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Process for preparing carboxylic esters

The invention relates to a batchwise process for preparing carboxylic esters by reacting dibasic or polybasic carboxylic acids or their anhydrides with alcohols.

Esters of polybasic carboxylic acids, for example phthalic acid, adipic acid, sebacic acid, maleic acid, and alcohols are widely used in surface coating resins, as constituents of paints and, in particular, as plasticizers for plastics.

It is known to prepare carboxylic esters by reacting carboxylic acids with alcohols. This reaction can be carried out autocatalytically or catalytically, for example by Brönstedt or Lewis acids. Quite independently of which type of catalysis is selected, a temperature-dependent equilibrium is always formed between the starting materials (carboxylic acid and alcohol) and the products (ester and water). In order to shift the equilibrium in favor of the ester, in many esterifications an entrainer is used to remove the reaction water from the batch. If one of the starting materials (alcohol or carboxylic acid) boils lower than the ester formed and forms a miscibility gap with water, a starting material can be used as entrainer and after water is removed, can be recirculated back to the batch. In the esterification of dibasic or polybasic acids, generally the alcohol used is the entrainer. For many applications the ester thus prepared must have a low acid number, that is to say the reaction of the carboxylic acid should proceed virtually quantitatively. Otherwise the yield is decreased and the acid must be removed, for example by neutralization. This is complex and can lead to byproducts which must be disposed of. In order to obtain as high as possible a conversion of the carboxylic acid, esterifications are generally carried out with an alcohol excess. However, an alcohol excess has the disadvantage that in the case of low-boiling alcohols, the reaction temperature at atmospheric pressure is so low that the reaction rate is too low for an industrial process. In order to counteract this effect, the reaction can be carried out under pressure, which leads to higher apparatus costs. A further disadvantage is that, with increasing alcohol excess, the maximum possible concentration of the target product in the reaction vessel decreases and thus the batch yield decreases. Furthermore, the

alcohol used in excess must be separated off from the ester, which is time and energy consuming.

5 Esterification reactions for the plasticizer esters dioctyl phthalate (DOP) and diisononyl phthalate (DINP) with organotitanium catalysis are well studied reactions and are described, for example, in GB 2 045 767, DE 197 21 347 or US 5 434 294.

These processes comprise the following steps:

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- reaction of one molecule of phthalic anhydride with one molecule of alcohol to give the half ester (ester carboxylic acid), autocatalytic
- addition of titanium catalyst, for example n-butyl titanate
- reaction of one molecule of half ester with one molecule of alcohol
- 15 with elimination of water to give the diphtalate
- simultaneous removal of the reaction water by distilling off an alcohol/water azeotrope
- destruction of the catalyst by addition of base
- distilling off the excess alcohol
- 20 - filtering off the catalyst residue
- purification of the phthalic diester by distillation, for example steam distillation.

25 These processes are batchwise and are not yet optimized with respect to maximum utilization of the reactors, that is to say space-time yield.

The object was therefore to improve the processes for the batchwise preparation of esters in order to make higher space-time yields possible (short reaction times, high batch yields).

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It has been found that the space-time yield of a batchwise esterification process in which the reaction water is removed by distillation as an azeotrope together with the alcohol used in excess and the resultant alcohol is replaced in whole or in part can be increased if the filling level of
35 the reactor is kept as constant as possible by replacing the amount of liquid separated off, that is to say alcohol and water, in whole or in part by alcohol.

The present invention therefore relates to a process for preparing carboxylic esters by reacting dicarboxylic acids or polycarboxylic acids or their anhydrides with alcohols, the reaction water being removed by azeotropic distillation together with the alcohol, the amount of liquid removed from the reaction by the azeotropic distillation being replaced in whole or in part with the alcohol.

The amount of liquid designated below is the volume of liquid which is removed from the reaction by azeotropic distillation and principally consists of reaction water and alcohol.

Complete replacement of the amount of liquid removed is preferred. This can be achieved, for example, by level-controlled feed of alcohol into the reactor. For technical reasons, complete replacement of the amount of liquid removed may not be achievable and may only be achievable with difficulty. In these cases, the amount of liquid removed is only partially replaced, for example only the alcohol, but not the reaction water removed, but, in all cases, is replaced by more than 90%, preferably from 95 to 98%.

It can also be necessary to recirculate more than the amount of liquid distilled off to the reactor, that is to say, in addition to the amount of alcohol removed, the reaction water is replaced, and, in addition, further alcohol is added. In this embodiment, from 110 to 100%, preferably 105 - 100%, of the amount of liquid removed is replaced by alcohol.

The inventive process has the advantage that, compared with known batchwise processes, the reaction rate is increased. As a result the cycle time can be reduced, which gives a higher space-time yield.

The inventive process is applicable in principle to all esterifications in which the reaction water is separated off by distillation together with an alcohol.

In the inventive process, the acid component used is dicarboxylic and polycarboxylic acids and their anhydrides. In the case of polybasic carboxylic acids, partial anhydrides can also be used. It is also possible to use mixtures of carboxylic acids and anhydrides. The acids can be aliphatic, carbocyclic, heterocyclic, saturated or unsaturated, and also aromatic. Aliphatic carboxylic acids have at least 4 carbon atoms.

Examples of aliphatic carboxylic acids and their anhydrides are maleic acid, fumaric acid, maleic anhydride, succinic acid, succinic anhydride, adipic acid, suberic acid, trimethyladipic acid, azelaic acid, decanedioic acid, dodecanedioic acid, brassylic acid. Examples of carbocyclic compounds are: hexahydrophthalic anhydride, hexahydrophthalic acid, cyclohexane-1,4-dicarboxylic acid, cyclohex-4-ene-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic anhydride, 4-methylcyclohexane-1,2-dicarboxylic acid, 4-methylcyclohexane-1,2-dicarboxylic anhydride, 4-methylcyclohex-4-ene-1,2-dicarboxylic acid, 4-methylcyclohex-4-ene-1,2-dicarboxylic anhydride. Examples of aromatic compounds are phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, trimellitic acid, trimesic acid, pyromellitic acid, pyromellitic anhydride or naphthalene dicarboxylic acids.

15 In the inventive process, preferably, branched or unbranched aliphatic alcohols having 4 to 13 carbon atoms are used. The alcohols are monohydric and can be secondary or primary.

The alcohols used can originate from various sources. Suitable starting materials are, for example, fatty alcohols, alcohols from the Alfol process or alcohols or alcohol mixtures which were produced by hydrogenation of saturated or unsaturated aldehydes, in particular those alcohols whose synthesis includes a hydroformylation step.

25 Alcohols which are used in the inventive process are, for example, n-butanol, isobutanol, n-octanol (1), n-octanol (2), 2-ethylhexanol, nonanols, decyl alcohols or tridecanols produced by hydroformylation or aldol condensation and subsequent hydrogenation. The alcohols can be used as pure compound, as a mixture of isomeric compounds or as a mixture of compounds having a different number of carbon atoms.

30 Preferred starting alcohols are mixtures of isomeric octanols, nonanols or tridecanols, the latter being able to be produced from the corresponding butene oligomers, in particular oligomers of unbranched butenes, by hydroformylation and subsequent hydrogenation. The butene oligomers can be prepared, in principle, by three processes. Acid-catalyzed oligomerization, in which, industrially, for example, zeolites or phosphoric acid is used on supports, gives the most highly branched oligomers. When unbranched butenes are used, for example, a C₈ fraction is formed which essentially consists of dimethylhexenes (WO 92/13818). A process which

is also carried out worldwide is oligomerization using soluble Ni complexes, known as the DIMERSOL process (B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, pages 261-263, Verlag Chemie 1996). In addition, oligomerization is practiced on nickel fixed-bed catalysts, for example the OCTOL process (Hydrocarbon Process., Int. Ed. (1986) 65 (2. Sect. 1), pages 31-33).

Very particularly preferred starting materials for the inventive esterification are mixtures of isomeric nonanols or mixtures of isomeric tridecanols which are prepared by oligomerizing unbranched butenes to give C₈ olefins and C₁₂ olefins by the Octol process, with subsequent hydroformylation and hydrogenation.

The inventive esterification can be carried out under autocatalytic or catalytic conditions. Esterification catalysts which can be used are Lewis acids or Brönstedt acids or organometallic substances which do not necessarily need to act as acids. Preferred esterification catalysts are alkoxides, carbonate salts or chelate compounds of titanium or zirconium, the catalyst molecule being able to contain one or more metal atoms. In particular, tetraisopropyl orthotitanate and tetrabutyl orthotitanate are used.

Esterification is carried out in a reaction vessel in which the reaction batch can be intensively mixed using an agitator or recirculation pump. The starting materials and the catalyst can be charged into the reactor simultaneously or sequentially. If one starting material is solid at the charging temperature it is expedient to introduce the liquid starting component first. Solid starting materials can be fed as powder, granules, crystals or melt. In order to shorten the batch time, it is advisable to start the heating during charging. The catalyst can be introduced in pure form or as solution, preferably dissolved in one of the starting materials, at the start or only after the reaction temperature has been reached. Carboxylic anhydrides frequently react with alcohols, even autocatalytically, that is to say non-catalyzed, to give the corresponding ester carboxylic acids (half esters); for example phthalic anhydride reacts to give phthalic acid monoester. Therefore, a catalyst is frequently not required until after the first reaction step.

The alcohol to be reacted, which serves as entrainer, can be used in a stoichiometric excess, preferably from 5 to 50%, particularly preferably from 10 to 30%, of the stoichiometrically required amount.

- 5 The catalyst concentration depends on the type of catalyst. In the case of the titanium compounds preferably used, this is from 0.005 to 1.0% by mass, based on the reaction mixture, in particular from 0.01 to 0.3% by mass.
- 10 The reaction temperatures when titanium catalysts are used are between 160°C and 270°C. The optimum temperatures depend on the starting materials, reaction progress and the catalyst concentration. They can readily be determined for each individual case by experiments. Higher temperatures increase the reaction rates and favor side reactions, for
- 15 example elimination of water from alcohols, or formation of colored byproducts. It is necessary, in order to remove the reaction water, that the alcohol can distill off from the reaction mixture. The desired temperature or the desired temperature range can be set by the pressure in the reaction vessel. In the case of low-boiling alcohols, the reaction is therefore carried
- 20 out at superatmospheric pressure, and in the case of higher-boiling alcohols, at reduced pressure. For example, in the reaction of phthalic anhydride with a mixture of isomeric nonanols, a temperature range of from 170°C to 250°C in the pressure range of from 1 bar to 10 mbar is employed.
- 25 The amount of liquid to be recycled to the reaction according to the invention can consist in part or in whole of alcohol which is produced by work-up of the azeotropic distillate. It is also possible to carry out the work-up at a later time point and to replace the amount of liquid removed in
- 30 whole or in part by fresh alcohol, that is to say alcohol being provided from a storage vessel.

In other embodiments of the invention, the liquid separated off is worked up to produce the alcohol.

- 35 During the reaction, an alcohol-water mixture is distilled off from the reaction mixture as azeotrope. The vapors leave the reaction vessel via a short column (internals or packing, 1 to 5, preferably 1 to 3, theoretical plates) and are condensed. The condensate can be separated into an

aqueous phase and an alcoholic phase; this can make cooling necessary. The aqueous phase is separated off and can, if appropriate after work-up, be discarded or used as stripping water in the aftertreatment of the ester.

- 5 The alcoholic phase which is produced after separating the azeotropic distillate can be recirculated to the reaction vessel in part or in whole. In practice, control of the reaction by a level controller has proved itself for feeding the alcohol.
- 10 It is possible to replace the amount of liquid removed by the azeotropic distillation completely or in part by separating the liquid separated off into an alcohol phase and a water phase and recirculating the alcohol phase to the esterification reaction.
- 15 Optionally, fresh alcohol can be added to the alcohol phase separated off.

There are various potential ways for feeding the alcohol to the esterification reaction. The alcohol can be added, for example, as reflux to the column. Another possibility is to pump the alcohol, if appropriate after
20 heating, into the liquid reaction mixture. Separating off the reaction water decreases the reaction volume in the apparatus. In the ideal case, during the reaction, as much alcohol is replenished as corresponds to the volume of the distillate separated off (water and if appropriate alcohol), so that the level in the reaction vessel remains constant. In the inventive process, by
25 increasing the alcohol excess, the equilibrium is shifted in the favor of the full esters.

When the reaction is complete, the reaction mixture, which essentially consists of full ester (target product) and excess alcohol, comprises, in
30 addition to the catalyst and/or its secondary products, small amounts of ester carboxylic acid(s) and/or unreacted carboxylic acid.

To work up these crude ester mixtures, the excess alcohol is removed, the acidic compounds are neutralized, the catalyst is destroyed and the
35 resultant solid byproducts are separated off. The majority of the alcohol is distilled off at atmospheric pressure or under reduced pressure. The last traces of the alcohol can be removed, for example, by steam distillation, in particular in the temperature range from 120 to 225°C. The alcohol can be separated off as the first or last work-up step.

The acidic substances, such as carboxylic acids, ester carboxylic acids or, if appropriate, the acid catalysts, are neutralized by adding basic compounds of the alkali metals and alkaline earth metals. These are used
5 in the form of their carbonates, hydrogencarbonates or hydroxides. The neutralizing agent can be used in solid form, or preferably as solution, in particular as aqueous solution. Here, sodium hydroxide solution is frequently used in the concentration range from 1 to 30% by weight, preferably from 20 to 30% by weight. The neutralizing agent is used in an
10 amount which corresponds to the stoichiometrically required amount to four times the stoichiometrically required amount, in particular the stoichiometrically required amount to twice the stoichiometrically required amount, as determined by titration. When the titanium catalysts are used, the neutralizing agent converts these into solid filterable substances.

15 Neutralization can be carried out immediately after ending the esterification reaction or after distilling off the majority of the excess alcohol. Preference is given to neutralization with sodium hydroxide solution immediately after completion of the esterification reaction at
20 temperatures above 150°C. The water introduced with the alkaline solution can then be distilled off together with the alcohol.

The solids present in the neutralized crude ester can be separated off by centrifuging, or preferably by filtration.

25 Optionally, after the esterification reaction, a filter aid and/or absorbent can be added during work-up for improved filterability and/or removal of colored substances or other byproducts.

30 The process described here can be carried out in one vessel or in a plurality of sequentially-connected vessels. Thus, for example, esterification and work-up can proceed in different vessels. When carboxylic anhydrides are used, there is the option of carrying out the reactions to give the half ester and the diester in different reactors.

35 The esters thus produced from polybasic carboxylic acids, for example phthalic acid, adipic acid, sebacic acid, maleic acid, and alcohols are widely used in resin coatings, as constituents of paints and, in particular, as plasticizers for plastics. Suitable plasticizers for PVC are diisononyl

phthalates and dioctyl phthalates. The use of the inventively prepared esters for these purposes is also subject-matter of the invention.

5 The alcohol separated off during work-up can, if appropriate after discharge of a portion, be used for the next batch.

The examples below are intended to describe the invention in more detail without limiting the range of protection as defined in the patent claims.

10 Examples

The esterification reactor used consists of a stirred tank having a heating coil (40 bar steam), a separation system for the reaction water/alcohol separation and a return line for the excess alcohol. The apparatus is
15 purged to be oxygen-free with nitrogen prior to charging.

Esterification of phthalic anhydride with a mixture of isomeric isononanols to give diisononyl phthalate (DINP)

20 **Example 1 (comparative example)**

Starting quantities:

1 000 kg of phthalic anhydride (liquid)

2 430 kg of isononanol

1 kg of butyl titanate

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As soon as 400 kg of isononanol had been charged into the reactor, heating was started. Phthalic anhydride in liquid form and the remaining amount of alcohol (2 030 kg) were fed in simultaneously. After the reaction mixture had achieved a temperature of 120°C, the titanium catalyst was
30 added. At 170°C the mixture began to boil. At this time point the maximum level of 80% was also established in the reactor. During the esterification, water was released and distilled off as isononanol azeotrope. The acid number of the reaction mixture decreased from an initial value of 100 mg KOH/g at the start of boiling to 10 mg KOH/g after 150 minutes, 1 mg/g
35 KOH after 290 minutes and 0.5 mg KOH/g after 330 minutes. The level in the reactor at this time point was still 76%.

Example 2 (according to the invention)

Starting quantities:

1 000 kg of phthalic anhydride (liquid)
2 430 kg of isononanol
110 kg of isononanol (supplement)
1 kg of butyl titanate

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As soon as 400 kg of isononanol had been introduced into the reactor, heating was started. Phthalic anhydride in liquid form and the remaining amount of alcohol (2 030 kg) were fed in simultaneously. After the reaction mixture had achieved a temperature of 120°C, the titanium catalyst was
10 added. At 170°C the mixture began to boil. At this time point the maximum level of 80% was also established in the reactor. During the esterification, water was released and distilled off as isononanol azeotrope. At a level of 78% in the reactor (approximately 2 h after the start of boiling), this was brought back to 80% with fresh isononanol (not present in the starting
15 amount) and this level was maintained by further supplementation of isononanol until the end of the reaction. When the reaction was completed (AN = 0.5), the isononanol excess was 110 kg higher than in the comparative example 1. The acid number of the reaction mixture decreased in this batch from an initial value of 100 mg KOH/g at the start
20 of boiling to 10 mg KOH/g after 150 minutes, 1 mg KOH/g after 270 minutes and 0.5 mg KOH/g after 300 minutes.

Therefore, the esterification time is decreased by the inventive process by 30 minutes or by 9%. (Yield based on phthalic anhydride greater than
25 99.8%)

Esterification of phthalic anhydride with 2-ethylhexanol to give bis (2-ethylhexyl) phthalate (DOP)

30 **Example 3 (comparative example)**

Starting quantities:

1 070 kg of phthalic anhydride (liquid)
2 350 kg of 2-ethylhexanol
1 kg of butyl titanate

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As soon as 400 kg of 2-ethylhexanol had been introduced into the reactor, heating was started. Phthalic anhydride in liquid form and the remaining amount of alcohol (1 950 kg) were fed in simultaneously. After the reaction mixture had reached a temperature of 120°C, the titanium catalyst was

added. At 170°C, the mixture began to boil. At this time point the maximum level of 80% was also established in the reactor. During the esterification, water was released and distilled off as 2-ethylhexanol azeotrope. The acid number of the reaction mixture decreased from an initial value of 110 mg KOH/g at the start of boiling to 10 mg KOH/g after 165 minutes, 1 mg KOH/g after 320 minutes and 0.5 mg KOH/g after 365 minutes. The level in the reactor at this time point was still 76%.

Example 4 (according to the invention)

10 Starting quantities:

1 070 kg of phthalic anhydride (liquid)

2 350 kg of 2-ethylhexanol

1 kg of butyl titanate

15 As soon as 400 kg of 2-ethylhexanol had been introduced into the reactor, heating was started. Phthalic anhydride in liquid form and the remaining amount of alcohol (1 950 kg) were fed in simultaneously. After the reaction mixture had achieved a temperature of 120°C, the titanium catalyst was added. At 170°C, the mixture began to boil. At this time point the maximum
20 level of 80% was also established in the reactor. During the esterification water was released and distilled off as 2-ethylhexanol azeotrope. At a level of 78% in the reactor (approximately 2 h after the start of boiling), this was brought back to 80% with fresh 2-ethylhexanol (not present in the starting amount) and this was maintained by further supplementation of 2-ethylhexanol until the end of the reaction. When the reaction was
25 completed (AN = 0.5), the 2-ethylhexanol excess was 120 kg higher than in comparative example 3. The acid number of the reaction mixture decreased in this batch from an initial value of 110 mg KOH/g at the start of boiling to 10 mg KOH/g after 165 minutes, 1 mg KOH/g after 300
30 minutes and 0.5 mg KOH/g after 325 minutes.

This pair of examples shows that the esterification time is decreased by the inventive process by 40 minutes or 11% (yield greater than 99.8% based on phthalic anhydride).



Patent claims:

1. A process for preparing carboxylic esters by reacting dicarboxylic or polycarboxylic acids or their anhydrides with alcohols, the reaction water being removed by azeotropic distillation together with the alcohol, which comprises replacing the amount of liquid removed from the reaction by the azeotropic distillation in whole or in part with the alcohol.
2. The process as claimed in claim 1, wherein the amount of liquid separated off by the azeotropic distillation is supplemented in whole or in part by separating the liquid separated off into a water phase and an alcohol phase and recirculating the alcohol phase to the esterification reaction.
3. The process as claimed in claim 1, wherein the amount of liquid separated off by azeotropic distillation is supplemented in whole or in part by separating the liquid separated off into a water phase and an alcohol phase and recirculating the alcohol phase, additionally admixed with fresh alcohol, to the esterification reaction.
4. The process as claimed in claim 1, wherein the amount of liquid removed from the reaction by the azeotropic distillation is replaced in whole or in part by fresh alcohol.
5. The process as claimed in claims 1 to 4, wherein the dicarboxylic or carboxylic acid used is phthalic acid or phthalic anhydride.
6. The process as claimed in claims 1 to 4, wherein the alcohol used is n-butanol, isobutanol, n-octanol (1), n-octanol (2), 2-ethylhexanol, nonanols, decyl alcohols or tridecanols.