



The present invention relates to a process for the manufacture of carboxylic acids by oxidation of an alkyl hydroperoxide compound.

- 5 It relates more particularly to the oxidation of cyclohexyl hydroperoxide to adipic acid by an oxidizing agent comprising molecular oxygen.

10 The manufacture of adipic acid by oxidation of cyclohexane is a process which has been studied for many years. This is because adipic acid is an important chemical compound used as starting material in many manufacturing operations, such as the production of polymers, for example polyamides, polyesters or  
15 polyurethanes.

Several processes for the manufacture of adipic acid from hydrocarbons, such as benzene, phenol, cyclohexene or cyclohexane, have been provided.  
20

The oxidation of cyclohexane, either directly or in two stages, are the most widely studied routes for producing adipic acid.

- 25 Thus, by way of illustration of the processes for the direct oxidation of hydrocarbons to dicarboxylic acids, United States Patent 2 223 493, published in December 1940, discloses the oxidation of cyclic hydrocarbons to the corresponding diacids, in a liquid phase generally  
30 comprising acetic acid, at a temperature of at least 60°C, using a gas comprising oxygen and in the presence of an oxidation catalyst, such as a cobalt compound.

35 Numerous other patents and articles disclose this reaction for the direct oxidation of cyclohexane to adipic acid. However, to obtain acceptable yields for the production of adipic acid, these documents disclose the use of acetic acid as solvent in the presence either of a homogeneous catalyst or of a heterogeneous



catalyst. Mention may be made, by way of illustration, of the article which appeared in the journal "Chemtech", 555-559 (September 1974), the author of which is K. Tanaka, which summarizes and comments upon the process for the direct oxidation of cyclohexane. Mention may also be made of United States Patents 3 231 608, 4 032 569, 4 158 73, 4 263 453 and 5 321 157 and European Patent 870 751, which disclose various homogeneous catalytic systems.

Provision has also been made for processes for the direct oxidation of cyclohexane in the presence of a heterogeneous catalyst, such as aluminophosphates substituted by cobalt, as in European Patent No. 519 569.

Provision has also been made for several processes for the oxidation in a single stage of cyclohexane to adipic acid without use of acetic acid. Some make provision for carrying out this reaction in the absence of solvents, others with solvents, such as organic esters, for example acetates (US 4 098 817), acetone (US 2 589 648) or alternatively alcohols, such as butanol, methanol or cyclohexanol, or acetonitrile (EP 784 045). Finally, Patent Application WO 01/66502 has provided a process for the direct oxidation of hydrocarbons to dicarboxylic acids in the presence of a carboxylic acid with a lipophilic nature as solvent. This solvent makes it possible to overcome the disadvantages exhibited by adipic acid.

These processes generally result in very low selectivities for adipic acid. Furthermore, the solvents used often exhibit low stability under the conditions for the oxidation of a hydrocarbon, such as cyclohexane. This low stability results in a high consumption of the solvent, which makes it difficult to exploit such processes industrially.

Manufacturing processes for the oxidation of hydrocarbons to dicarboxylic acids by two successive oxidation stages are used industrially on a large scale. These processes consist, in a first stage, in carrying out the oxidation of hydrocarbons to alcohols and ketones with oxygen or a gas comprising oxygen. In a second stage, the alcohols and/or ketones are oxidized to acids by oxidation with nitric acid. Various embodiments of these two stages are made use of. Thus, the first stage can comprise two substages; in a first substage, the hydrocarbon is oxidized to hydroperoxide. After separation of the hydroperoxide from the unreacted hydrocarbon, the hydroperoxide is decomposed in a separate reactor to alcohol and/or ketone. In another embodiment also made use of, the production of hydroperoxide and its decomposition to alcohol and/or ketone are carried out simultaneously in a single reactor.

Currently, the oxidation of alcohols and/or ketones is carried out with nitric acid. Such a reaction produces nitrous and nitric oxides as main effluent, requiring the presence of a treatment process for these oxides to reduce the effect on the environment. This treatment of the effluents has a damaging effect economically on the two-stage oxidation processes.

One of the aims of the present invention is to provide a process for the oxidation of hydrocarbons to produce acids or polyacids which does not require the use as oxidation agent of nitric acid or one of its derivatives and thus which does not produce nitrogen oxide discharges.

To this end, the invention provides a process for the manufacture of carboxylic acids, characterized in that it consists in reacting a hydroperoxide of hydrocarbons with oxygen or a gas comprising oxygen in the presence

of an oxidation catalyst comprising a metal belonging to the transition metal groups.

The catalyst can advantageously comprise a metal  
5 element chosen from the group consisting of Cu, Ag, Au, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Al, Sc, In, Tl, Y, Ga, Ti, Zr, Hf, Ge, Sn, Pb, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, the lanthanides, such as Ce, and the combinations of these.

10 These catalytic elements are employed either in the form of compounds advantageously at least partially soluble in the liquid oxidation medium under the conditions of implementation of the oxidation reaction  
15 or supported on, absorbed on or bonded to an inert support, such as silica or alumina, for example.

In the case of heterogeneous catalysis, the catalytically active metal elements are supported on or  
20 incorporated in a micro- or mesoporous inorganic matrix or in a polymeric matrix or are in the form of organometallic complexes grafted to an organic or inorganic support. The term "incorporated" is understood to mean that the metal is an element of the  
25 support or that the operation is carried out with complexes sterically trapped in porous structures under the conditions of the oxidation.

In a preferred embodiment of the invention, the  
30 homogeneous or heterogeneous catalyst is composed of salts or of complexes of metals from Groups IVb (Ti group), Vb (V group), VIb (Cr group), VIIb (Mn group), VIII (Fe or Co or Ni group) and Ib (Cu group), and cerium, alone or as mixtures. The preferred  
35 elements are in particular Co and/or Mn and/or Cr and/or Zr, Hf, Ce and/or Zr, Hf. The concentration of metal in the liquid oxidation medium varies between 0.00001 and 5% (weight%), preferably between 0.0001% and 2%.

According to the invention, the hydroperoxides which are employed in the process of the invention are generally primary or secondary hydroperoxides deriving  
5 from alkanes, cycloalkanes, alkylaromatic hydrocarbons, the aromatic ring of which optionally comprises one or more substituents, such as, in particular, an alkyl group or halogen atom, more particularly chlorine atom, alkenes and cycloalkenes having from 3 to 20 carbon  
10 atoms.

Mention may be made, by way of examples of such hydroperoxides, of cyclohexyl hydroperoxide, cyclododecyl hydroperoxide, tetralin hydroperoxide,  
15 ethylbenzene hydroperoxide or pinane hydroperoxide.

Among these hydroperoxides, one of the most advantageous is very certainly cyclohexyl hydroperoxide, the oxidation of which results in adipic  
20 acid as main dicarboxylic acid, one of the base compounds for the manufacture of polyamides, more particularly of poly(hexamethylene adipate).

These hydroperoxides can be obtained by various  
25 processes and can be used in the process of the invention in the purified form or as a mixture with other compounds originating in particular from their manufacturing processes.

30 The process of the invention can be carried out preferably in the presence of a solvent advantageously composed of the hydrocarbon used for the manufacture of the hydroperoxide. However, recourse may be had to various solvents, such as alkanes, among which will  
35 more particularly be mentioned hexane, heptane and isooctane, cycloalkanes, among which will be mentioned, by way of illustration, cyclohexane and cyclooctane, aromatic hydrocarbons, such as benzene, toluene and xylene, halogenated hydrocarbons, alcohols, ketones,

ethers, nitriles, carboxylic acids, such as acetic acid, and mixtures of these solvents.

5 However, it should be noted that, as the hydroperoxide is generally produced in the form of a solution in a hydrocarbon, for example cyclohexane, by oxidation of the latter, the oxidation reaction is advantageously carried out on a solution originating from the oxidation of the hydrocarbon (cyclohexane). This  
10 solution can be used as it is or after removing certain constituents in a way known per se. It is also possible to use a solution of hydroperoxide in the solvent, for example cyclohexane, which is substantially pure.

15 Thus, the process of the invention can be carried out on a solution originating from the oxidation of a hydrocarbon to hydroperoxide, as is or after removal of certain by-products by, for example, washing the solution with water to remove in particular water-  
20 soluble acids, or on the hydroperoxide purified by conventional purification processes, such as distillation, extraction or any other conventional method.

25 The oxidation reaction is carried out at a temperature of between 50°C and 250°C, preferably between 70°C and 200°C. It can be carried out at atmospheric pressure. However, it is generally carried out under pressure in order to keep the components of the reaction medium in  
30 the liquid form. The pressure can be between 10 kPa (0.1 bar) and 20 000 kPa (200 bar), preferably between 100 kPa (1 bar) and 10 000 kPa (100 bar).

The oxygen used can be in the pure form or as a mixture  
35 with an inert gas, such as nitrogen or helium. Use may also be made of air enriched to a greater or lesser extent with oxygen.

The oxidation process can be carried out continuously or according to a batchwise process. Advantageously, the liquid reaction medium which has left the reactor is treated according to known processes which make it possible, on the one hand, to separate and recover the acids produced and, on the other hand, to recycle the nonoxidized or partially oxidized organic compounds, such as cyclohexane, cyclohexanol and/or cyclohexanone, the catalyst and optionally the solvent.

The amount of catalyst, expressed as percentage by weight of metal with respect to the reaction mixture, generally lies between 0.00001% and 5% and preferably between 0.0001% and 2%, without these values being critical. However, it is a matter of having a sufficient activity while not using excessively large amounts of a catalyst which subsequently has to be separated from the final reaction mixture and recycled.

It can be advantageous also to employ a compound which initiates the oxidation reaction, such as, for example, a ketone, an aldehyde or a hydroperoxide. Cyclohexanone, which is a reaction intermediate in the case of the oxidation of cyclohexane, is very particularly indicated. Generally, the initiator represents from 0.01% to 20% by weight of the weight of the reaction mixture employed, without these proportions having a critical value. The initiator is of use in particular during the start of the oxidation and when the oxidation is carried out at a temperature of less than 120°C. It can be introduced from the beginning of the reaction.

It is also possible, without thereby departing from the scope of the invention, to add, to the reaction medium, another compound which can have in particular the effect of improving the productive output and/or the selectivity of the oxidation reaction for adipic acid,

such as, for example, improving the dissolution of the oxygen.

Mention may in particular be made, as examples of such  
5 compounds, of nitriles, carboxylic acids, more particularly lipophilic acids, halogenated compounds, more advantageously fluorinated compounds, and precursors of these compounds. Mention may be made, as  
10 compounds which are more particularly suitable, of nitriles, such as acetonitrile or benzonitrile, halogenated derivatives, such as dichloromethane, or fluorinated compounds, such as:

- cyclic or acyclic fluorinated or perfluorinated aliphatic hydrocarbons or fluorinated aromatic  
15 hydrocarbons, such as perfluorotoluene, perfluoromethylcyclohexane, perfluorohexane, perfluoroheptane, perfluorooctane, perfluorononane, perfluorodecalin, perfluoromethyldecalin,  $\alpha,\alpha,\alpha$ -trifluorotoluene or 1,3-bis(tri-  
20 fluoromethyl)benzene
- perfluorinated or fluorinated esters, such as perfluoro(alkyl octanoate)s or perfluoro(alkyl nonanoate)s
- fluorinated or perfluorinated ketones, such as  
25 perfluoroacetone
- fluorinated or perfluorinated alcohols, such as perfluorohexanol, perfluorooctanol, perfluorononanol, perfluorodecanol, perfluoro-t-butanol, perfluoroisopropanol or 1,1,1,3,3,3-hexafluoro-  
30 2-propanol
- fluorinated or perfluorinated nitriles, such as perfluoroacetonitrile
- fluorinated or perfluorinated acids, such as trifluoromethylbenzoic acids, pentafluorobenzoic  
35 acid, perfluorohexanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid or perfluoroadipic acid
- fluorinated or perfluorinated halides, such as perfluoroiodooctane or perfluorobromooctane

- fluorinated or perfluorinated amines, such as perfluorotripropylamine, perfluorotributylamine or perfluorotripentylamine
- carboxylic acids, such as valeric acid, glutaric acid, succinic acid, aminocaproic acid derivatives, or acids with a lipophilic nature, such as the tert-butyl of benzoic acid.

Mention may be made, as lipophilic carboxylic acids suitable for the invention, of hexanoic acid, heptanoic acid, octanoic acid, 2-ethylhexanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid or stearic (octadecanoic) acid and their permethylated derivatives (complete substitution of the hydrogens of the methylene groups by the methyl group), 2-octadecylsuccinic acid, 2,5-di(tert-butyl)benzoic acid, 4-(tert-butyl)benzoic acid, 4-octylbenzoic acid, tert-butyl hydrogen orthophthalate, naphthenic or anthracenic acids substituted by alkyl groups, preferably of tert-butyl type, substituted derivatives of phthalic acids, or fatty diacids, such as fatty acid dimer. Mention may also be made of acids belonging to the preceding families carrying various electron-donating substituents (groups with heteroatom of the O or N type) or electron-withdrawing substituents (halogens, sulphonamides, nitro or sulphonanato groups, or the like).

It can also be carried out in the presence of water introduced from the initial stage of the process or by controlling the amount of water in the reaction medium, either by addition or removal.

As indicated above, the reaction mixture resulting from the oxidation is subjected to various operations for separating some of its constituents in order, for example, to make possible their recycling in the oxidation and the recovery of the acids produced.

According to a first alternative form of the process, the crude reaction mixture can first of all be subjected to cooling to a temperature of 16°C to 30°C, for example, which brings about the crystallization of  
5 at least a portion of the acid formed. A medium comprising a solid phase composed essentially of acids, at least one liquid organic phase, comprising essentially the unreacted compound to be oxidized, possibly the solvent and the oxidation intermediates or  
10 other products resulting from the oxidation, and a liquid aqueous phase, comprising essentially acidic by-products from the oxidation and the water formed, is this obtained. The catalyst may be found in one of the organic phases, if it is soluble in the said phase, or  
15 in the lower aqueous phase.

After filtering off or centrifuging the solid, the liquid organic and aqueous phases constituting the filtrate or the centrifugate are separated by settling,  
20 if this occurs: the organic phase or phases can be recycled in a new oxidation reaction.

It can be advantageous to concentrate the reaction mixture prior to the operation for crystallization of  
25 the acid.

According to a second alternative form of the process, the final crude reaction mixture can be withdrawn under hot conditions, for example at a temperature which can  
30 reach 75°C. The reaction mixture then separates by settling into at least two liquid phases: one or more organic phases, comprising essentially the unreacted hydrocarbon, the solvent and the oxidation intermediates, and a liquid aqueous phase, comprising  
35 essentially the acids formed and the water formed. Depending on the solubility and the nature of the catalyst, the latter can be present in the organic phase or phases, recovered by solid/liquid separation before precipitation or crystallization of the acid

formed in the case of a heterogeneous catalysis or, if it is soluble in the aqueous phase, extracted by liquid/liquid extraction, through a resin or electro-dialysis.

5

As in the first alternative form, the liquid phases are separated: the organic phase or phases can be recycled in a new oxidation reaction.

10 In these implementational examples of the invention, water can be added to the reaction medium to obtain better dissolution of the acidic by-products from the oxidation and better recovery of the acid formed.

15 The acid is generally recovered by precipitation during the cooling of the reaction medium. The acid thus recovered can be purified according to the standard techniques disclosed in numerous patents. Mention may be made, by way of example, of French patents  
20 Nos. 2 749 299 and 2 749 300.

If the liquid nonorganic or aqueous phase comprises the catalyst, the latter is extracted either before the crystallization of the acid formed, by precipitation or  
25 extraction according to known processes, such as liquid-liquid extraction, electrodialysis or treatment through ion-exchange resins, for example, or after crystallization of the acid formed, by extraction techniques described above or the like.

30

Another subject-matter of the invention is a process for the manufacture of carboxylic acid which consists, in a first stage, in oxidizing a hydrocarbon to hydroperoxide with oxygen or a gas comprising oxygen.

35 The medium obtained, after optionally concentrating by evaporating a portion of the unreacted hydrocarbon, is subjected to a second stage of oxidation of the hydroperoxide to carboxylic acids in accordance with the process of the invention described above.

According to preferred embodiments of the invention, the reaction medium resulting from the first oxidation stage is subjected to various treatments for separating  
5 and removing by-products in order to purify the hydroperoxide. These treatments can comprise washing the oxidation medium with water or a slightly basic solution.

10 Other advantages and details of the invention will become more clearly apparent in the light of the examples given below solely by way of indication and illustration.

15 **Example 1**

2.9 mg of Mn(III) acetylacetonate and 4.51 g of a purified solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the  
20 following composition, expressed as % by weight:

|                          |        |
|--------------------------|--------|
| Cyclohexyl hydroperoxide | 10.59% |
| Cyclohexanone            | 2.06%  |

are charged to a 30 ml autoclave made of Hastelloy C22.

25 The autoclave is immediately pressurized to 100 bar of air at ambient temperature and placed in an oven. The mixture is heated to 130°C with stirring by shaking.

After reacting for 180 minutes, the autoclave is cooled  
30 and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

The following results are obtained:

DC (cyclohexyl hydroperoxide) = 95%  
35 DC (cyclohexane) = 2.4%  
Adipic acid: 42 mg

The term "DC" is understood to mean the degree of conversion of the product, calculated by the ratio of

the difference between the number of starting molecules and the number of final molecules with respect to the number of starting molecules.

## 5 **Example 2**

9.4 mg of Mn(III) acetylacetonate and 4.51 g of a solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

- cyclohexyl hydroperoxide (CHHPO) 10.76%
- cyclohexanol/cyclohexanone 2.58%
- cyclohexane 85.61%
- 15 - carboxylic acids 0.13%

are charged to a 30 ml autoclave made of Hastelloy C22.

The autoclave is immediately pressurized to 100 bar of air at ambient temperature and placed in an oven. The mixture is heated to 130°C with stirring by shaking.

After reacting for 180 minutes, the autoclave is cooled and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

25

The following results were obtained:

DC (cyclohexyl hydroperoxide) = 99.8%

DC (cyclohexane) = 0.02%

Adipic acid: 489 mg

30

## **Example 3**

7.6 mg of  $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$  and 4.56 g of a solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

- cyclohexyl hydroperoxide (CHHPO) 10.93%
- cyclohexanol/cyclohexanone 2.29%
- cyclohexane 85.67%

- carboxylic acids 0.19%

are charged to a 30 ml autoclave made of Hastelloy C22.

5 The autoclave is immediately pressurized to 100 bar of  
air at ambient temperature and placed in an oven. The  
mixture is heated to 130°C with stirring by shaking.

After reacting for 180 minutes, the autoclave is cooled  
and then degassed. The reaction mass collected is  
10 analysed by gas chromatography (GC).

The following results were obtained:

DC (cyclohexyl hydroperoxide) = 86.8%

DC (cyclohexane) = 0%

15 Adipic acid: 105 mg

#### **Example 4**

0.4 mg of cobalt(II) chloride tetrahydrate and 4.50 g  
20 of a solution of cyclohexyl hydroperoxide originating  
from the oxidation of cyclohexane, with the following  
composition, expressed as % by weight, for the main  
components:

|    |                                    |        |
|----|------------------------------------|--------|
|    | - cyclohexyl hydroperoxide (CHHPO) | 10.93% |
| 25 | - cyclohexanol/cyclohexanone       | 2.29%  |
|    | - cyclohexane                      | 85.67% |
|    | - carboxylic acids                 | 0.19%  |

are charged to a 30 ml autoclave made of Hastelloy C22.

30 The autoclave is immediately pressurized to 100 bar of  
air at ambient temperature and placed in an oven. The  
mixture is heated to 130°C with stirring by shaking.

After reacting for 180 minutes, the autoclave is cooled  
35 and then degassed. The reaction mass collected is  
analysed by gas chromatography (GC).

The following results were obtained:

DC (cyclohexyl hydroperoxide) = 93.3%

DC (cyclohexane) = 1.3%

Adipic acid: 98 mg

### Example 5

5

3 mg of Mn(III) acetylacetonate, 142 mg of valeric acid and 4.57 g of a solution, washed with water, of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

- cyclohexyl hydroperoxide (CHHPO) 9.85%
- cyclohexanol/cyclohexanone 5.35%
- cyclohexane 84.80%

are charged to a 30 ml autoclave made of Hastelloy C22.

15

The autoclave is immediately pressurized to 100 bar of air at ambient temperature and placed in an oven. The mixture is heated to 130°C with stirring by shaking.

20 After reacting for 180 minutes, the autoclave is cooled and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

The following results were obtained:

25 DC (cyclohexyl hydroperoxide) = 93.5%  
DC (cyclohexane) = 0.6%  
Adipic acid: 527 mg

### Example 6

30

3 mg of Mn(III) acetylacetonate, 455 mg of para-(tert-butyl)benzoic acid and 4.5 g of a solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

- cyclohexyl hydroperoxide (CHHPO) 10.76%
- cyclohexanol/cyclohexanone 2.58%
- cyclohexane 85.61%
- carboxylic acids 0.13%

are charged to a 30 ml autoclave made of Hastelloy C22.

The autoclave is immediately pressurized to 100 bar of air at ambient temperature and placed in an oven. The mixture is heated to 130°C with stirring by shaking.

After reacting for 180 minutes, the autoclave is cooled and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

10

The following results were obtained:

DC (cyclohexyl hydroperoxide) = 95.4%

DC (cyclohexane) = 3.2%

Adipic acid: 540 mg

15

#### **Example 7**

32 mg of Mn(III) acetylacetonate and 41.4 g of a solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

- |    |                                    |        |
|----|------------------------------------|--------|
|    | - cyclohexyl hydroperoxide (CHHPO) | 10.76% |
|    | - cyclohexanol/cyclohexanone       | 2.58%  |
| 25 | - cyclohexane                      | 85.61% |
|    | - carboxylic acids                 | 0.13%  |

are charged to a 180 ml autoclave made of titanium.

The autoclave is immediately pressurized to 75 bar of air at ambient temperature. The reactor is subsequently heated to 130°C and is then connected to an oxygen supply which provides, during the time of the reaction, an oxygen partial pressure of 20 bar for a total pressure of the autoclave of 100 bar. The unit is stirred at 1 000 revolutions per minute throughout the duration of the reaction.

After reacting for 80 minutes, the autoclave is cooled and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

5 The following results were obtained:

DC (cyclohexyl hydroperoxide) = 99.9%

DC (cyclohexane) = 6.2%

Adipic acid: 7.34 g

10 After cooling the solution and filtering, a white solid comprising predominantly adipic acid is obtained. The productive output associated with this test is of the order of 100 grams of adipic acid produced per litre of reaction medium and per hour.

15

#### **Example 8**

73 mg of Mn(III) acetylacetonate and 42.6 g of a solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

|    |                                     |        |
|----|-------------------------------------|--------|
|    | - cyclohexyl hydroperoxide (CHHPPO) | 10.76% |
|    | - cyclohexanol/cyclohexanone        | 2.58%  |
| 25 | - cyclohexane                       | 85.61% |
|    | - carboxylic acids                  | 0.13%  |

are charged to a 180 ml autoclave made of titanium.

30 The autoclave is immediately pressurized to 75 bar of air at ambient temperature. The reactor is subsequently heated to 130°C and is then connected to an oxygen supply which provides, during the time of the reaction, an oxygen partial pressure of 20 bar for a total pressure of the autoclave of 100 bar. The unit is stirred at 1 000 revolutions per minute throughout the duration of the reaction.

35

After reacting for 55 minutes, the autoclave is cooled and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

5 The following results were obtained:

DC (cyclohexyl hydroperoxide) = 100%

DC (cyclohexane) = 6.3%

Adipic acid: 7.32 g

10 After cooling the solution and filtering, a white solid comprising predominantly adipic acid is obtained. The productive output associated with this test is of the order of 130 grams of adipic acid produced per litre of reaction medium and per hour.

15

#### **Example 9**

10 mg of Mn(II) acetate (54 ppm by weight), 4.5 mg of Co(II) acetate (26 ppm by weight) and 41.7 g of a solution of cyclohexyl hydroperoxide originating from the oxidation of cyclohexane, with the following composition, expressed as % by weight, for the main components:

|    |                                     |       |
|----|-------------------------------------|-------|
|    | - cyclohexyl hydroperoxide (CHHPPO) | 7.2%  |
| 25 | - 6-hydroxyhexanoic acid            | 0.5%  |
|    | - cyclohexanol/cyclohexanone        | 8.0%  |
|    | - cyclohexane                       | 84.1% |
|    | - carboxylic acids                  | 0.2%  |

are charged to a 180 ml autoclave made of titanium.

30

The autoclave is immediately pressurized to 75 bar of air at ambient temperature. The reactor is subsequently heated to 130°C and is then connected to an oxygen supply which provides, during the time of the reaction, an oxygen partial pressure of 20 bar for a total pressure of the autoclave of 100 bar. The unit is stirred at 1 000 revolutions per minute throughout the duration of the reaction.

After reacting for 55 minutes, the autoclave is cooled and then degassed. The reaction mass collected is analysed by gas chromatography (GC).

5 The following results were obtained:

DC (cyclohexane) = 8.5%

Adipic acid: 3.94 g

CLAIMS

1. Process for the manufacture of carboxylic acids, characterized in that it consists in reacting an  
5 organic hydroperoxide with an oxidizing agent comprising molecular oxygen and in the presence of an oxidation catalyst.

2. Process according to Claim 1, characterized in  
10 that the organic hydroperoxide is chosen from the group consisting of primary or secondary hydroperoxides deriving from alkanes, cycloalkanes, alkylaromatic hydrocarbons, the aromatic ring of which optionally comprises one or more substituents, such as, in  
15 particular, an alkyl group or halogen atom, more particularly chlorine atom, alkenes and cycloalkenes having from 3 to 20 carbon atoms.

3. Process according to either of Claims 1 and 2,  
20 characterized in that the organic hydroperoxide is chosen from the group consisting of cyclohexyl hydroperoxide, cyclododecyl hydroperoxide, tetralin hydroperoxide, ethylbenzene hydroperoxide and pinane hydroperoxide.

25 4. Process according to one of the preceding claims, characterized in that the hydroperoxide to be oxidized is obtained by oxidation of a hydrocarbon by an oxidizing agent comprising molecular oxygen.

30 5. Process according to Claim 4, characterized in that the reaction medium resulting from the oxidation of a hydrocarbon to hydroperoxide is used as product reacted with the oxidizing agent.

35 6. Process according to Claim 5, characterized in that the reaction medium resulting from the oxidation of a hydrocarbon is washed with water before being reacted with an oxidizing agent.

7. Process according to Claim 5 or 6, characterized in that the reaction medium resulting from the oxidation of a hydrocarbon is treated to remove the by-products of the oxidation other than the hydroperoxide.

8. Process according to one of the preceding claims, characterized in that the catalyst is soluble in the liquid medium under the conditions of implementation of the oxidation reaction.

9. Process according to Claim 8, characterized in that the catalyst is insoluble in the liquid medium under the conditions of implementation of the oxidation reaction.

10. Process according to Claim 9, characterized in that the catalyst is a supported catalyst comprising an inorganic or polymeric support.

11. Process according to one of the preceding claims, characterized in that the oxidation reaction is carried out in the presence of a solvent.

12. Process according to Claim 11, characterized in that the solvent is chosen from the group consisting of alkanes, cycloalkanes, aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ketones, ethers and the mixtures of these solvents.

13. Process according to Claim 12, characterized in that the solvent is chosen from the group consisting of hexane, heptane, isooctane, cyclohexane, cyclooctane, benzene, toluene and xylene.

14. Process according to Claim 11, characterized in that the solvent is the hydrocarbon corresponding to the hydroperoxide to be oxidized.

15. Process according to one of the preceding claims, characterized in that the liquid medium, after oxidation, is separated by settling into at least one organic phase, formed by the nonoxidized hydroperoxide and the solvent, and an aqueous or solid phase, the said organic phases being recycled in a new oxidation and the acid produced being extracted from the aqueous phase.
16. Process according to Claim 15, characterized in that the acid is extracted from the aqueous phase by crystallization.
17. Process according to one of the preceding claims, characterized in that the catalyst is recycled with the organic phase or phases.
18. Process according to one of the preceding claims, characterized in that the catalyst is separated from the liquid medium by separation by settling or solid/liquid separation.
19. Process according to either of Claims 13 and 14, characterized in that the catalyst soluble in the aqueous phase is extracted by liquid/liquid extraction, separation through resins or by electrodialysis.
20. Process according to one of the preceding claims, characterized in that the catalyst comprises manganese as catalytically active element.
21. Process for the manufacture of carboxylic acids from hydrocarbons, characterized in that it comprises
- a first stage of oxidation of the hydrocarbons to hydroperoxides by oxygen or a gas comprising oxygen,
  - a second stage of concentration of hydroperoxide in the reaction medium by extraction of at least a portion of the nonoxidized hydrocarbons,

- a third stage of oxidation of hydroperoxides to carboxylic acids according to one of the preceding claims.

- 5 22. Process according to Claim 21, characterized in that the oxidation medium obtained after the second stage is subjected to a treatment to extract by-products other than the hydroperoxides.