Method for preparing alicyclic carboxylic acids or their derivatives

The invention relates to preparing alicyclic carboxylic acids or their derivatives, in particular carboxylic esters, by selective hydrogenation of the corresponding aromatic carboxylic acid(s) (derivatives) in at least three series-connected reactors, at least the two first being operated in the loop operating mode.

Alicyclic polycarboxylic esters, for example the esters of cyclohexane-1,2-dicarboxylic acid, are used as lubricating oil components and as aids in metal processing. In addition, they are used as plasticizers for polyolefins and PVC.

For plasticizing PVC, predominantly use is made of esters of phthalic acid, for example dibutyl, dioctyl, dinonyl or didecyl esters of phthalic acid. Since the use of these phthalates is increasingly under discussion in recent time as controversial, their use in plastics could be restricted. Alicyclic polycarboxylic esters, of which some are already described in the literature as plasticizers for plastics could then be used as suitable substitutes.

In most cases, the most economical route for preparing alicyclic polycarboxylic esters is nuclear hydrogenation of the corresponding aromatic polycarboxylic esters, for example of the abovementioned phthalates. Some methods are already known for this:

In US 5,286,898 and US 5,319,129, methods are described by which dimethyl terephthalate can be hydrogenated in the presence of supported Pd catalysts which are doped with Ni, Pt and/or Ru at temperatures greater than or equal to 140°C and at a pressure between 50 and 170 bar to give the corresponding hexahydrodimethyl terephthalate.

US 3,027,398 discloses the hydrogenation of dimethyl terephthalate in the presence of supported Ru catalysts at 110 to 140°C and 35 to 105 bar.

In DE 28 23 165, aromatic carboxylic esters are hydrogenated to the corresponding alicyclic carboxylic esters in the presence of supported Ni, Ru, Rh and/or Pd catalysts at 70 to 250°C and 30 to 200 bar. In this case use is made of a macroporous support having a mean pore size

of 70 nm and a BET surface area of approximately 30 m^2/g.

Further supported ruthenium catalysts for preparing alicyclic polycarboxylic esters by hydrogenating aromatic polycarboxylic esters are claimed in the patent documents WO 99/32427, WO 00/78704, DE 102 25 565.2 and DE 102 32 868.4.

WO 2004/046078 describes the hydrogenation of benzenepolycarboxylic acids or their derivatives in the presence of a catalyst which has the active catalyst metal applied on a support, the support having one or more materials with ordered mesopores.

The aromatic polycarboxylic esters are hydrogenated in US 3,027,398 batchwise, in US 5,286,898, US 5,319,129, DE 28 23 165, WO 99/32427 and WO 00/78704 continuously in a tubular reactor without or with recirculation (loop operating mode) of the hydrogenation output.

In DE 102 32 868.4 and DE 102 25 565.2, the aromatic polycarboxylic esters are hydrogenated to the corresponding alicyclic polycarboxylic esters in two series-connected reactors, the first being operated in loop operating mode (partial recirculation of the reactor output) and the second being operated in straight through-flow passage. The first loop reactor can also be replaced by a plurality of small series- or parallel-connected loop reactors, these reactors having a shared circuit.

Since the technically known methods are not completely satisfactory with respect to the space-time yield and/or the selectivity, the object of the invention was to develop a hydrogenation method which does not have one or more of these disadvantages and which provides a hydrogenation product which can be used as such or after only little effort in terms of purification.

It has now been found that in the hydrogenation of aromatic carboxylic esters to the corresponding alicyclic carboxylic esters, the space-time yield and/or the product quality can be increased, i.e. a smaller amount of byproducts is obtained, when the hydrogenation is carried out in at least three series-connected hydrogenation units, at least the two first

hydrogenation units being operated in loop operating mode, i.e. with recirculation of a part of the respective hydrogenation output and the residence time of the series-connected hydrogenation units being different and lower in the first reactor than in the second reactor.

A hydrogenation unit, here and in the text hereinafter, is taken to mean a hydrogenation reactor or a plurality of series-connected reactors or a plurality of parallel-connected reactors or a reactor group which consists of parallel- and series-connected reactors, that is to say a reactor or a reactor arrangement which can perform the function of a reactor in the inventive method.

The present invention therefore relates to a method for the continuous preparation of alicyclic carboxylic acids or their derivatives by catalytic hydrogenation of the corresponding aromatic carboxylic acids or their derivatives using a hydrogen-containing gas in the presence of solid catalysts disposed in the fixed bed, which comprises carrying out the hydrogenation in at least three series-connected hydrogenation units, operating at least the first two hydrogenation units in loop operating mode and operating at least two hydrogenation units which are series-connected and operated in loop operating mode with different residence times, the residence time in one of the hydrogenation units operated in loop operating mode being less than in a directly following hydrogenation unit operated in loop operating mode.

If, in the context of the present invention, residence times are mentioned, mean residence times (reciprocal LHSV) are meant. These are defined as the quotient of the given reaction volume or the bulk volume of the catalyst (in the case of heterogeneous reaction systems this is to be set as equal) and the total volumetric flow rate (without recycle stream) of the starting material (of the starting material to be hydrogenated).

The inventive method has the advantage that, by a simple series connection of at least two loop reactors, the space-time yield can be increased compared with the methods described in the prior art. By the use of at least two loop reactors, in addition, a more stable and flexible operation is possible. For instance, in the event of loss of one of the loop reactors, if necessary, with this reactor being bypassed, the hydrogenation can be operated further. Owing to the use of the at least two loop reactors, therefore, higher breakdown security is also

ensured. In addition, simpler maintenance of the reactor system and a higher service life of the catalysts is achieved.

The inventive method is described by way of example hereinafter without the intention of limiting the invention to the exemplary embodiments. Where hereinafter ranges, general formulae or classes of compounds are specified, these are intended not only to comprise the corresponding ranges or groups of compounds which are explicitly mentioned, but also all partial ranges and partial groups of compounds which can be obtained by omitting individual values (ranges) or compounds.

The inventive method for the continuous preparation of alicyclic carboxylic acids or their derivatives by catalytic hydrogenation of the corresponding aromatic carboxylic acids or their derivatives by a hydrogen-containing gas in the presence of catalysts disposed in the fixed bed is distinguished by the fact that the hydrogenation is carried out in at least three series-connected hydrogenation units, that at least the first two hydrogenation units are operated in loop operating mode and that at least two hydrogenation units which are series-connected and operated in loop operating mode are operated with different residence times, the residence time in one of the hydrogenation units operated in loop operating mode being less than in a directly following hydrogenation unit operated in loop operating mode. It can be advantageous if all hydrogenation units are operated in loop operating mode. Likewise, it can be advantageous if the last hydrogenation unit is operated in straight through-flow passage.

The ratio of the residence times in the series-connected loop reactors is preferably from 0.01 to less than 1, preferably from 0.1 to 0.9, and particularly preferably from 0.2 to 0.5. The residence times are preferably set in such a manner that, in the first of the series-connected loop reactors, a conversion rate of 40 to 90% is achieved, preferably from 60 to 90%, and in the second loop reactor, a conversion rate of 2 to 60%, preferably of 2 to 40%, based on the starting concentration of the compound to be hydrogenated at the input of the respective reactor.

Owing to the use of two series-connected loop reactors with differing residence time and an operating mode in the range of the particularly preferred conversion rates, in the

hydrogenation of diisononyl phthalates or didecyl phthalates (diisodecyl phthalates), optimum utilization of the catalyst volume is achieved.

Of course, more than two series-connected loop reactors can be present in the inventive method. It is also possible in the inventive method when more than two series-connected loop reactors are present, that one or more of these reactors are run in such a manner that series-connected loop reactors are not run with different residence times, in which the front reactor is operated with a lower residence time than the following reactor, as long as at least two series-connected loop reactors are present in which the front reactor is operated at a lower residence time than the following reactor.

In the inventive method, an aromatic carboxylic acid or a derivative thereof or a mixture of aromatic carboxylic acids or their derivatives can be continuously hydrogenated in the liquid phase or liquid/gas mixed phase in the presence of a catalyst disposed in the fixed bed in at least three series-connected hydrogenation units with hydrogen to form the corresponding alicyclic carboxylic acids or their derivatives. A variant of the inventive method with three hydrogenation units is shown as block diagram in Fig. 1. It must be emphasized that the variant shown here also applies mutatis mutandis to methods having more than three hydrogenation units.

In the embodiment of the invention shown in Fig. 1, the first two hydrogenation units are operated in loop operating mode and the third hydrogenation unit is operated in the straight through-flow passage. Other embodiments are possible in which all three hydrogenation units are operated in loop operating mode, or in which more than three hydrogenation units are present. If the hydrogenation is carried out in a hydrogenation plant having more than three hydrogenation units, according to the invention, the first two hydrogenation units are operated in loop operating mode and the following hydrogenation units can optionally be operated in loop operating mode or in straight through-flow passage.

In the variant of the inventive method shown in Fig. 1, each individual reactor is charged with hydrogenation gas. In order to minimize hydrogen consumption and the output losses caused by the offgas streams, it can be expedient to use the offgas of one hydrogenation unit as

hydrogenation gas for another hydrogenation unit. For example, in a method as shown in Fig. 1, the offgas (6) from the first hydrogenation unit (3) can be fed into the second hydrogenation unit (11) instead of the hydrogenation gas (1b), and the offgas (14) of the second hydrogenation unit (11) can be fed into the third hydrogenation unit (18) instead of the hydrogenation gas (1c). In this case, liquid starting material/product phase and hydrogenation gas flow in the same sequence through the reactors. Likewise, it can be expedient to allow hydrogenation gas and starting material/product phase to flow through the reactors in opposite direction. In this case, fresh hydrogenation gas is introduced into the last reactor and offgas from the first reactor is discharged. Furthermore, two or more reactors can have a shared hydrogenation gas system and other reactors can be charged separately therefrom with hydrogenation gas. When the offgas of one reactor is used as hydrogenation gas of another reactor, if desired, the pressure drop can be compensated for by intermediate compression.

Preferably, the offgas quantities and gas streams are set in such a manner that in all reactors good fluid dynamics is present, i.e. a low wall flow and a high interfacial area for mass transfer.

As hydrogenation gases, use can be made of any desired hydrogen-containing gas mixtures which do not comprise harmful amounts of catalyst poisons, for example carbon monoxide or hydrogen sulfide. The use of inert gases is optional, preferably, hydrogen at a purity greater than 95%, in particular greater than 98%, is used. Inert gas fractions can be, for example, nitrogen or methane. Preferably, sufficient hydrogen is present in the hydrogenation units so that it is present in excess, in particular in an excess of 200%, preferably in an excess of from 5 to 100%, and particularly preferably in an excess of from 10 to 50%, based on the stoichiometric amount which is required to achieve the conversion rate which is possible or desired in the hydrogenation unit. Without setting a sufficient excess of hydrogen, the hydrogenation of the aromatic bonds is achieved only incompletely, which leads to losses of yield.

According to the inventive method, aromatic carboxylic acids or their derivatives, such as aromatic mono-, di- or polycarboxylic acids or their derivatives, for example their esters or anhydrides, in particular their alkyl esters, can be reacted to give the corresponding alicyclic

carboxylic acid compounds. As aromatic di- or polycarboxylic acid derivatives, not only full esters, but also partial esters can be hydrogenated using the inventive method. Full ester is intended to mean a compound in which all acid groups are esterified. Partial esters are compounds having at least one free acid group (or if appropriate one anhydride group) and at least one ester group. If polycarboxylic esters are used in the inventive method, these preferably comprise 2, 3 or 4 ester functions.

In the inventive method, as aromatic di- or polycarboxylic acids or their derivatives, use is preferably made of benzene-, diphenyl-, naphthalene-, diphenyl oxide- or anthracene-polycarboxylic acids, their anhydrides and/or the corresponding esters. The alicyclic di- or polycarboxylic acids or their derivatives obtained by the inventive method consist of one or more C_6 rings, if appropriate linked by a C-C bond, or fused.

In a preferred embodiment, the present invention relates to a method for hydrogenating 1,2-, 1,3- or 1,4-benzenedicarboxylic acid or derivatives thereof, in particular esters thereof, and/or 1,2,3-, 1,2,4- or 1,3,5-benzenetricarboxylic acid or derivatives thereof, in particular esters thereof, i.e. the isomers of 1,2-, 1,3- or 1,4-cyclohexanedicarboxylic acid or derivatives thereof, in particular esters thereof, or 1,2,3-, 1,3,5- or 1,2,4-cyclohexanetricarboxylic acid or derivatives thereof, in particular esters thereof are obtained.

In the inventive method, for example, the following aromatic carboxylic acids or derivatives thereof, in particular esters, can be used: 1,2-naphthalenedicarboxylic acid, 1,3-naphthalene-dicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 1,7-naphthalenedicarboxylic acid, 1,8-naphthalene-dicarboxylic acid, phthalic acid (benzene-1,2-dicarboxylic acid), isophthalic acid (benzene-1,3-dicarboxylic acid), terephthalic acid (benzene-1,4-dicarboxylic acid), benzene-1,2,3-tri-carboxylic acid, benzene-1,2,4-tricarboxylic acid (trimellitic acid), benzene-1,3,5-tricarboxylic acid (trimesic acid), benzene-1,2,3,4-tetracarboxylic acid. In addition, use can be made of acids or their derivatives, in particular esters, which are formed from said acids by substitution by alkyl, cycloalkyl or alkoxyalkyl groups of one or more hydrogen atoms bound to the aromatic nucleus.

As aromatic monocarboxylic acids or their derivatives, use can be made in the inventive method of, e.g. benzoic acid, 1-naphthoic acid or 2-naphthoic acid or their derivatives, in particular their esters. Furthermore, use can be made of monocarboxylic acids or their derivatives, in particular esters, which are formed from said monocarboxylic acids by substitution by alkyl, cycloalkyl or alkoxyalkyl groups of one or more hydrogen atoms bound to the aromatic nucleus.

Particularly preferably, use can be made in the inventive method of the aromatic carboxylic esters of the abovementioned aromatic carboxylic acids. The alcohol component of the aromatic carboxylic esters preferably used preferably consists of branched or linear (unbranched) alkyl, cycloalkyl or alkoxyalkyl groups having 1 to 25 carbon atoms, preferably 3 to 15, particularly preferably 8 to 13, carbon atoms, and very particularly preferably 9 or 10 carbon atoms. The alcohol component can have one or more hydroxyl groups. If more than one carboxyl group is present in a molecule, the alcohol components in a molecule of an aromatic polycarboxylic ester used can be identical or different, i.e. they can have identical or different isomers or chain lengths. Obviously, isomers with respect to the substitution pattern of the aromatic system can also be used in the form of a mixture, e.g. a mixture of phthalic ester and terephthalic ester.

In the inventive method, as ester of an aromatic di- or polycarboxylic acid, use can be made of, for example the following compounds: terephthalic acid monomethyl ester, terephthalic acid dimethyl ester, terephthalic acid diethyl ester, terephthalic acid di-n-propyl ester, terephthalic acid dibutyl ester, terephthalic acid diisobutyl ester, terephthalic acid di-tert-butyl ester, terephthalic acid monoglycol ester, terephthalic acid diglycol ester, terephthalic acid diisoheptyl ester, terephthalic acid n-octyl ester, terephthalic acid diisooctyl ester, terephthalic acid di-2-ethylhexyl ester, terephthalic acid di-n-nonyl ester, terephthalic acid diisononyl ester, terephthalic acid di-n-decyl ester, terephthalic acid diisodecyl ester, terephthalic acid dipropylheptyl ester, terephthalic acid di-n-undecyl ester, terephthalic acid diisododecyl ester, terephthalic acid ditridecyl ester, terephthalic acid di-n-octadecyl ester, terephthalic acid diisooctadecyl ester, terephthalic acid di-n-eicosyl ester, terephthalic acid monocyclohexyl ester; phthalic acid monomethyl ester, phthalic acid dimethyl ester, phthalic acid di-n-propyl ester, phthalic acid di-n-butyl ester, phthalic acid diisobutyl ester, phthalic acid di-tert-butyl

ester, phthalic acid monoglycol ester, phthalic acid diglycol ester, phthalic acid diisoheptyl ester, phthalic acid di-n-octyl ester, phthalic acid diisooctyl ester, phthalic acid diethylhexyl ester, phthalic acid di-n-nonyl ester, phthalic acid diisononyl ester, phthalic acid di-n-decyl ester, phthalic acid di-2-propylheptyl ester, phthalic acid diisodecyl ester, phthalic acid di-n-undecyl ester, phthalic acid diisoundecyl ester, phthalic acid ditridecyl ester, phthalic acid di-n-octadecyl ester, phthalic acid diisooctadecyl ester, phthalic acid di-n-eicosyl ester, phthalic acid monocyclohexyl ester; phthalic acid dicyclohexyl ester, isophthalic acid monomethyl ester, isophthalic acid dimethyl ester, isophthalic acid dimethyl ester, isophthalic acid diethyl ester, isophthalic acid di-n-propyl ester, isophthalic acid di-n-butyl ester, isophthalic acid diisobutyl ester, isophthalic acid di-tert-butyl ester, isophthalic acid monoglycol ester, isophthalic acid diglycol ester, isophthalic acid diisoheptyl ester, isophthalic acid di-n-octyl ester, isophthalic acid diisooctyl ester, isophthalic acid di-2-ethylhexyl ester, isophthalic acid di-n-nonyl ester, isophthalic acid diisononyl ester, isophthalic acid di-n-decyl ester, isophthalic acid diisodecyl ester, isophthalic acid dipropylheptyl ester, isophthalic acid di-n-undecyl ester, isophthalic acid diisododecyl ester, isophthalic acid di-n-dodecyl ester, isophthalic acid ditridecyl ester, isophthalic acid di-n-octadecyl ester, isophthalic acid diisooctadecyl ester, isophthalic acid di-n-eicosyl ester, isophthalic acid monocyclohexyl ester.

In the inventive method, as ester of the monocarboxylic acids, use can be made of, e.g. benzoates of diols, for example glycol dibenzoate, diethylene glycol dibenzoate, triethylene glycol dibenzoate or dipropylene glycol dibenzoate, or else benzoic acid alkyl ester, for example decyl or isodecyl benzoate, nonyl or isononyl benzoate, octyl or isooctyl benzoate, 2-ethylhexyl benzoate or tridecyl or isotridecyl benzoate.

In the inventive method, use can also be made of mixtures of two or more carboxylic acids or carboxylic acid derivatives, in particular mixtures of carboxylic esters. Such mixtures can be obtained, for example, in the following ways:

a) a di- or polycarboxylic acid is partially esterified with an alcohol in such a manner that full and partial esters are present simultaneously.
b) a mixture of at least two carboxylic acids is esterified with an alcohol, a mixture of at least two full esters being formed.

c) a di- or polycarboxylic acid is esterified with an alcohol mixture, in which case a corresponding mixture of full esters can be formed.

d) a di- or polycarboxylic acid is partially esterified with an alcohol mixture.

e) a mixture of at least two carboxylic acids is partially esterified with an alcohol mixture.

f) a mixture of at least two di- or polycarboxylic acids is partially esterified with an alcohol mixture.

In these reactions, instead of the polycarboxylic acids, the corresponding anhydrides can also be used.

On a large scale, aromatic esters, in particular the full esters, are prepared by route c) frequently from alcohol mixtures. Corresponding alcohol mixtures are, for example:

C_5-alcohol mixtures, prepared from linear butenes by hydroformylation and subsequent hydrogenation;

C_5-alcohol mixtures, prepared from isobutene or butene mixtures which comprise linear butenes and isobutene, by hydroformylation and subsequent hydrogenation;

C_6-alcohol mixtures, prepared from a pentene or a mixture of two or more pentenes, by hydroformylation and subsequent hydrogenation;

C_7-alcohol mixtures, prepared from triethylene or dipropene or a hexene isomer or another mixture of hexene isomers by hydroformylation and subsequent hydrogenation;

C_8-alcohol mixtures, such as 2-ethylhexanol (2 isomers), prepared by aldol condensation of n-butyraldehyde and subsequent hydrogenation;

C_9-alcohol mixtures, prepared from C_4-olefins by dimerization, hydroformylation and hydrogenation. For preparation of the C_9-alcohols, starting materials which can be used are isobutene or a mixture of linear butenes or mixtures with linear butenes and isobutene. The C_4-olefins can be dimerized using different catalysts, for example proton acids, zeolites, organometallic nickel compounds or solid nickel-containing contact catalysts. The C_8-olefin mixtures can be hydroformylated using rhodium or cobalt catalysts. There is therefore a multiplicity of technical C_9-alcohol mixtures.

C_{10}-alcohol mixtures prepared from tripropylene by hydroformylation and subsequent hydrogenation; 2-propylheptanol (2 isomers), prepared by aldol condensation of valeraldehyde and subsequent hydrogenation;

C_{10}-alcohol mixtures, prepared from a mixture of at least two C_5-aldehydes by aldol condensation and subsequent hydrogenation;
C_{13}-alcohol mixtures, prepared from dihexene, hexaethylene, tetrapropylene or tributene by hydroformylation and subsequent hydrogenation.

Further alcohol mixtures can be produced by hydroformylation and subsequent hydrogenation from olefins or olefin mixtures which arise, for example, in Fischer-Tropsch syntheses, in dehydrogenations of hydrocarbons, metathesis reactions, in the polygas method or other industrial processes. Furthermore, olefin mixtures comprising olefins of different carbon numbers can also be used for preparing alcohol mixtures.

In the inventive method, use can be made of all ester mixtures prepared from aromatic carboxylic acids and the abovementioned alcohol mixtures. According to the invention, use is preferably made of esters prepared from phthalic acid, phthalic anhydride or benzoic acid and a mixture of isomeric alcohols having from 6 to 13 carbon atoms.

Examples of technical phthalates which can be used in the inventive method are the following products having the trade names:
Vestinol C (di-n-butyl phthalate) (CAS No. 84-74-2); Vestinol IB (diisobutyl phthalate) (CAS No. 84-69-5); Jayflex DINP (CAS No. 68515-48-0); Jayflex DIDP (CAS No. 68515-49-1); Palatinol 9P (68515-45-7), Vestinol 9 (CAS No. 28553-12-0); TOTM (CAS No. 3319-31-1); Linplast 68-TM, Palatinol N (CAS No. 28553-12-0); Jayflex DHP (CAS No. 68515-50-4); Jayflex DIOP (CAS No. 27554-26-3); Jayflex UDP (CAS No. 68515-47-9); Jayflex DIUP (CAS No. 85507-79-5); Jayflex DTDP (CAS No.68515-47-9); Jayflex L9P (CAS No. 68515-45-7); Jayflex L911P (CAS No. 68515-43-5); Jayflex L11P (CAS No. 3648-20-2); Witamol 110 (CAS No. 68515-51-5); Witamol 118 (di-n-C8-C10-alkyl phthalate) (CAS No. 71662-46-9); Unimoll BB (CAS No. 85-68-7); Linplast 1012 BP (CAS No. 90193-92-3); Linplast 13XP (CAS No.27253-26-5); Linplast 610P (CAS No. 68515-51-5); Linplast 68 FP (CAS No. 68648-93-1); Linplast 812 HP (CAS No. 70693-30-0); Palatinol AH (CAS No. 117-81-7); Palatinol 711 (CAS No. 68515-42-4); Palatinol 911 (CAS No. 68515-43-5); Palatinol 11 (CAS No. 3648-20-2); Palatinol Z (CAS No. 26761-40-0); Palatinol DIPP (CAS No. 84777-06-0); Jayflex 77 (CAS No. 71888-89-6); Palatinol 10 P (CAS No. 533-54-0);

Vestinol AH (CAS No. 117-81-7).

It must be noted that in the nuclear hydrogenation of aromatic di- or polycarboxylic acids or their esters from each isomer used, at least two stereoisomeric hydrogenation products can form. The mass ratios of the resultant stereoisomers to one another depend on the catalyst used and on the hydrogenation conditions. All hydrogenation products having any ratio(s) of the stereoisomers to one another can be used without separation, or after a separation. Generally, the hydrogenation products are used without separation.

In the inventive method, solid hydrogenation catalysts are used which preferably comprise at least one metal of the eighth subgroup of the Periodic Table of the Elements. Preferably, use is made of, as active metals of the eighth subgroup of the Periodic Table of the Elements, platinum, rhodium, palladium, cobalt, nickel or ruthenium, or a mixture of two or more thereof, in particular ruthenium being used as active metal.

In addition to the abovementioned metals, in addition at least one metal of the first and/or seventh subgroup of the Periodic Table of the Elements may be present in the catalysts. Preferably, use is made of rhenium and/or copper.

The content of the active metals, i.e. of the metals of the first and/or seventh and/or eighth subgroup of the Periodic Table of the Elements, is preferably from 0.1 to 30% by mass. The noble metal content, i.e. of the metals of the eighth subgroup of the Periodic Table of the Elements and of the fifth or sixth period, e.g. palladium, ruthenium, calculated as metal, is preferably in the range from 0.1 to 10% by mass, in particular in the range from 0.8 to 5% by mass, very particularly between 1 and 3% by mass.

Preferably, the catalysts used are supported catalysts. As supports, use can be made, for example, of the following materials: activated carbon, silicon carbide, aluminum oxide, silicon oxide, aluminosilicate, titanium dioxide, zirconium dioxide, magnesium oxide and/or zinc oxide or their mixtures. Particularly preferably, use is made of a catalyst which has a titanium dioxide support. In addition, these support materials can comprise alkali metals, alkaline earth metals and/or sulfur.

In the inventive method, preferably use is made of ruthenium catalysts which are claimed in the patent documents DE 102 25 565.2 and DE 102 32 868.4.

In the inventive method, the hydrogenation units preferably each consist of a hydrogenation reactor. This can be a tubular reactor, tube-bundle reactor, or preferably a shaft furnace.

The individual reactors can be operated adiabatically, polytropically or virtually isothermally, i.e. having a temperature increase of typically less than 10°C. In this case, in particular the reactors operated in the loop operating mode are preferably run quasiisothermally, preferably having a temperature increase less than 10°C, particularly preferably less than 5°C.

The inventive method is carried out preferably in the liquid/gas mixed phase or liquid phase, in three-phase reactors in cocurrent flow, the hydrogenation gas being distributed in a manner known per se in the liquid starting material/product stream. In the interest of even liquid distribution, an improved removal of heat of reaction and/or a high space-time yield, the reactors operated in the loop operating mode are preferably run at high liquid loadings of from 10 to 400, preferably from 20 to 200, and particularly preferably from 40 to 150m^3 per m^2 cross-sectional area of the empty reactor and hour.

The liquid loadings can be identical or different in the reactors operated in the loop operating mode. Preferably, the liquid loading is greatest in the first reactor and decreases in the subsequent reactors operated in loop operating mode. In a plant according to the invention having two series-connected loop reactors the liquid loading in the first reactor is preferably in the range from 20 to 200, in particular in the range from 40 to 150 $m^3/(m^2 \cdot h)$ and in the second reactor, preferably in the range from 20 to 180, in particular in the range from 40 to 140 $m^3/(m^2 \cdot h)$.

The loading of the reactor operated in the straight through-flow passage is preferably from 2 to 100 $m^3/(m^2 \cdot h)$, in particular from 10 to 80 $m^3/(m^2 \cdot h)$.

The hydrogenation can be carried out in the absence, or preferably in the presence, of a

solvent. As solvent, use can be made of all liquids which form a homogeneous solution with the starting material and product, which are inert under hydrogenation conditions and may readily be separated off from the product. The solvent can also be present in a mixture of a plurality of substances, and if appropriate water.

Use can be made, for example, of the following substances as solvent: straight-chain or cyclic ethers, for example tetrahydrofuran or dioxane and also aliphatic alcohols in which the alkyl radical has 1 to 13 carbon atoms. Alcohols which can preferably be used as solvents are isopropanol, n-butanol, isobutanol, n-pentanol, 2-ethylhexanol, nonanols, technical nonanol mixtures, decanol, technical decanol mixtures, tridecanols. The use of alcohols is only preferred when the carboxylic acid derivatives intended for hydrogenation are esters. When alcohols are used as solvent, it can be expedient to use that alcohol or alcohol mixture which would be formed on saponification of the product. As a result, byproduct formation due to transesterification would be excluded. A further preferred solvent is the hydrogenation product itself.

By using a solvent, the aromatics concentration in the reactor feed can be limited, as a result of which better temperature control in the reactor can be achieved. This can have as consequence a minimization of side reactions and thus an increase in product yield. Preferably, the aromatics content in the reactor feed is between 1 and 70%. The desired concentration range can, in those reactors which are operated in the loop operating mode, be set by the circulation ratio (ratio of recirculated hydrogenation output to starting material). The aromatics concentration in the reactor feed (mixture of fresh starting material or hydrogenation output of the previous reactor and of circulation stream) preferably decrease from the first to the last reactor. For example, in a plant according to Fig. 1, the aromatics concentration in the feed to the first reactor (3) is in the range from 70 to 5% by mass, in the feed to the second reactor (11) in the range from 40 to 2% by mass, and in the feed to the third reactor (18) in the range from 20 to 1% by mass.

The inventive method is carried out preferably in a pressure range from 0.3 to 30 MPa, in particular from 1.5 to 20 MPa, very particularly preferably from 5 to 20 MPa. The pressure in the individual reactors can be identical or different. Preferably, the pressures are identical or

approximately identical.

The hydrogenation temperatures are preferably from 50 to 250°C, more preferably from 80 to 200°C. The hydrogenation temperatures in individual reactors can be identical or different.

The hydrogenation product which is formed in the inventive hydrogenation of an aromatic carboxylic acid or its derivatives, in particular an aromatic di- or polycarboxylic ester or a mixture of aromatic di- or polycarboxylic esters by the inventive method has preferably a content of alicyclic carboxylic acids or their derivatives, in particular esters, of greater than 96% by mass, in particular greater than 98% by mass, very particularly preferably greater than 99% by mass. This mixture can be used directly or after a purification. Byproducts can be separated off, for example by distillation, or by stripping with an inert gas such as nitrogen or steam. Preferably, small amounts of low boilers are separated off by stripping with steam in the temperature range from 120°C to 240°C, in particular in the range from 150 to 200°C and at a pressure of from 5 kPa to 10 kPa . Then, by reducing the pressure to below 5 kPa, the product can be dried.

Products which are obtained by the inventive method are mixtures which have alicyclic carboxylic acids or their derivatives, in particular alicyclic carboxylic esters, and particularly preferably alicyclic di- or polycarboxylic acids.

The present invention further relates to the use of the inventively prepared mixtures of alicyclic carboxylic esters as plasticizers in plastics. Preferred plastics are PVC, homo- and copolymers based on ethylene, propylene, butadiene, vinyl acetate, glycidyl acrylate, glycidyl methacrylate, methacrylates, acrylates, acrylates having, bound to the oxygen atom of the ester group, alkyl radicals of branched or unbranched alcohols having one to ten carbon atom(s), styrene, acrylonitrile, homo- or copolymers of cyclic olefins.

As representatives of the above groups, the following plastics may be mentioned by way of example:
polyacrylates having identical or different alkyl radicals having 4 to 8 carbon atoms, bound to the oxygen atom of the ester group, in particular having the n-butyl, n-hexyl, n-octyl and

2-ethylhexyl radical and isononyl radical, polymethacrylate, polymethylmethacrylate, methylacrylate-butylacrylate copolymers, methylmethacrylate-butylmethacrylate copolymers, ethylene-vinylacetate copolymers, chlorinated polyethylene, nitrile rubber, acrylonitrile-butadiene-styrene copolymers, ethylene-propylene copolymers, ethylene-propylene-diene copolymers, styrene-acrylonitrile copolymers, acrylonitrile-butadiene rubber, styrene-butadiene elastomers, methyl methacrylate-styrene-butadiene copolymers and/or nitrocellulose.

Furthermore, the inventively prepared alicyclic carboxylic esters can be used for modifying plastic mixtures, in particular for blending a polyolefin with a polyamide. Mixtures of plastics and the inventively prepared alicyclic polycarboxylic esters are likewise subject matter of the present invention. Suitable plastics are the abovementioned compounds. Such mixtures preferably comprise at least 5% by mass, particularly preferably 10-80% by mass, very particularly preferably 20-70% by mass, of the alicyclic polycarboxylic esters.

Mixtures of plastics, in particular PVC, which comprise one or more of the inventively prepared alicyclic polycarboxylic esters can, for example, be present in the following products, or be used for their preparation:
hoses, cables, wire sheathings, insulating tapes, in motor vehicle and furniture construction, plastisols, in floor coverings, medical articles, food packaging, seals, films, composite films, plates, artificial leather, toys, wallpaper, packaging vessels, adhesive tape films, clothing, coatings, coatings of textiles, shoes, underseal, seam seals, modeling compositions, or balls.

In addition to the abovementioned applications, the inventively prepared alicyclic carboxylic esters can be used as lubricating oil component, as constituent of cooling fluids and metal processing liquids. Likewise, they can be used as component in paints, varnishes, inks and adhesives.

The inventive method can be carried out in various embodiments. A preferred embodiment of the present invention is shown by way of example as a block diagram in the figure Fig. 1. This diagram has three reactors or reactor units of which two are operated in the loop operating mode. Of course, the inventive method can also be carried out using more than three reactors

(or reactor units), or all three reactors can be operated in the loop operating mode.

In the variant of the inventive method according to Fig. 1, hydrogen (1a), starting material (2) and a part (8) of the liquid hydrogenation output (7) from the reactor (3) are fed into the hydrogenation unit (3). The hydrogenation output (4) from the hydrogenation unit (3) is separated in the still (5) into offgas (6) and liquid phase (7). A part (9) of the stream (7) is passed together with the part (16) of the liquid phase (15) from the second hydrogenation unit (11) and hydrogen (1b) into the hydrogenation unit (11). The hydrogenation output (12) from the hydrogenation unit (11) is separated in the still (13) into offgas (14) and liquid phase (15). A part (17) of the stream (15) is fed together with hydrogen (1c) into the hydrogenation unit (18). The hydrogenation output (19) from the hydrogenation unit (18) is separated in the still (20) into offgas (21) and crude product (22). Crude product (22) is either used as such or, after purification, in a plant which is not shown.

The present invention is described by way of example in the examples hereinafter, without the invention being intended to be limited to the embodiments specified in the examples.

Examples

The hydrogenation reactor was a tubular reactor and was operated continuously, optionally in straight through-flow passage, or in loop operating mode. In all experiments, the liquid phase and the hydrogenation gas flowed cocurrently from top to bottom.

The tubular reactor was packed with 1350 ml of ruthenium catalyst (1% Ru/TiO_2). This catalyst was prepared from the TiO_2 support Aerolyst 7711 and an aqueous ruthenium nitrate solution as described in DE 102 32 868.4. The catalyst consisted of cylindrical rod extrudates having the circle diameter of 1.5 mm and a length of 4 to 6 mm.

In both experiments, diisononyl phthalate, abbreviated form DINP, of Oxeno Olefinchemie GmbH having the trade name Vestinol 9 was used. As hydrogenation gas, use was made of hydrogen at a purity of greater than 99.9%.

In both examples the liquid hydrogenation output of one hydrogenation stage is the feed

product of the next hydrogenation stage. The individual hydrogenation stages were carried out one after the other in the same reactor using the same catalyst and same catalyst quantity. The hydrogenation output of the first stage, after the quasisteady-state equilibrium is achieved, was collected and used for the second stage. In example 1, in addition, the hydrogenation output of the second stage was collected as feed material for the third stage. For better comparability, the pressure, the reaction temperature and the offgas amount were identical in all hydrogenation steps.

Example 1 (according to the invention)

The hydrogenation was carried out in three stages. In the first two stages, the reactor was operated in loop operating mode, and in the third stage in straight through-flow passage. The operating parameters and the mass flow rates of example 1 are compiled in table 1.

Table 1:

	1st stage	2nd stage	3rd stage
Temperature (°C)	100	100	100
Pressure (MPa)	10	10	10
Offgas (l(S.T.P.)/h)	50	50	50
Circulation rate (l/h)	30	30	0
Feed (l/h)	9.54	3.18	1.05
DINP concentration in the feed (%) (based on fresh DINP or hydrogenation output of the previous reactor)	100	59.7	19.9
Hydrogenation output (l/h) *	9.592	3.197	1.053
DINP concentration in the hydrogenation output (%)	59.7	19.9	< 0.05
LHSV (h^{-1}) **	7.06	2.35	0.78

* Volume of the hydrogenation output, calculated assuming a density of 0.975 g/l and ignoring the offgas losses

** LHSV: liters of fresh DINP or liters of hydrogenation output from the previous reactor per liter of catalyst per hour

The target product (hydrogenation output of the third stage) had a purity of greater than 99.5% by mass. The DINP conversion rate was virtually quantitative.

Taking into account the fact that the hydrogenation output of one stage is the feed material of the next stage, starting from 9.54 l/h of fresh DINP, for a continuous hydrogenation taking into account the differing densities of DINP and DINCH, gave the following feed streams (without recycle streams) to the reactors:
First reactor: 9.54 l/h
Second reactor: 9.592 l/h
Third reactor: 9.643 l/h

Maintaining the LHSV identified in table 1 gave, for the just mentioned volumetric flow rates, the following catalyst amounts:
First reactor: 1.35 l
Second reactor: 4.07 l
Third reactor: 12.36 l

The (total) catalyst volume in the two loop reactors corresponds accordingly to 5.432 l. The feed of 9.54 l/h of fresh DINP to the first reactor, over the two loop reactors, gave a total LHSV of 1.75 h^{-1}.

Example 2 (comparison)
The hydrogenation was carried out in two stages. In the first stage, the reactor was operated in loop operating mode, and in the second stage in straight through-flow passage.

The operating parameters and the mass flow rates of example 2 are listed in table 2.

Table 2:

	1st stage	2nd stage
Temperature (°C)	100	100
Pressure (MPa)	10	10
Offgas (l(S.T.P.)/h)	50	50
Circulation rate (l/h)	30	0
Feed (l/h)	1.59	1.05
DINP concentration in the feed (%) (based on fresh DINP or hydrogenation output of the previous reactor)	100	19.9
Hydrogenation output (l/h)	1.625	1.053
DINP concentration in the hydrogenation output (%)	19.9	< 0.05
LHSV (h^{-1})	1.18	0.78

In the hydrogenation of a pure DINP to a residual content of 19.9%, the hydrogenation was performed in two series-connected loop reactors (example 1) having an LHSV of 1.75 h^{-1}, in the hydrogenation to the same residual content using only one loop reactor (example 2), in contrast, the LHSV was 1.18 h^{-1}. It was thus found that the inventive method has a higher space-time yield compared with a conventional method.

Patent claims:

1. A method for the continuous preparation of alicyclic carboxylic acids or their derivatives by catalytic hydrogenation of the corresponding aromatic carboxylic acids or their derivatives using a hydrogen-containing gas in the presence of solid catalysts disposed in a fixed bed, which comprises carrying out the hydrogenation in at least three series-connected hydrogenation units, operating at least the first two hydrogenation units in loop operating mode and operating at least two hydrogenation units which are series-connected and operated in loop operating mode with different residence times, the residence time in one of the hydrogenation units operated in loop operating mode being less than in a directly following hydrogenation unit operated in loop operating mode.

2. The method as claimed in claim 1,
   wherein
   all hydrogenation units are operated in loop operating mode.

3. The method as claimed in claim 1,
   wherein
   the last hydrogenation unit is operated in straight through-flow passage.

4. The method as claimed in one of claims 1 to 3,
   wherein
   the hydrogenation is carried out in an apparatus which has more than two hydrogenation units.

5. The method as claimed in one of claims 1 to 3,
   wherein
   the hydrogenation is carried out in an apparatus which has three hydrogenation units.

6. The method as claimed in one of claims 1 to 5,
   wherein
   use is made of a catalyst which comprises at least one metal of the eighth subgroup of the

Periodic Table of the Elements.

7. The method as claimed in claim 6,
wherein
use is made of a catalyst which comprises ruthenium.

8. The method as claimed in one of claims 1 to 7,
wherein
use is made of a catalyst which has a titanium dioxide support.

9. The method as claimed in one of claims 1 to 8,
wherein
as aromatic carboxylic acids or their derivatives, use is made of mono-, di- or polycarboxylic acids or their derivatives.

10. The method as claimed in one of claims 1 to 9,
wherein
as aromatic di- or polycarboxylic acids or their derivatives, use is made of benzene-, diphenyl-, naphthalene-, diphenyl oxide- or anthracene di- or polycarboxylic acids, their anhydrides, and/or their corresponding esters.

11. The method as claimed in claim 9,
wherein
as aromatic monocarboxylic acid, use is made of benzoic acid, 1-naphthoic acid, or 2-naphthoic acid , their anhydrides or their esters.

12. The method as claimed in at least one of claims 1 or 11,
wherein
as aromatic carboxylic acid derivatives, use is made of the carboxylic esters.

13. The method as claimed in claim 12,
wherein

when di- or polycarboxylic acid derivatives are used, the partial and/or full esters are used.

14. The method as claimed in claim 12 or 13,
wherein
the alcohol components of the aromatic carboxylic esters used have branched or unbranched alkoxyalkyl, cycloalkyl and/or alkyl groups having 1 to 25 carbon atoms.

15. The method as claimed in at least one of claims 12 to 14,
wherein
the alcohol components of the aromatic di- and/or polycarboxylic esters used are in each case identical or different.

16. The method as claimed in at least one of claims 9 to 14,
wherein
as aromatic dicarboxylic acid derivative, use is made of diisononyl phthalate or didecyl phthalate.

17. The method as claimed in claim 11,
wherein
as aromatic monocarboxylic acid derivative, use is made of isononyl benzoate or decyl benzoate.

18. The method as claimed in at least one of claims 1 to 17,
wherein
the ratio of the residence times in the series-connected loop reactors is from 0.01 to less than 1.