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**LOW PRESSURE PROCESS FOR THE MANUFACTURE
OF CYCLOHEXANEDICARBOXYLATE ESTERS**

5 This invention pertains to a process for the manu-
facture of dialkyl cyclohexanedicarboxylates by the low
pressure, catalytic hydrogenation of the corresponding
dialkyl benzenedicarboxylate. More particularly, this
invention pertains to the low pressure, catalytic
hydrogenation of a dialkyl benzenedicarboxylate wherein
10 the formation/accumulation of carbon monoxide is
suppressed to maintain the activity of the precious
metal catalyst.

Dimethyl 1,4-cyclohexanedicarboxylate has been
manufactured on a commercial scale for over 30 years as
15 an intermediate in the production of cyclohexanedimeth-
anol, a diol which is used extensively as a monomer in
the preparation of condensation polymers, particularly
polyesters. Dimethyl cyclohexanedicarboxylates also are
valuable chemical intermediates useful, for example, in
20 the manufacture of polyester resins used in the
formulation of coating compositions.

The manufacture of dimethyl 1,4-cyclohexanedicar-
boxylate and 1,4-cyclohexanedimethanol using dimethyl
terephthalate as the feedstock and a heterogenous mode
25 of operation is described in U.S. Patent 3,334,149.
This patent describes a continuous process wherein
molten dimethyl terephthalate flows over and through a
bed of a supported palladium catalyst in a mode of
operation referred to as trickle bed operation. The
30 continuous process described requires the use of high
pressures, e.g., greater than 346 bars absolute (34,600
kPa), and utilizes a palladium on alumina catalyst in
the hydrogenation of dimethyl terephthalate to dimethyl
1,4-cyclohexanedicarboxylate. The specific palladium on
35 alumina employed is in the form of 3 mm chips and

contains 0.5 weight percent palladium deposited on alumina, the crystalline phase of which is a mixture of bayerite and boehmite.

5 It is apparent that chemical processes which require the use of high pressures such as pressures in excess of 340 bars (34,000 kPa) are inherently expensive due to the increased operating costs and the cost of the apparatus required including the high pressure-rated reactor and the compressors. However, when the
10 hydrogenation of dimethyl terephthalate to dimethyl 1,4-cyclohexanedicarboxylate is carried out at pressures less than 135 bars absolute (13,500 kPa) using the above-described palladium on alumina catalyst, commercially acceptable hydrogenation rates cannot be
15 achieved and/or maintained. For example, when operating at 125 bars absolute (12,500 kPa), the hydrogenation rate typically is significantly less than the rates achieved at approximately 410 bars absolute (41,000 kPa) pressure. In some cases, the hydrogenation reaction can
20 decrease to a rate of zero. The reduced hydrogenation rate is due to decreased activity of the palladium catalyst which, we have discovered, is related to the generation of carbon monoxide during the hydrogenation at lower pressures. It has been found that the
25 hydrogenation of dimethyl benzenedicarboxylates at relatively low pressures, e.g., pressures of less than 175 bars absolute (17,500 kPa), results in the formation of carbon monoxide, possibly by the decomposition of the methanol liberated from the dimethyl ester. The problem
30 of carbon monoxide formation and/or catalyst deactivation is not encountered when the hydrogenation is carried out at the high pressures described in U.S. Patent 3,334,149. It is known that the presence of carbon monoxide in hydrogen gas used in catalytic

hydrogenation processes is detrimental to such processes. However, the production of carbon monoxide and the extreme sensitivity of the above-described palladium on alumina catalyst to parts per million (ppm) amounts of carbon monoxide is surprising.

The present invention is concerned with a process whereby a dimethyl benzenedicarboxylate is catalytically hydrogenated to the corresponding dimethyl cyclohexanedicarboxylate using moderate pressures and readily available catalysts. The present invention provides a continuous process for the manufacture of a dimethyl cyclohexanedicarboxylate which comprises the steps of;

- (1) continuously feeding hydrogen gas and a liquid mixture of the dimethyl cyclohexanedicarboxylate product and the corresponding dimethyl benzenedicarboxylate reactant to a hydrogenation zone containing at least one fixed bed of a palladium on alumina hydrogenation catalyst; and
- (2) continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product from the hydrogenation zone;

wherein the dimethyl benzenedicarboxylate is hydrogenated to the dimethyl cyclohexanedicarboxylate at a pressure of 10 to 205 bars absolute (1,000 to 20,500 kPa) and a temperature of 150 to 230°C and the concentration of carbon monoxide in the hydrogen gas removed from the hydrogenation zone is maintained at less than 200 parts per million by volume (ppmv). Our novel process may be used to produce dimethyl cyclohexanedicarboxylate esters at a conversion of 99% or greater and space-time yields (based on the volume of catalyst) of 1000 g per liter-hour or greater.

Various process conditions and/or modes of operation may be controlled or modified to maintain the



carbon monoxide concentration at levels which do not retard significantly the hydrogenation rate of the process. Thus, the concentration of carbon monoxide may be maintained at low levels simply by venting all of the gaseous effluent from the process and feeding only fresh hydrogen which is essentially free of carbon monoxide. However, this mode of operation is economically feasible only if the off-gas consisting primarily of hydrogen and a small amount, e.g., 500 ppmv, of carbon monoxide can be transferred to and used in another chemical process or if the off-gas can be purified to remove the carbon monoxide. Since purging all, or substantially all, of the hydrogen from the hydrogenation process frequently is not practical, the amount of gas which may be purged from the system to control carbon monoxide levels normally is up to about 10 volume percent of the amount of fresh hydrogen fed to the hydrogenation process.

Carbon monoxide formation can be suppressed by operating in a mode which provides a large amount of hydrogen to the catalyst surface. The mass transfer of hydrogen to the catalyst sites must be high enough to avoid having a lower dissolved hydrogen concentration than desired. A recycle stream of hydrogen may be used to increase the gas velocity through the catalyst bed to decrease the liquid hold-up in the reactor which decreases the liquid around the catalyst through which the hydrogen must diffuse. The gas hourly space velocity (GHSV) for the hydrogen normally should be at least 2 and preferably in the range of about 3 to 10. The particular hydrogen GHSV which will give satisfactory or optimal results can depend on other process parameters such as the feed rate of the liquid phase comprising the dimethyl cyclohexanedicarboxylate product and dimethyl benzenedicarboxylate reactant to



the hydrogenation zone and the temperatures and pressures employed and on the characteristics of the catalyst.

5 The rate of the exothermic hydrogenation process of
the present invention is moderated by feeding the
dimethyl benzenedicarboxylate reactant with the dimethyl
cyclohexanedicarboxylate product as an inert diluent.
The weight ratio of the dimethyl benzenedicarboxylate to
10 the dimethyl cyclohexanedicarboxylate may be in the
range of 1:50 to 1:5 although weight ratios of 1:20 to
1:10 are preferred. The dimethyl
cyclohexanedicarboxylate inert diluent may be provided
in the form of a recycle stream of the product effluent.
This recycle stream may be passed through a heat
15 exchanger to increase or, more commonly, decrease the
temperature of the stream to control the temperature of
the hydrogenation zone. In commercial operation, 80 to
95 weight percent of the product effluent may be
recycled to the hydrogenation zone after being combined
20 with fresh dimethyl benzenedicarboxylate reactant.

 The dimethyl benzenedicarboxylate reactant must be
fed to the hydrogenation zone at a rate which will
result in substantially complete conversion of the
reactant to the cyclohexanedicarboxylate product.
25 Incomplete conversion of the reactant may cause the
formation of hot spots within the catalyst bed and/or
runaway reactions. The liquid hourly space velocity
(LHSV) of the dimethyl benzenedicarboxylate reactant
feed to the hydrogenation zone typically is 0.3 to 5 and
30 preferably 0.5 to 2. The most suitable LHSV for the
reactant feed is dependent upon the particular
temperature and pressure used which, as mentioned
hereinabove, can depend upon the flow rate and/or purity
of the hydrogen.

The hydrogenation process of the present invention may be carried out over a temperature range of 150 to 230°C. Generally, higher temperatures favor carbon monoxide formation and therefore the use of temperatures in the upper part of the range require means for removing carbon monoxide from the hydrogenation zone, e.g., by purging all, or substantially all, of the hydrogen effluent of the process. We have demonstrated, for example, that when all other operating conditions are kept constant, decreasing the feed temperature to the primary hydrogenation reactor from 183°C to 174°C results in a decrease in (i) the DMT content of the product stream from conduit 34 and (ii) the carbon monoxide concentration in the hydrogen purge gas. When the off-gas purged from the process is 30 volume percent or less of the amount of fresh hydrogen fed, the process preferably is operated within a temperature range of 160 to 200°C.

The hydrogenation process may be performed within a pressure range of 10 to 205 bars absolute (1,000 to 20,500 kPa). At pressures below this range, the hydrogenation rate is low resulting in an unacceptable production rate whereas at pressures above 205 bars absolute (20,500 kPa), the benefits and advantages provided by our invention are much less significant. The hydrogenation preferably is carried out at a pressure in the range of 40 to 140 bars absolute (4,000 to 14,000 kPa). It also is preferred to maintain the concentration of carbon monoxide in the hydrogen gas removed from the hydrogenation zone at less than 100 parts per million by volume. Our improved process may be used to manufacture 1,2- 1,3- and 1,4- cyclohexanedicarboxylate ester by the hydrogenation of the corresponding benzenedicarboxylate ester isomers.

The 1,3- and, especially, the 1,4- isomers are the most important products of the process.

The precious metal catalysts useful in our novel process comprise supported palladium catalysts, especially palladium on alumina catalysts wherein palladium comprises 0.1 to 5.0 weight percent of the catalyst. The preferred palladium on alumina catalysts have the following characteristics:

- (1) palladium comprises 0.5 to 2.0 weight percent of the catalyst;
- (2) the palladium dispersion is at least 20 percent;
- (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 200 microns from the surface of the alumina; and
- (4) the crystalline phase of the alumina is alpha, theta, delta, gamma, eta or a mixture thereof.

The nitrogen BET surface area of the palladium on alumina catalysts used in the process of our invention is in the range of 20 to 300 square meters per gram (m^2/g) with the range of 30 to 150 m^2/g being preferred. It is well known in the art that BET surface area is a function of crystalline phases and calcination history and should be as high as possible while maintaining the appropriate oxide phase. Catalysts having the characteristics described hereinabove may be prepared according to conventional impregnation or deposition techniques using procedures well known to those skilled in the art. The catalyst may be used in the hydrogenation process in the form of pellets, spheres, extrudates and the like. The particular form is not critical so long as the catalyst form does not lead to excessive channeling of the liquid feed through the reactor, e.g., in continuous operation using a fixed bed of catalyst through which the reactant is passed.



Preferably, the surface area:volume ratio of the catalyst is at least 500 and preferably greater than 1500.

5 The accompanying Figure is a process flow diagram illustrating the principles of the process of the present invention. Those skilled in the art will recognize that the hydrogenation process may be operated by modifying the particular equipment depicted in the
10 Figure.

Referring to the Figure, reactor 10 is fed with a liquid mixture of dimethyl benzenedicarboxylate reactant and dimethyl cyclohexanedicarboxylate diluent by means of conduits 12 and 14 and hydrogen is supplied to
15 reactor 10 by conduits 16 and 18. Reactor 10 constitutes the primary hydrogenation zone of the process system depicted in the Figure and may be a generally columnar pressure vessel containing one or more fixed beds of a palladium on alumina hydrogenation
20 catalyst. A portion of the liquid product and hydrogen gas is removed from the base of vessel 10 by conduit 20, passed through heat exchanger 22 and recycled by means of conduits 24 and 14 to the top or upper portion of reactor 10. Heat exchanger 22 is used to increase or,
25 more typically, to decrease the temperature of the recycle stream and thus aid in the control of the temperature within the primary hydrogenation reactor including the temperature gradient over the length of the catalyst bed or beds contained therein.

30 The recycle stream of conduits 20, 24 and 14 provides all of the cyclohexanedicarboxylate diluent which is combined with dimethyl benzenedicarboxylate reactant fed via conduit 12 and fed to reactor 10. The recycle liquid typically constitutes 80 to 90 weight

percent of the total liquid effluent of reactor 10. The degree of conversion of the dimethyl benzenedicarboxylate reactant fed to reactor 10 usually is 92 to 99 mole percent, preferably 95 to 98 mole percent.

5 A second portion of the liquid product and hydrogen gas is removed from the base of vessel 10 by conduit 26, passed through heat exchanger 28 and fed by conduit 30 to the top or upper portion of reactor 32 wherein the overall conversion of the dimethyl benzenedicarboxylate reactant fed to hydrogenation process is increased to at least 99.9 mole percent. Reactor 32 constitutes the secondary hydrogenation zone of the process system depicted in the Figure and may be a generally columnar, pressure vessel containing one or more fixed beds of a
10 palladium on alumina hydrogenation catalyst. Dimethyl cyclohexanedicarboxylate product is removed from reactor 32 by means of conduit 34. The product normally has a purity of at least 99 mole percent.

15 The hydrogen gas effluent of reactor 32 is recycled by conduits 36 and 18 to reactor 10. Approximately 30 to 100 volume percent of this gas recycle stream is purged from the process through conduit 38 to aid in the maintenance of the carbon monoxide in the stream to less than 200 ppmv. To suppress the formation/accumulation
20 of carbon monoxide within the catalyst beds, the gas hourly space velocity of the hydrogen gas is in the range of 2 to 10. The volume ratio of recycle hydrogen supplied via conduit 36 to fresh hydrogen supplied via conduit 16 usually is in the range of about 0.1:1 to
25 1:1.

30 In a preferred embodiment of the present invention, the hydrogenation process is carried out using at least 2 hydrogenation zones: a primary zone and a secondary zone comprising a total of two or more reactors. A



5 mixture of fresh dimethyl benzenedicarboxylate reactant
and dimethyl cyclohexanedicarboxylate diluent is fed to
the primary hydrogenation zone along with a mixture of
fresh and recycled hydrogen. About 92 to 99, preferably
10 95 to 98, mole percent of the dimethyl benzenedicarbox-
ylate reactant is converted to dimethyl cyclohexanedi-
carboxylate product in the primary hydrogenation zone.
Approximately 80 to 95 weight percent of the liquid
effluent exiting the primary hydrogenation zone is
15 recycled and fed to the primary zone along with the
fresh dimethyl benzenedicarboxylate reactant.

The remainder of the liquid effluent (the portion
not recycled) and the off-gas from the primary
hydrogenation zone is fed to the secondary hydrogenation
15 zone wherein the overall conversion of the dimethyl
benzenedicarboxylate reactant to dimethyl cyclohex-
anedicarboxylate product is increased to at least 99.0,
preferably at least 99.9, mole percent. The vapor
effluent comprising hydrogen from the secondary
20 hydrogenation zone is recycled and fed to the primary
hydrogenation zone. Normally, a portion, e.g., 5 to 30
volume percent, of this recycle stream is purged from
the hydrogenation system to maintain the carbon monoxide
concentration in the recycle fed to the primary zone to
25 less than 200 ppmv.

The above-described preferred embodiment of our
invention therefore concerns a process for the
manufacture of a dimethyl cyclohexanedicarboxylate which
comprises the steps of:

- 30 I. continuously feeding hydrogen gas and a liquid
mixture of the dimethyl cyclohexanedicarboxylate
product and the corresponding dimethyl benzenedi-
carboxylate reactant to a primary hydrogenation
zone containing at least one fixed bed of a



palladium on alumina hydrogenation catalyst wherein the dimethyl benzenedicarboxylate is hydrogenated to the dimethyl cyclohexanedicarboxylate;

5 II. continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product and unreacted dimethyl benzenedicarboxylate from the primary hydrogenation zone;

10 III. continuously recycling 80 to 95 weight percent of the liquid product from II to the primary hydrogenation zone;

15 IV. continuously feeding the liquid product which is not recycled and the hydrogen gas from II to a secondary hydrogenation zone wherein unreacted dimethyl benzenedicarboxylate is hydrogenated to the dimethyl cyclohexanedicarboxylate;

20 V. continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product at a dimethyl benzenedicarboxylate conversion rate of at least 99 mole percent from the secondary hydrogenation zone;

25 VI. purging from 5 to 30 volume percent of the hydrogen gas from V from the hydrogenation process; and

VII. recycling the hydrogen gas from V which is not purged from the process to the primary hydrogenation zone;

30 wherein the hydrogenation is carried out at a pressure of 10 to 205 bars absolute (1,000 to 20,500 kPa) and a temperature of 150 to 230°C and the concentration of carbon monoxide in the hydrogen gas removed from the hydrogenation zone is maintained at less than 200, preferably less than 100, parts per million by volume (ppmv).



The process provided by our invention is further illustrated by the following experiments wherein amounts of materials are specified in parts by weight except for the amount of hydrogen which is specified in parts by volume. The continuous experiments were carried out using the process system depicted in the Figure. Primary hydrogenation reactor 10 contained 12 parts of a hydrogenation catalyst comprising 0.5% palladium on alumina and secondary hydrogenation reactor 32 contained 6 parts of the same hydrogenation catalyst.

EXAMPLE 1

A mixture of 10 weight percent dimethyl 1,4-benzenedicarboxylate (dimethyl terephthalate, DMT) and 90 weight percent dimethyl 1,4-cyclohexanedicarboxylate (DMCD) was fed to reactor 10 at a rate of 96 parts per hour and a temperature of 186°C. Hydrogen gas comprising approximately 33 volume percent fresh hydrogen supplied by conduit 12 and approximately 67 volume percent supplied by conduit 36 was fed to reactor 10 through conduit 14 at a rate of 0.9 parts per hour. The hydrogen feed rate represented a GHSV of about 6.8 based on the volume of catalyst in both reactors 10 and 32. About 90 weight percent of the liquid effluent of reactor 10 was recycled by conduits 20, 24 and 14. The pressure within reactors 10 and 32 was maintained at approximately 124 bars absolute (12,400 kPa) $\pm$ 1 bar (100 kPa).

The reactor 10 liquid and gas effluents not recycled were transported by conduit 26, heat exchanger 28 and conduit 30 and fed to secondary hydrogenation reactor 32 at a temperature of 194°C. DMCD containing less than about 0.2 weight percent DMT was removed from reactor 32 by conduit 34 at a rate of 9.9 parts per



hour. The hydrogen gas effluent of reactor 32 was recycled by conduits 36 and 18 to primary hydrogenation reactor 10. Hydrogen gas was purged from the process by conduit 38 at a rate of 0.03 parts per hour.

5 While the process system was operated at the production rates described above, the system was stable as evidenced by the fact that the temperature of the liquid fed and the liquid removed from reactor 10 remained substantially the same. When the feed of DMT
10 to reactor 10 was increased to 10.9 parts per hour, the temperature of the liquid removed from reactor 10 decreased, rather than increased, and continued to decrease with time, showing a decrease in reaction rate within reactor 10. This decreased reaction rate was
15 further established by an increase in the amount of DMT in the product and an increase of 13 weight percent of the DMT in the recycle stream of conduit 20. Upon reducing the DMT feed rate to 8.6 parts per hour, the system returned to normal as evidence by the DMT content
20 of the recycle liquid and product.

EXAMPLE 2

 The process was operated as described in Example 1 except that (i) the DMT feed rate to reactor 10 was 10.9
25 parts per hour and (ii) the hydrogen purge rate via conduit 38 was 0.3 parts per hour. Thus, hydrogen comprising 50 volume percent fresh hydrogen and 50 volume percent recycle hydrogen was fed to reactor 10 through conduit 18 at a rate of 1.2 parts per hour. The
30 use of these process parameters resulted in smooth, steady state operation of the process. The increase in the amount of the hydrogen gas purge permitted an increase in the rate of DMT addition without a decrease

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in reaction rate caused by the formation/accumulation of carbon monoxide in the catalyst bed.

5 The hydrogen purge rate then was decreased to approximately 0.15 parts per hour. The carbon monoxide concentration in the gas purged through conduit 38 increased from 74 ppmv to over 100 ppmv, showing that carbon monoxide is not in equilibrium and that higher
10 purge rates reduce the concentration of carbon monoxide which provides more stable operation.

EXAMPLE 3

15 The process was operated as described in Example 1 except that (i) the DMT feed rate to reactor 10 was 10.9 parts per hour and (ii) the hydrogen purge rate via conduit 38 was 0.3 parts per hour. Thus, hydrogen comprising 100 volume percent fresh hydrogen and 0 volume percent recycle hydrogen was fed to reactor 10 through conduit 18 at a rate of about 0.6 parts per
20 hour. The DMT content of the material transported by lines 20 and 26 was 6.5 weight percent. The velocity of the hydrogen gas within conduit 18 was increased resulting in an increase of the hydrogen feed rate to reactor 10 to 1.2 parts per hour. The DMT content of the liquid on lines 20 and 26 decreased to 2.9 weight
25 percent and the carbon monoxide content of the hydrogen gas purged via conduit 38 decreased from greater than 100 ppmv to 58 ppmv. This process modification demonstrates the advantages provided by increasing the flow rate of the hydrogen gas.

30 The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and

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modifications can be effected within the spirit and scope of the invention.



CLAIMS

We claim:

1. Continuous process for the manufacture of a dimethyl cyclohexanedicarboxylate which comprises the steps of:
 - (1) continuously feeding hydrogen gas and a liquid mixture of the dimethyl cyclohexanedicarboxylate product and the corresponding dimethyl benzenedicarboxylate reactant to a hydrogenation zone containing at least one fixed bed of a palladium on alumina hydrogenation catalyst; and
 - (2) continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product from the hydrogenation zone;
- wherein the dimethyl benzenedicarboxylate is hydrogenated to the dimethyl cyclohexanedicarboxylate at a pressure of 10 to 205 bars absolute (1,000 to 20,500 kPa) and a temperature of 150 to 230°C and the concentration of carbon monoxide in the hydrogen gas removed from the hydrogenation zone is maintained at less than 200 parts per million by volume (ppmv).
2. Process according to Claim 1 wherein the gas hourly space velocity of the hydrogen through the hydrogenation zone is at least 2.
3. Process according to Claim 1 wherein the gas hourly space velocity of the hydrogen through the hydrogenation zone is at least 2 and the weight ratio of the dimethyl benzenedicarboxylate to the dimethyl cyclohexanedicarboxylate is in the range of 1:20 to 1:10.

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4. Continuous process for the manufacture of a dimethyl cyclohexanedicarboxylate which comprises the steps of:

- 5 (1) continuously feeding hydrogen gas and a liquid mixture of the dimethyl cyclohexanedicarboxylate product and the corresponding dimethyl benzenedicarboxylate reactant to a hydrogenation zone containing at least one fixed bed of a palladium on alumina hydrogenation catalyst; and
- 10 (2) continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product from the hydrogenation zone;

wherein the dimethyl benzenedicarboxylate is hydrogenated at a conversion rate of at least 99 mole percent to the dimethyl cyclohexanedicarboxylate at a pressure of 10 to 205 bars absolute (1,000 to 20,500 kPa) and a temperature of 150 to 230°C, the concentration of carbon monoxide in the hydrogen gas removed from the hydrogenation zone is maintained at less than 100 parts per million by volume, the gas hourly space velocity of the hydrogen through the hydrogenation zone is 3 to 10, the weight ratio of the dimethyl benzenedicarboxylate to the dimethyl cyclohexanedicarboxylate is in the range of 1:20 to 1:10 and the liquid hourly space velocity of the dimethyl benzenedicarboxylate is 0.3 to 5.

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5. Process for the manufacture of a dimethyl cyclohexanedicarboxylate which comprises the steps of:

- 30 I. continuously feeding hydrogen gas and a liquid mixture of the dimethyl cyclohexanedicarboxylate product and the corresponding dimethyl benzenedicarboxylate reactant to a primary hydrogenation zone containing at least one fixed bed of a

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- palladium on alumina hydrogenation catalyst wherein the dimethyl benzenedicarboxylate is hydrogenated to the dimethyl cyclohexanedicarboxylate;
- 5 II. continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product and unreacted dimethyl benzenedicarboxylate from the primary hydrogenation zone;
- 10 III. continuously recycling 80 to 95 weight percent of the liquid product from II to the primary hydrogenation zone;
- 15 IV. continuously feeding the liquid product which is not recycled and the hydrogen gas from II to a secondary hydrogenation zone wherein unreacted dimethyl benzenedicarboxylate is hydrogenated to the dimethyl cyclohexanedicarboxylate;
- 20 V. continuously removing hydrogen gas and a liquid product comprising dimethyl cyclohexanedicarboxylate product having a purity of at least 99 mole percent from the secondary hydrogenation zone;
- 25 VI. purging from 5 to 30 volume percent of the hydrogen gas from V from the hydrogenation process; and
- 30 VII. recycling the hydrogen gas from V which is not purged from the process to the primary hydrogenation zone;
- wherein the hydrogenation is carried out at a pressure of 10 to 205 bars absolute (1,000 to 20,500 kPa) and a temperature of 150 to 270°C and the concentration of carbon monoxide in the hydrogen gas removed from the hydrogenation zone is maintained at less than 200 parts per million by volume (ppmv).

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