred for 1 hour and then filtered. A new method for decoloration was used; in which, the ester was washed with sodium chlorate/hydrogen peroxide.

RESULTS AND DISCUSSION

Plasticizer quality

One of the principal items of plasticizer quality is its colour. Many factors can affect the colour; some of these are discussed below:-

- 1) Product colour is a function of time x temperature. In general, the longer the time of and/or the greater the temperature of reaction, the higher will be the colour of the ester product. In sulphuric acid catalysed reactions, the temperature has to be kept low in order to avoid forming coloured compound due to reaction with the sulphuric acid catalyst. The low temperature increases the reaction time and generally results in colour formation, which is normally treated using activated carbon; leading to a partial removal of the colour. The use of titanate catalyst, which is neutral, allows the use of higher temperatures (up to 220°C if the operating pressure of the reaction system and the oil heating system are compatible with higher temperature) without any colour formation problems. Faint yellowing of the colour as a minimal and by simple treatment; a colourless material was successfully obtained after the treatment with sodium chlorate/hydrogen peroxide.
- 2) The quality of the reagents used in the reaction can have a significant bearing on product colour. The carbonyl content of the alcohol (a measure of the aldehyde content) is probably the most important and should be less than 0.01%^[15]. Carbonyl containing compounds are very reactive species known to form coloured compounds.
- 3) In order to reduce colour formation, it was vitally important to ensure that the plant was purged with nitrogen before start up and that no air was introduced during the subsequent operations.

Reaction time

From the above it can be seen that the length of reaction time can affect product colour. There are many factors which can affect reaction time, some of these are discussed below:-

- 1) Because the esterification reaction is reversible, the reaction time is affected by the standing water content in the reactor. With titanate catalyst the

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standing water is also important because of the hydrolysis of the titanate catalyst. The standing water concentration is primarily determined by the boil up in the reactor, where alcohol is used as the entrainer for the water created during the reaction.

- In these reactions the separated alcohol from the boil up contains some water. As known from the literatures^[16], with butanol, water is soluble to about 20% in butanol and hence, although a good physical separation between water and butanol have been achieved in the alcohol/ water separator, the returning alcohol contains a significant amount of water. In order to reduce this water content of the alcohol it would be worth considering the fitting of a reflux stripper. This is a small packed column through which the vapour from the reactor and the returning alcohol reflux pass and are contacted counter currently. The stripper has the effect of drying the alcohol reflux, thus reducing the standing water content of the reaction mixture in the reactor.
- Alcohol excess above stoichiometry also affects the reaction time. A minimum of 20% excess alcohol needs to be used^[17]. This is because during the reaction some breakdown products are formed from the alcohol and some non alcohol components are present in the alcohol as supplied e.g. paraffins, heavy ends. In large scale production, these components are concentrated in the course of the reaction, so that gradually the recycled alcohol contains less real alcohol and the excess must be increased to account for this fact.

In general, when the temperature had reached that selected for the experiment, a weighed amount of catalyst was added with a syringe. For solid catalysts a small amount of the used alcohol 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 end of the reaction was taken to be 99.7%-99.8% (an acid value of about 0.4-0.24 mg KOH/g)^[13].

The progress of the reaction was followed by withdrawing samples at intervals by means of a syringe. Each sample was added to a known weight of cold alcohol

to quench the reaction, weighed and titrated against standard potassium hydroxide solution in ethanol using bromthymol blue as indicator. The results were used to calculate the amount of un-reacted half ester present and a graph was plotted of conversion against time from injection of catalyst (Figure 1).

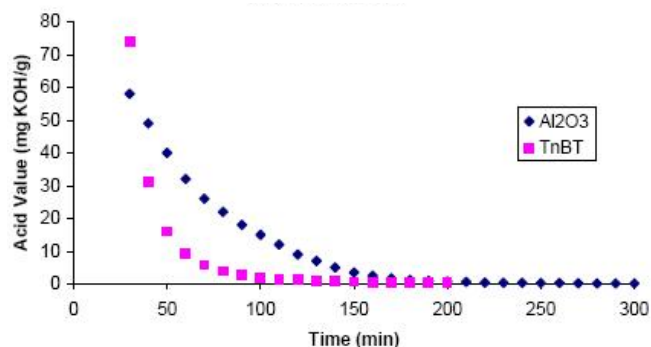


Figure 1: Comparison of the catalytic activity of aluminium oxide and tetra-n-butyltitanate (TnBT) in the Synthesis of DOP

Neutralisation

The use of caustic soda as a neutralisation agent requires care. Because sodium hydroxide is a strong base, it was used in a dilute aqueous solution (2%) and the neutralisation has been carried out at a low a temperature - the neutralisation was carried at 30°C or less. The use of sodium hydroxide as the neutralising agent gives better filtration characteristics to the titanate residues, than sodium carbonate does. In addition, the volume of water used washes the ester and removes some impurities. The use of sodium hydroxide at too high temperature or too high concentration produces back reaction and can increase the acid value.

The advantage of sodium hydroxide neutralisation is that most of the sodium salt of the monoester was removed with the water layer. This improves the volume resistivity of the ester, as compared with a carbonate neutralisation, which is important if the ester end use is in the electrical area. Figure 2 shows the ¹H NMR spectra of a purified DBP sample. The chemical shift at (7.6-7.8) ppm, corresponds to the four protons of the aromatic unit, and the chemical shift between 4.1 and 4.3 ppm, corresponds to four protons of the butyl group (near to oxygen atom). The chemical shift of the middle eight protons of the two butyl groups appear between 1.6 and 1.9 ppm. The last chemical shift appearing at (0.98-1.1) ppm is dew to the six protons of the methyl groups; one methyl for each butyl group. The purity of

the produced DBP is confirmed from the determined integrated intensity ratio of the chemical shifts mentioned above which was (4:4:4:4:6) and in correspondence with DBP structure. In addition, Figure 3 which is a typical IR spectrum for DBP is shown. From these two figures, it is clear that the produced DBP is pure and free from all impurities. This is a good indicative result which proves that the synthesis and purification processes are successful.

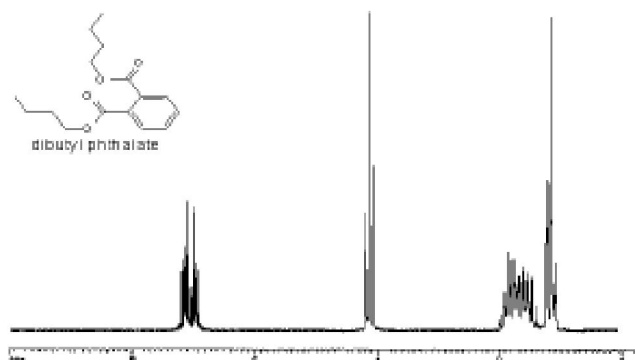


Figure 2: $^1\text{H-NMR}$ of DBP

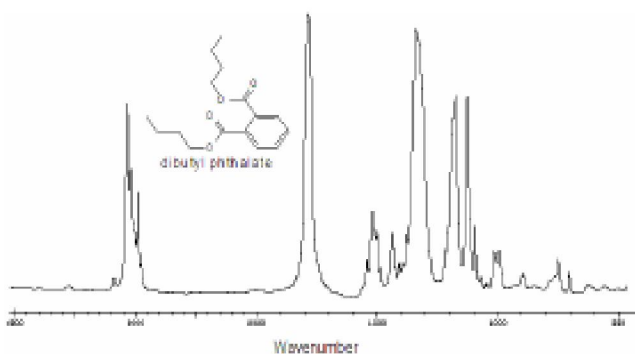


Figure 3: FT-IR of DBP

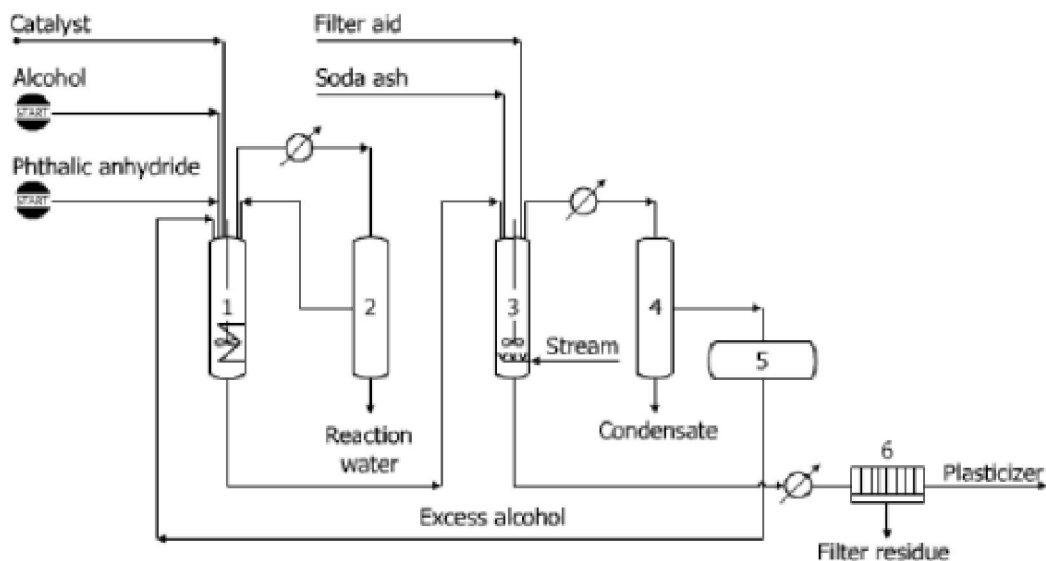


Figure 5: Batch esterification process.

Figure 4 shows the GC result of DBP which give a single peak (retention time = 9.6 min). This is another indication about the purity of the prepared DBP.

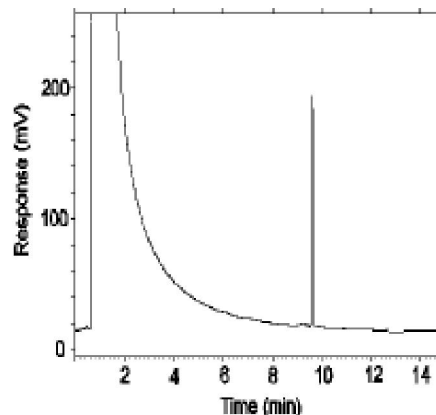


Figure 4: GC of DBP

Ester recovery

The cake discharged from the filter contains 70-80% w/w of ester. It was not possible to reduce this content by mechanical means. A process was developed, in which the filter cake was dropped into hot water and agitated to give a three phases mixture with a supernatant layer of ester, which was collected and recycled; a process which is very important in the large scale production. In general, under the optimal reaction conditions and based on the acid value calculation, the conversion reached 98% after 2 h with respect to tetra-*n*-butyltitanate (TnBT) catalyst and after 3 h with respect to (aluminum oxide/sodium hydroxide) catalyst.

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Pilot plant

A laboratory scale pilot plant in standard steel components was performed to scale up the plasticizer productivity to 50 litres. A schematic representation of the process sequence is shown in Figure 5. In this process, alcohol and PA are fed into the esterification reactor (1). Then the excess alcohol from the previous charge as well as catalyst are added and the reaction mixture is heated to the required esterification temperature. Evaporated water and alcohol are condensed and separated (2), so that the alcohol can be recycled to the esterification reactor. After completion of the reaction, traces of unreacted monoester are neutralized (3), followed by steam stripping of the excess alcohol. The overhead vapor mixture is condensed, the alcoholic phase being separated (4) from water and collected in the excess alcohol tank (5). The condensate is worked up internally to avoid environmental problems. After drying the ester with nitrogen, filter aid is added and the ester is cooled and filtered (6).

Production equipment

The equipment consists of two reactors:

Reactor 1: Esterification

The reactor 1 (Figure 6) consists of a heating system, stirrer, feeding system for nitrogen, the alcohol,

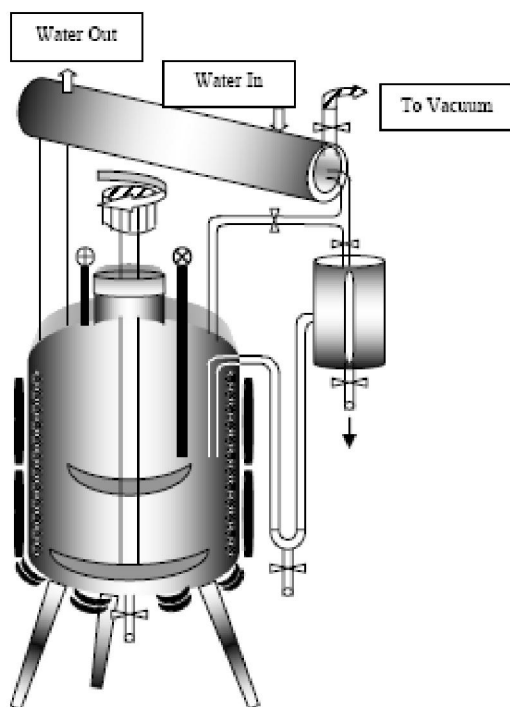


Figure 6: Esterification reactor; steel components

PA and the catalyst. Connected to the reactor is a condenser (water cooled) with vacuum pump and a separator for the separation of alcohol and water and the recirculation of the alcohol. The raw DOP is transferred to reactor 2 for work up.

Reactor 2: Work up

The reactor 2 (Figure 6) for the treatment of the raw plasticizer (from reactor 1) consists of the reactor with a heating system, feeding tubes for additives (filter aids etc.) water, alkali. The reactor is connected to a condenser with a vacuum pump for the separation of water and low boiling components. The purified plasticizer is separated from insoluble substances (e.g. filter aids, catalyst hydrolysates, etc.) in a filter preferably in a plate filter press. The production equipment is made of stainless steel.

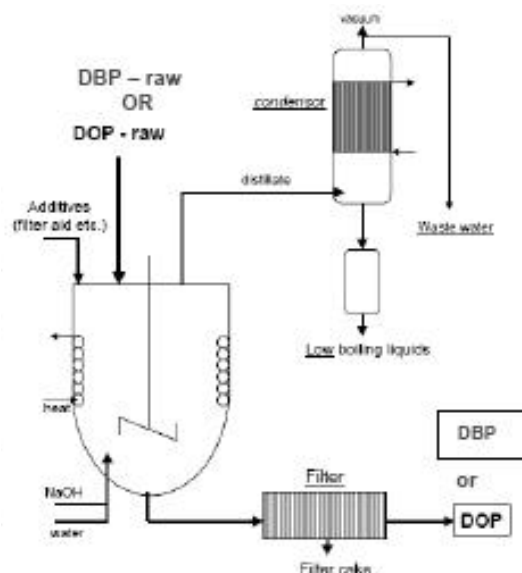


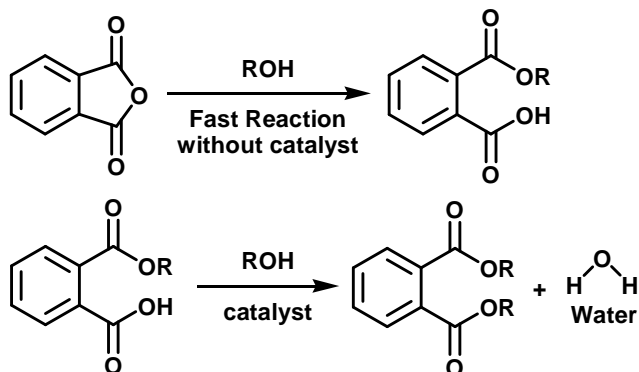
Figure 6: Purification reactor; steel components

Production steps

Esterification

The reactor 1 is purged with nitrogen to prevent oxygen reaction with the reactants and products and to maintain a dry atmosphere (the titanate catalyst is sensitive to moisture). The preheated alcohol (80-100°C) and PA are introduced into the reactor. The molar ratio of PA to alcohol typically is 1: 2 up to 1: 25. The catalyst is added at about 120 - 150 °C either as pure material or dissolved in some water free alcohol as last ingredient. One has to take care that the recycled alcohol contains some water and is not suitable for direct mixing with the titanate.

Together with the PA, alcohol and the catalyst; some additives also are fed into the reactor to improve the product quality and to facilitate the work up, e.g. carbon black or filter aids. The formation of the half-ester by the addition reaction is very fast (max. 20 min.)^[17] and slightly exothermic.



This half ester can be made also in a separate step in a separate reactor. The esterification starts at about 180 °C, visible in the formation of water in the separator. The temperature is continuously raised and monitored by the stream of recycled alcohol. The esterification is endothermic. When the recirculation of the alcohol drops a slight vacuum is applied.

The alcohol acts as entrainer for the water. The alcohol/water azeotrope is separated after the condensation in the separator. The water is let off from time to time. The reaction runs at normal pressure. The end of the reaction is indicated by the slow formation of water. The degree of reaction is measured by determination of the acid value. When the acid value has reached 1 - 2, the pressure in the reactor is slowly reduced under full reflux whereby the reaction is further completed and the acid value further drops. The temperature should not exceed 210-220°C to avoid discoloration. After reaching an acid value of 0.3 - 0.5 the excess of alcohol was distilled off under a vacuum. This raw plasticizer is transferred to the reactor 2 for work at a temperature of about 180 °C.

Work up

The work up was mainly for the purification of the crude plasticizer.

- decomposition of catalyst
- removal of the catalyst
- neutralization of acidic product
- de-coloration
- deodorization

The next step after the transfer of the raw material from reactor 1 to reactor 2 was the post treatment. The relatively high stability of the plasticizer allows a relatively hard treatment. At 170-180°C water steam was injected via nozzles at reduced pressure to remove residual amounts of alcohol and additionally olefins, ethers and other small amounts of by products such as odor components by water steam distillation. At the same time the titanate catalyst was decomposed and could not cause saponification reactions. The titanate was hydrolyzed to polymeric titanium dioxide. The addition of filter aid helped achieving a good, rapid filtration of this polymeric titanium dioxide. Removal of catalyst was easy, where aluminum oxide or titanium dioxide was as easily filtered solid^[18]. The filtration aid can be added prior to the esterification step, before injection of water steam or shortly before filtration. For the neutralization^[11] of residual acid, the addition of alkali such as NaOH or NaHCO₃, was added. The amount of water and NaOH added in the example of a 20 kg charge production of plasticizer were 5 L water and 500 mL NaOH (20 %). After this agitation the crude plasticizer was dried under vacuum (2 mbar) at 100°C for about 0.5 hours and filtered. Good filter types were plate filter types. For improved purification, the treatment of the ester with the alkali addition, washing with water, addition of filter aids drying and filtration was repeated, confirmed by ¹HNMR, FTIR and GC.

CONCLUSION

Both tetra-n-butyltitanate (TnBT) and (aluminum oxide/sodium hydroxide) catalysts have relatively high catalytic activities for esterification of phthalic anhydride with 2-ethylhexanol and 1-butanol. Under the optimal reaction conditions, the conversion reached 98% after 2 h with respect to tetra-n-butyltitanate (TnBT) catalyst and after 3 h with respect to (aluminum oxide/sodium hydroxide) catalyst. These two catalysts are excellent for the technical manufacture of plasticizers and both systems were easy to be separated. They offer decisive advantages compared with other catalyst systems: high product quality, waste reduction, easy processability and cost saving. A laboratory scale pilot plant in standard steel components was successfully performed to scale up the plasticizer productivity to 50 litres.

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