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Multistage process for the preparation of oxo aldehydes
and/or alcohols

The present invention relates to a process for the
5 preparation of aldehydes having 7 to 25 carbon atoms by
multistage cobalt- or rhodium-catalyzed hydroform-
ylation of the corresponding olefins.

Prior art

10 As will be known, higher aldehydes, in particular those
having 7 to 25 carbon atoms, can be prepared by
catalytic hydroformylation (referred to usually in
industry as oxo process) of the olefins which have one
fewer carbon atom. The aldehydes are used, for example,
15 as synthesis precursors for the production of
carboxylic acids and as fragrances. In industry they
are often converted into the corresponding alcohols by
catalytic hydrogenation, such alcohols being used inter
alia as intermediates for the preparation of
20 plasticizers and detergents.

A large number of processes for the hydroformylation of
olefins are described in the literature. The choice of
catalyst system and optimal reaction conditions for the
25 hydroformylation are dependent on the reactivity of the
olefin used. The effect of the structure of the olefin
used on its reactivity in the hydroformylation is
described, for example, by J. FALBE, "New Syntheses
with Carbon Monoxide", Springer Verlag, 1980, Berlin,
30 Heidelberg, New York, pages 95 et seq.

As a general rule, the rate of hydroformylation
reactions under constant general conditions decreases
with increasing carbon number and with increasing
35 degree of branching of the olefin. Thus, the reaction
rate of linear olefins can exceed that of the branched
isomers by more than a factor of ten. In addition, the
position of the double bond in the olefin has a

decisive influence on the reactivity. Olefins with a terminal double bond react markedly more quickly than isomers with the double bond inside the molecule. The varying reactivity of isomeric octenes has been investigated, for example, by B.L. HAYMORE, A. van HASSELT, R. BECK, *Annals of the New York Acad. Sci.*, 1983, 415, 159-175. A general overview and further literature are given by B. CORNILS, W.A. HERRMANN, "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1&2, VCH, Weinheim, New York, 1996.

Industrial olefin mixtures which are used as starting materials for the hydroformylation synthesis often contain olefin isomers of very different structures having differing degrees of branching and different double bond positions, and olefins of varying molar masses. This is true in particular of olefin mixtures produced by di-, tri- or continuing oligomerization of olefins having 2 to 8 carbon atoms or other readily accessible higher olefins, or by cooligomerization of said olefins. Possible examples of typical olefin mixtures which are relevant industrially for the hydroformylation are tri- and tetrapropene, and di-, tri- and tetrabutenes.

In the case of a hydroformylation carried out industrially, it is desired to achieve, in addition to a high conversion, a high selectivity in order to ensure optimal utilization of the raw material. To achieve a high conversion, in the case of olefins which react slowly, a relatively long reaction time and/or relatively high reaction temperatures must often be accepted. By contrast, more reactive olefins are converted to the aldehydes under the same reaction conditions in a much shorter time. If mixtures of olefins of varying reactivity are hydroformylated together, this leads to the need for relatively long

reaction times in order to achieve adequate conversion also of the olefins which are more difficult to oxidize. However, the aldehydes produced from olefins which can be more readily converted are formed relatively quickly and are then present in the reactor alongside the olefins which are more difficult to hydroformylate. This leads to undesired secondary and consecutive reactions of the aldehydes, e.g. to hydrogenation, to condensation reactions and to the formation of acetals and hemiacetals. Primarily because of the varying reactivity of the olefin isomers, it is therefore difficult to achieve high conversions and also high selectivities during the hydroformylation.

As well as the disadvantageous effect on the selectivity, there are two further aspects which oppose a joint hydroformylation of olefin mixtures in one stage to high conversions. Firstly, the relatively long reaction times for a pregiven capacity (or reactor performance) require relatively large reactor volumes. This is disadvantageous particularly since hydroformylation processes are processes which proceed at increased pressure, and the investment costs for pressurized reactors increase exponentially with size. Secondly, control of the product properties of the aldehydes is limited, e.g. determined by the n/i ratio.

Processes for the two-stage hydroformylation of olefins are known. EP 562 451 and EP 0 646 563 describe the hydroformylation of mixtures comprising 1- and 2-butene where, in the first stage, the 1-butene is reacted in a heterogeneous reaction, i.e. in a multiphase system, optionally with the addition of a phase transfer reagent or solubility promoter and, in the second stage, a homogeneously dissolved catalyst is used. According to EP 0 562 451, rhodium catalysts are used in both stages, while according to EP 0 646 563, rhodium catalysts are used in the first stage and

cobalt catalysts are used in the second stage. According to EP 0 562 451, the olefin which is unreacted in the first stage, largely 2-butene, is hydroformylated in a second stage in homogeneous phase and in the presence of rhodium as catalyst. In EP 0 646 563 this procedure is specified inasmuch as the unreacted olefin in the first stage leaves the reactor in gaseous form, together with carbon monoxide, hydrogen and butane produced by hydrogenation. This gas, optionally at compression, is passed to the second hydroformylation stage. The procedure according to these two publications cannot advantageously be used for the hydroformylation of higher olefins, i.e. having more than 5 carbon atoms, because the unreacted olefins can no longer be discharged in gaseous form from the first stage with viable expenditure because of their relatively high boiling points.

GB 1 387 657 describes a two-stage hydroformylation in which the reaction product from the first stage is discharged in gaseous form and, after the aldehydes or alcohols have been condensed out, some of the offgas from the first stage, which comprises unreacted olefins, is returned to the first stage, and the remainder is passed to the second reactor. This process concept is suitable for the hydroformylation of volatile olefins having no more than 5 carbon atoms, e.g. for ethylene or propylene. Like the processes mentioned above, it is not advantageous for the reaction of higher olefins since the vapor pressures of the olefins (and those of the aldehydes) are too low and the process therefore has to inevitably be carried out in the liquid phase.

WO 95/08525 describes a two-stage hydroformylation process in which the reaction mixture is discharged from the first stage in gaseous form. Allegedly, olefins having 2 to 20 carbon atoms, in particular 2 to

8 carbon atoms, can be reacted by the process. The hydroformylation is rhodium-catalyzed, and the catalyst is identical in both stages. The example describes the hydroformylation of propylene. As with the processes
5 described above, higher olefins having more than 5 carbon atoms cannot advantageously be converted on an industrial scale because of the relatively high boiling points of the starting materials and products. Conversion in the gas phase is therefore energetically
10 unfavorable.

A further variant of a two-stage hydroformylation is described in DE 3 232 557. In the first stage, the olefins are hydroformylated using a cobalt catalyst
15 with conversions of 50-90%, the cobalt catalyst is separated off from the reaction mixture, and the aldehydes formed are introduced into a second hydroformylation stage together with the unreacted olefins. The ligand-modified cobalt catalyst used here
20 effects not only further hydroformylation of the olefins, but also hydrogenation of the aldehydes to give the alcohols. In addition, the aldehydes produced in the first stage are exposed to the energetic reaction conditions of the second stage. This leads to
25 consecutive reactions, in particular to condensation reactions with the formation of high-boiling components.

Object of the invention

30 The object of the invention was therefore to provide a process for the preparation of higher oxo aldehydes or the corresponding alcohols from olefins or olefin mixtures which combines high conversions with high selectivities, accordingly produces fewer byproducts
35 and/or secondary products, is additionally distinguished by high space-time yields and offers more room for maneuver for controlling the product properties.

The present invention therefore provides a process for the multistage cobalt- or rhodium-catalyzed hydroformylation of olefins having 6 to 24 carbon atoms to
5 give alcohols and/or aldehydes, where the olefins

- a) are hydroformylated in a hydroformylation step to a conversion of from 20 to 98%,
- b) the catalyst is removed from the resulting liquid
10 reactor discharge,
- c) the resulting liquid hydroformylation mixture is separated into a low-boiler fraction comprising olefins and paraffins, and a bottoms fraction comprising aldehydes and/or alcohols,
- 15 d) the olefins present in the low-boiler fraction are reacted in further process stages comprising the process steps a, b and c
and the bottoms fractions of process steps c) of all process stages are combined.

20

The process according to the invention is preferably carried out such that the liquid reactor discharge of hydroformylation step a) is a homogeneous liquid phase. The cobalt or rhodium catalysts are preferably employed
25 such that they are dissolved homogeneously in the liquid reactor discharge of hydroformylation step a).

The unreacted olefins are separated from the aldehydes formed following removal of excess synthesis gas and
30 catalyst in one or more separation steps or distillation steps. The hydroformylation products from the first process stage are therefore not again subjected in one or more further stages to the conditions of a hydroformylation reaction which favor
35 consecutive reactions.

Description of the variants of the invention

The process according to the invention can in each case be carried out discontinuously or continuously, preferably with two process stages. For a continuous
5 procedure various process variants are possible, which are shown by way of example as two-stage processes in Figures 1 to 3. These embodiments are referred to below as variants 1, 2 and 3. It should be emphasized that the procedures described here are of course also
10 applicable for processes with more than two process stages.

The crude aldehyde obtained by means of the process according to the invention which, in addition to the
15 process products aldehyde and alcohol, also comprises formates, condensation products and other high-boiling components, are worked up either by distillation to isolate the aldehyde, or are firstly hydrogenated and then distilled to isolate the alcohols.

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Variant 1

The process according to Variant 1 is shown as a block diagram in Fig. 1. The olefin mixture 3, the synthesis gas 2 (carbon monoxide and hydrogen), and catalyst
25 solution or the precursors of the catalyst 4 are fed to the first hydroformylation reactor 1. The resulting hydroformylation mixture 5 is decompressed, the decompression gas 7 (unconsumed synthesis gas) is drawn off and the decompressed hydroformylation mixture is
30 freed from the catalyst 4 in the first catalyst removal 6, the catalyst, optionally after removal of a small partial stream and after topping up with fresh catalyst, being returned to the first hydroformylation reactor 1. The term catalyst here also refers to
35 precursors of catalysts, e.g. cobalt(II) salt solutions. The hydroformylation mixture 8 freed from the catalyst is separated in the distillation column 9 into low-boiling components 10, which consist

predominantly of unreacted olefins, and crude aldehyde 11. The low-boiling components 10, synthesis gas 13 and catalyst solution 16 are introduced into the second hydroformylation reactor 12. The hydroformylation step
5 of the second process stage can be carried out using the same catalyst system (both metal and ligand or their respective concentration) or using another catalyst system to the first stage. The hydroformylation mixture 14 from the second
10 hydroformylation reactor 12 is again decompressed, and the decompression gas 17 is drawn off. The decompressed hydroformylation mixture 14 is freed from the catalyst 16 in the second catalyst removal 15, the catalyst in turn, optionally after removal of a small partial
15 stream and after topping up with fresh catalyst, being returned to the second hydroformylation reactor 12. The catalyst-free hydroformylation mixture 18 can be separated in the column 19 into the low-boiling components 20, which consist predominantly of saturated
20 hydrocarbons, and crude aldehyde 21. In some instances, some of the low-boiling components 20 may be returned to the reactor 12. (Line not shown in Fig. 1).

A further arrangement of this process variant consists
25 in the hydroformylation mixture 18 freed from catalyst being passed together with the crude aldehyde 11 to the hydrogenation 22 without distillation in the column 19 (line 24). The crude aldehydes 11 and 21 or 11 and 24 are hydrogenated in the hydrogenation reactor 22 with
30 hydrogen to give the crude alcohol 23, which can optionally be worked up in a distillation (not shown) to give pure alcohol. If the aldehyde is the actual target product, the hydrogenation unit 22 is bypassed and, where necessary, the crude aldehyde (11 and 21 or
35 11 and 24) is worked up in a distillation (not shown) to give pure aldehyde.

In this variant of the invention, each process stage has a hydroformylation step a), a catalyst removal step b) and a distillation step c), with the proviso that the catalyst separated off in b) is returned, directly
5 or after work-up, to the hydroformylation step a) of the respective process stage.

Optionally, this process variant can also be carried out such that the last process stage does not have a
10 distillation step c).

Variant 2

The block diagram of a further process variant of the invention is shown in Fig. 2. The olefin mixture 3, the
15 synthesis gas 2 (carbon monoxide and hydrogen), and catalyst 4 or its precursor are fed to the first hydroformylation reactor 1. The resulting hydroformylation mixture 5 is decompressed, the decompression gas 7 (unconsumed synthesis gas) is drawn
20 off and the decompressed hydroformylation mixture is freed from the catalyst 4 in the first catalyst removal 6, the catalyst, optionally after removal of a small partial stream and after topping up with fresh catalyst, being returned to the first hydroformylation
25 reactor 1. The hydroformylation mixture 8 freed from the catalyst is passed to the distillation 9. There, together with the catalyst-free hydroformylation mixture 18 from the second hydroformylation reactor 12, it is separated into a low-boiler fraction 10, which
30 comprises the unreacted olefins and inert paraffins, and crude aldehyde 19. The low-boiling components 10 are, after removal of a partial stream 11 for removal of saturated hydrocarbons (paraffins) and other nonolefinic compounds, passed together with synthesis
35 gas 13 and catalyst 16 to the second hydroformylation reactor 12. The resulting hydroformylation mixture 14 is decompressed, the decompression gas 17 is drawn off, and the decompressed hydroformylation mixture is freed

from the catalyst 16 in the second catalyst removal 15, the catalyst, optionally after removal of a small partial stream and after topping up with fresh catalyst, being returned to the second hydroformylation reactor 12. The catalyst-free second hydroformylation mixture 18 is fed with the hydroformylation mixture 8 from the first stage, as already mentioned, to the distillation column 9. The crude aldehyde 19 can be hydrogenated in the hydrogenation unit 20 with hydrogen to give the crude alcohol 21. This alcohol can in turn be worked up in a distillation (not shown) to give pure alcohol. If an aldehyde is the target product, the crude aldehyde 19 is, with bypass of the hydrogenation unit, worked up in a distillation (not shown) to give pure aldehyde.

The term catalyst here may also mean precursors of catalysts, e.g. cobalt(II) salt solutions. The second and each further process stage can be carried out using the same catalyst system (both metal and ligand or their respective concentration) or using a system different to the first stage.

Instead of being removed via the partial stream 11, the saturated hydrocarbons can also be removed by working up a partial stream of the hydroformylation product 18 freed from the catalyst (not shown). On an industrial scale, this can be carried out, for example, by separating this partial stream by distillation into low-boiling components, which are removed, and aldehydes, which are returned to the catalyst-free hydroformylation mixture 18 or the crude aldehyde 19.

This variant of the invention has, for each process stage, a hydroformylation step a) and a catalyst removal step b), the combined liquid hydroformylation mixtures being separated in a common distillation step c) into a low-boiler fraction and bottoms fraction,

with the proviso that the catalyst separated off in steps b) is returned, directly or after work-up, to the hydroformylation step a) of the respective process stage.

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Variant 3

A further variant of the process according to the invention is shown in Fig. 3. The olefin mixture 3, the synthesis gas 2 (carbon monoxide and hydrogen), and catalyst solution or precursor thereof 4 are fed to the first hydroformylation reactor 1. The resulting hydroformylation mixture 5 is decompressed together with the hydroformylation mixture 14 from the second hydroformylation reactor 12 as combined hydroformylation discharges 15, and the decompression gas 7 (unconsumed synthesis gas) is drawn off. The combined hydroformylation discharges are freed from the catalyst 16 in the catalyst removal 6, giving a mixture 8 comprising the formed aldehydes, alcohols and unreacted olefins. The catalyst 16 is, optionally after removal of a partial amount and topping up with fresh catalyst, subdivided into the two partial streams 4 and 17. Partial stream 4 is returned to the first hydroformylation reactor 1 and partial stream 17 is returned to the second hydroformylation reactor 12. The catalyst-free hydroformylation discharge 8 is separated in the distillation column 9 into the low-boiling components 10 and the crude aldehyde 18. The low-boiler fraction 10, which comprises the unreacted olefins, is, optionally after removal of a partial amount 11 (to remove saturated hydrocarbons or other nonolefinic compounds), fed together with synthesis gas 13 and catalyst 17 to the second hydroformylation reactor 12. The crude aldehyde 18 can be hydrogenated in the hydrogenation unit 19 with hydrogen to give the crude alcohol 20. The latter can in turn be worked-up in a distillation (not shown) to give pure alcohol. If the aldehyde is the target product, the hydrogenation unit

19 is bypassed and the crude aldehyde 18 is worked up by distillation to give pure aldehyde (not shown).

5 In the case of variant 3 too, it is possible to remove saturated hydrocarbons via a separate work-up of a partial stream of the hydroformylation mixture 14, for example by distillative removal of the low-boiling components.

10 This variant of the process according to the invention is notable for the fact that the combined reactor discharges of all hydroformylation steps a) pass through only a catalyst removal step b) and a distillation step c), with the proviso that the
15 catalyst separated off in the process steps b) is divided, directly or after work-up, and returned to the hydroformylation steps a) of the individual process stages.

20 In this variant too, catalyst also encompasses precursors of catalysts, e.g. cobalt(II) salt solutions.

25 In this process variant, the same catalyst, i.e. cobalt or rhodium as active catalyst metal, must be used in all hydroformylation steps or process stages. It is, however, possible to use different catalyst concentrations in different process stages or hydroformylation steps thereof.

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In the process according to the invention it is possible to return all or some of the separated-off excess synthesis gas to the process. A particularly interesting possibility arises when the hydro-
35 formylation reactors are operated at different pressures. The offgas from reactors which are operated at higher pressure than others can be separated off at a pressure above the operating pressure of the other

reactors, meaning that it can be used in the other reactors without compression.

The common feature of the invention or of variants 1 to 3 is the hydroformylation of olefins or olefin mixtures in a plurality, preferably in two, stages, where in the first stage predominantly the more reactive olefins are converted and in the further stages predominantly the less reactive olefins are converted. Another essential feature of the invention is the removal of unreacted olefins present in the low-boiling components from the hydroformylation product of the first stage discharged as liquid, after removal of the catalyst, preferably by distillation. The essential differences between the individual variants consist in the complexity of working up the reaction discharges. By virtue of the separately operating catalyst cycles, variant 1 permits the use of different catalysts, of different catalyst concentrations or of different ligand systems in the reactors. In variant 1, these separate distillations guarantee the best removal of paraffins produced in the process. It is, however, possible to save at least one of the distillations and to separate the discharges from the various hydroformylation reactors in just one distillation step (variant 2). A further reduction in the required apparatus is achieved by combining the catalyst cycles (variant 3). Although different catalysts can no longer be used in the process stages, the concentration of the catalyst in the reactors can still be adjusted by means of the splitting ratio (partial streams 4 and 17 in the case of a two-stage process according to Figure 3) of the recycled catalyst. Also, the reaction conditions such as pressure, temperature, etc. can still be chosen freely independently of one another for each hydroformylation step.

The reactors in which the hydroformylation is carried out can be identical or different in all process stages. Examples of types of reactor which can be used are bubble columns, loop reactors, jet-nozzle reactors, stirred reactors and tubular reactors, some of which may be cascaded and/or provided with internals.

Description of the starting materials, process conditions and products

10 The starting materials for the process are olefins or mixtures of olefins having 6 to 24 carbon atoms, advantageously having 6 to 20 carbon atoms, in particular having 8 to 20 carbon atoms, and having terminal or internal C-C double bonds. The mixtures can
15 consist of olefins of identical, similar (± 2) or significantly different ($> \pm 2$) carbon number. Examples of olefins, which can be used as starting material either in pure form, in an isomer mixture or in a mixture with further olefins of different carbon
20 number, which may be mentioned are: 1-, 2- or 3-hexene, 1-heptene, linear heptenes having an internal double bond (2-heptene, 3-heptene etc.), mixtures of linear heptenes, 2- or 3-methyl-1-hexene, 1-octene, linear octenes having an internal double bond, mixtures of
25 linear octenes, 2- or 3-methylheptene, 1-nonene, linear nonenes having an internal double bond, mixtures of linear nonenes, 2-, 3- or 4-methyloctenes, 1-, 2-, 3-, 4- or 5-decene, 2-ethyl-1-octene, 1-dodecene, linear dodecenes having an internal double bond, mixtures of
30 linear dodecenes, 1-tetradecene, linear tetradecenes having an internal double bond, mixtures of linear tetradecenes, 1-hexadecene, linear hexadecenes having an internal double bond, mixtures of linear hexadecenes. Suitable starting materials are also,
35 inter alia, the mixture of isomeric hexenes (dipropene) produced during the dimerization of propene, the mixture of isomeric octenes (dibutene) produced during the dimerization of butenes, the mixture of isomeric

nonenes (tripropene) produced during the trimerization of propene, the mixture of isomeric dodecenes (tetrapropene or tributene) produced during the tetramerization of propene or the trimerization of butenes, the hexadecene mixture (tetrabutene) produced during the tetramerization of butenes, and olefin mixtures prepared by cooligomerization of olefins of different carbon number (preferably 2 to 4), optionally after distillative separation into fractions of identical or similar (± 2) carbon number. It is also possible to use olefins or olefin mixtures which have been prepared by Fischer-Tropsch synthesis. Moreover, olefins which have been prepared by olefin metathesis or by other industrial processes can be used. Preferred starting materials are mixtures of isomeric octenes, nonenes, dodecenes or hexadecenes, i.e. oligomers of lower olefins, such as n-butenes, isobutene or propene. Other likewise highly suitable starting materials are oligomers of C₅-olefins.

For the oligomerization of butenes to mixtures comprising essentially C₈-olefins there are in principle three process variants. The oligomerization over acid catalysts has been known for a long time, zeolites or phosphoric acid on supports, for example, being used in industry. This process produces isomer mixtures of branched olefins which are essentially dimethylhexenes (WO 92/13818). A process which is likewise used throughout the world is the oligomerization using soluble Ni complexes, known as DIMERSOL process (B. CORNILS, W.A. HERRMANN, "Applied Homogeneous Catalysis with Organometallic Compounds"; Vol. 1&2, VCH, Weinheim, New York 1996). The third process variant is the oligomerization over nickel fixed-bed catalysts; the process has gained access into the literature as the OCTOL process (Hydrocarbon Process., Int. Ed. (1986), 65 (2. Sect. 1) page 31-33).

For the preparation according to the invention of a C₉-alcohol mixture which is particularly suitable for the preparation of plasticizers, preference is given to using a C₈-olefin mixture which has been obtained from
5 linear butenes by the OCTOL process.

In the synthesis gas used for the hydroformylation carbon monoxide and hydrogen are generally present in the molar ratio from 1:4 to 4:1 and preferably in an
10 approximately stoichiometric ratio.

The process of the invention is carried out using cobalt or rhodium catalysts, and with or without complex-stabilizing additives, such as organic
15 phosphines or phosphites. In all of the hydroformylation steps of the process it is possible to use either rhodium catalysts or cobalt catalysts. It is also possible to use a cobalt catalyst (alternatively: rhodium catalyst) in the hydroformylation step a) in
20 the first process stage, and to use rhodium catalysts (alternatively: cobalt catalyst) in the hydroformylation steps of the further process stages. It is an advantage of the process according to the invention that different catalysts can be used in the
25 individual stages, meaning that in cases of more than two process stages it is also possible to use different catalysts, e.g. cobalt/rhodium/cobalt.

The choice of catalyst and of reaction conditions
30 (concentration of the catalyst, temperature, pressure, residence time) depends, inter alia, on the number of carbon atoms and the composition of the starting olefins. If a high proportion of terminally hydroformylated olefin is a criterion for high product
35 quality, then, for example in the case of the dimerization mixture of n-butenes known as di-n-butene, very good product quality is achieved coupled with satisfactory yield if, in the case of a two-stage

process, unmodified cobalt catalysts are used in both stages. If an unmodified cobalt catalyst is used in the first stage and an unmodified rhodium catalyst is used in the subsequent stages, then the yield improves, while the product quality is somewhat diminished. A further improvement in yield and a reduction in product quality arise if unmodified rhodium catalysts are used in all stages. If a low proportion of terminally hydroformylated olefin is a criterion for high product quality, then, for example in the case of the dimerization mixture of n-butenes known as di-n-butene, good product quality is achieved coupled with a very high yield if, in the case of a two-stage process, unmodified rhodium catalysts are used in both stages. If ligand-modified catalysts are used, in particular if rhodium and phosphorus ligands are used, there is also further scope for influencing the proportion of terminally or nonterminally hydroformylated olefin via the choice of ligand. For a given starting olefin, the optimum number of process stages, and in the individual hydroformylation steps, the optimal catalysts can be determined without difficulty by exploratory experiments. The catalyst concentrations in the individual stages can be identical or different.

The temperatures and the pressures in the hydroformylation steps of the various process stages can vary within wide limits, depending on the catalyst and olefin mixtures. Since in the first stage the more reactive olefins react in preference, in the hydroformylation steps of the further stages more energetic reaction conditions with regard to temperature, amount of catalyst, residence time are advantageously used.

The optimal conditions can vary from case to case depending on the objective: thus, for example, the space-time yield achieved overall, the increase in the

selectivity or the desired product properties may be an optimization criterion. As a rule, the composition of the starting olefin and the choice of catalyst systems and/or reaction conditions decide which of the possible
5 embodiments of the process according to the invention is the economically optimal.

In the process according to the invention, olefin conversions in the hydroformylation steps of the
10 individual process stages of from 20 to 98%, in particular from 40 to 80%, particularly preferably 50 to 75% are obtained (in each case single pass).

In the hydroformylation steps a) of the further process
15 stages which follow the first process stage, the olefins can in each case be reacted to a conversion of at least 50%, preferably 55 to 98%.

It is an advantage of the process according to the
20 invention that different reaction conditions can be set in the hydroformylation reactors. This allows the hydroformylation conditions to be matched to the reactivity of the olefin mixture introduced. To minimize secondary products and byproducts it is, for
25 example, sensible to react the reactive olefins under the mildest conditions possible, so that virtually no secondary products and byproducts form therein. Then, in the following reactor, the olefin mixture which remains, which largely consists of the unreactive
30 olefins, is hydroformylated under, where necessary, more severe conditions. It is therefore possible to influence the isomer distribution of the aldehydes formed via the varying reaction conditions in the reactors.

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Rhodium- and cobalt-catalyzed hydroformylation processes differ mostly by virtue of their operating parameters. However, the main difference is in the

fundamentally different catalyst removal and recycle. The two processes are described separately below.

Cobalt-catalyzed hydroformylation process

5 In the cobalt-catalyzed hydroformylation of olefins it is possible to use unmodified and/or modified catalysts which may be identical or different for each process stage. The hydroformylation process in each of the cobalt-catalyzed process stages can be carried out by a
10 one-stage process described in DE 196 54 340. According to this process, the starting materials, the cobalt salt solution, the organic phase and the synthesis gas are simultaneously introduced into the reactor in cocurrent from below, preferably using a mixing nozzle.

15 The cobalt compounds used are preferably cobalt salts, such as formates, acetates or salts of carboxylic acids which are water-soluble. Cobalt acetate has proven particularly successful; this is used as an aqueous
20 solution with a cobalt content of from 0.5 to 3% by weight, preferably from 1.0 to 2.0% by weight, calculated as metal.

The organic phase comprises the olefin to be
25 hydroformylated and optionally additionally an aldehyde and/or alcohol, the aldehyde or alcohol preferably being the reaction products formed during the hydroformylation.

30 In the cobalt-catalyzed process, particular importance is attached to the metered addition of the starting materials into the reactor. The metering device must ensure good phase mixing and the production of the greatest possible phase exchange area. In the case of
35 cobalt-catalyzed hydroformylation, it is therefore advantageous to divide the reactor space of the hydroformylation reactors by incorporating a small number of perforated sheets (minimum number = 1)

arranged perpendicularly to the flow direction of the reactant and product stream. As a result of the reactor cascading, the backmixing is considerably reduced compared with the simple bubble column and the flow behavior approximates that of a tubular reactor. This process engineering measure results in both the yield and the selectivity of the hydroformylation being improved.

- 10 If, according to the invention, hydroformylation steps with cobalt catalyst are used, then these are operated at temperatures of from 100 to 250°C and under pressures of from 100 to 400 bar. Temperatures of from 140 to 210°C and synthesis gas pressures of from 200 to 300 bar have proven particularly successful. The volume ratio of the carbon monoxide to the hydrogen in the synthesis gas is generally between 2:1 and 1:2, in particular in the volume ratio 1:1. The synthesis gas is advantageously used in excess, for example in up to three times the stoichiometric amount.

The hydroformylation of olefins is carried out under cobalt catalysis in the first process stage, in which the more reactive olefins are converted, at temperatures between 140 and 195°C, preferably at 160 to 185°C. Olefin conversions between 20 and 90%, preferably between 50 and 80%, are strived for in this process stage.

- 30 After leaving the reactor of the first process stage or of the first hydroformylation step, the product discharge is decompressed to 10 to 15 bar and passed to the decobalting (catalyst removal, 6 in Fig. 1). In the decobalting step, the product discharge (organic phase) is freed from cobalt carbonyl complexes in the presence of "process water" using air or oxygen at temperatures of from 130 to 190°C. The decobalting processes are well known and described in the literature in detail,

such as e.g. by J. FALBE, in "New Syntheses with Carbon Monoxide", Springer Verlag (1980), Berlin, Heidelberg, New York, page 158 et seq.

- 5 The decobalting is preferably carried out in a pressurized container filled with dumped packing, such as, for example, Raschig rings in which the highest possible phase exchange area is generated. The cobalt-free organic product phase is separated from the
10 aqueous phase in a downstream separation container. The aqueous phase, the "process water", which contains the back-extracted cobalt recovered from the organic phase in the form of cobalt acetate/formate, is, wholly or following removal of a small fraction, returned to the
15 oxo reactor of the respective process stage and preferably used as starting material for the in situ preparation of the cobalt catalyst complexes.

- Precarbonylation, catalyst extraction and the actual
20 hydroformylation are preferably carried out in one reactor according to DE 196 54 340. It is also possible to separate these process stages from one another in terms of apparatus.

- 25 The organic reactor discharge, which contains the unreacted olefins, aldehydes, alcohols, formic esters and high-boiling components is, after the hydroformylation step and the catalyst removal, passed to a distillation step. Here, the reactor discharge
30 freed from the cobalt catalyst and excess synthesis gas is separated by distillation into the crude aldehydes/alcohols (bottoms fraction) and a low-boiler fraction which, depending on the process variant and conditions of the hydroformylation step, consists
35 predominantly of the unreacted, less reactive olefins and/or paraffins produced by hydrogenation of the olefins.

The unreacted olefins freed from the products of value in the distillation step are then passed to the hydroformylation step of the next process stage.

- 5 According to the process of the invention, the cobalt-catalyzed hydroformylation is carried out in the further process stages following the first stage or hydroformylation steps at temperatures of from 160 to 220°C, preferably from 175 to 195°C. Here, olefin
10 conversions of at least 50%, preferably between 50 and 95%, preferably between 55 and 98% are strived for.

The multistage process according to the invention offers the possibility of bringing the olefin
15 conversion in the first stage to the strived-for value by adapting the reaction conditions, for example by choosing low cobalt concentrations. In the following stages, where the more slowly reacting olefins are converted, the reaction conditions can then be
20 intensified, for example by increasing the catalyst concentration.

The process stages according to the invention using cobalt catalyst are particularly suitable for the
25 hydroformylation of mixtures of isomeric olefins prepared by oligomerization of propene and butenes. Typical oligomerization products which are preferably used as raw material base for the hydroformylation according to the novel process include di-, tri- and
30 tetrapropene, and di-, tri-, and tetrabutene.

Rhodium-catalyzed hydroformylation

In rhodium-catalyzed hydroformylation processes it is possible to use modified and/or unmodified catalysts
35 which may be identical or different for each rhodium-catalyzed hydroformylation step.

These rhodium catalysts can be introduced into the process in the form of their active complexes, although in industry it is usually simpler to generate the active catalysts in situ from stable, readily storable rhodium compounds. Suitable rhodium compounds for this purpose are, for example, rhodium(II) and rhodium(III) salts, such as rhodium(III) chloride, rhodium(III) nitrate, rhodium(III) sulfate, potassium rhodium sulfate, rhodium(II) and rhodium(III) carboxylate, rhodium(II) and rhodium(III) acetate, rhodium(II) octanoate, rhodium(II) nonanoate, rhodium(III) oxide, salts of rhodic(III) acid, trisammonium hexachlororhodate(III). Also suitable are rhodium complexes, such as acetylacetonatodicarbonylrhodium, acetylacetonatobisethylenerrhodium(I). Rhodium acetate, rhodium octanoate and rhodium nonanoate are particularly suitable.

In general, approximately 1 to 500 and, preferably, 3 to 50 mol of ligand are added per mole of rhodium. Fresh ligand can be added to the reaction at any time in order to keep the concentration of free ligand constant.

The concentration of the rhodium in the hydroformylation reactor is between 1 ppm and 500 ppm, preferably between 5 ppm and 200 ppm.

The choice of ligands added is not restricted in the process according to the invention, but depends on the olefin used and on the desired products. Preferred ligands are ligands which contain nitrogen, phosphorus, arsenic or antimony atoms, particular preference being given to phosphorus ligands. The ligands can be monodentate or polydentate, and in the case of chiral ligands either the racemate or an enantiomer or diastereomer can be used. Phosphorus ligands which are to be mentioned are, in particular, phosphines,

phosphine oxides, phosphites, phosphonites and phosphinites. Examples of phosphines are triphenylphosphine, tris(p-tolyl)phosphine, tris(m-tolyl)phosphine, tris(o-tolyl)phosphine, tris(p-methoxyphenyl)phosphine, tris(p-fluorophenyl)phosphine, tris(p-chlorophenyl)phosphine, tris(p-dimethylaminophenyl)phosphine, ethyldiphenylphosphine, propyldiphenylphosphine, t-butyldiphenylphosphine, n-butyldiphenylphosphine, n-hexyldiphenylphosphine, c-hexyldiphenylphosphine, dicyclohexylphenylphosphine, tricyclohexylphosphine, tricyclopentylphosphine, triethylphosphine, tri(1-naphthyl)phosphine, tri-2-furylphosphine, tribenzylphosphine, benzyldiphenylphosphine, tri-n-butyldiphenylphosphine, tri-i-butyldiphenylphosphine, tri-t-butyldiphenylphosphine, bis(2-methoxyphenyl)phosphine, neomenthyldiphenylphosphine, the alkali metal, alkaline earth metal, ammonium or other salts of sulfonated triphenylphosphines, such as tris(m-sulfonylphenyl)phosphine, (m-sulfonylphenyl)diphenylphosphine, 1,2-bis(dicyclohexylphosphino)ethane, bis(dicyclohexylphosphino)methane, 1,2-bis(diethylphosphino)ethane, 1,2-bis(2,5-diethylphospholano)benzene [Et-DUPHOS], 1,2-bis(2,5-diethylphospholano)ethane [Et-BPE], 1,2-bis(dimethylphosphino)ethane, bis(dimethylphosphino)methane, 1,2-bis(2,5-dimethylphospholano)benzene [Me-DUPHOS], 1,2-bis(2,5-dimethylphospholano)ethane [Me-BPE], 1,2-bis(diphenylphosphino)benzene, 2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene [NORPHOS], 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [BINAP], 2,2'-bis(diphenylphosphino)-1,1'-biphenyl [BISBI], 2,3-bis(diphenylphosphino)butane, 1,4-bis(diphenylphosphino)butane, 1,2-bis(diphenylphosphino)ethane, bis(2-diphenylphosphinoethyl)phenylphosphine, 1,1'-bis(diphenylphosphino)ferrocene, bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)propane, 2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl, O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [DIOP], 2-(diphenylphosphino)-2'-methoxy-1,1'-

binaphthyl, 1-(2-diphenylphosphino-1-naphthyl)iso-
quinoline, 1,1,1-tris(diphenylphosphino)ethene,
tris(hydroxypropyl)phosphine.

5 A particularly preferred phosphine used is triphenylphosphine.

Examples of phosphites are trimethyl phosphite, triethyl phosphite, tri-n-propyl phosphite, tri-
10 isopropyl phosphite, tri-n-butyl phosphite, tri-isobutyl phosphite, tri-t-butyl phosphite, tris(2-ethylhexyl) phosphite, triphenyl phosphite, tris(2,4-di-t-butylphenyl) phosphite, tris(2-t-butyl-4-methoxyphenyl) phosphite, tris(2-t-butyl-4-methylphenyl) phosphite, tris(p-cresyl) phosphite. Also
15 sterically hindered phosphite ligands, as are described inter alia in EP 155 508, US 4 668 651, US 4 748 261, US 4 769 498, US 4 774 361, US 4 835 299, US 4 885 401, US 5 059 710, US 5 113 022, US 5 179 055, US 5 260 491, US 5 264 616, US 5 288 918, US 5 360 938, EP 472 071, EP 518 241 and WO 97/20795. Preference is given to
20 using substituted triphenyl phosphites having in each case 1 or 2 isopropyl and/or tert-butyl groups on the phenyl rings, preferably in the ortho-position relative
25 to the phosphite ester group.

Examples of phosphonites are methyldiethoxyphosphine, phenyldimethoxyphosphine, phenyldiphenoxyposphine, 6-phenoxy-6H-dibenz[c,e][1,2]oxaphosphorine and deriva-
30 tives thereof, in which the hydrogen atoms are wholly or partially replaced by alkyl or aryl radicals or halogen atoms, and ligands which are described in patents WO 98/43935, JP 09-268152 and DE 198 10 794 and in the German patent applications DE 199 54 721 and
35 DE 199 54 510.

Common phosphonite ligands are described inter alia in US 5 710 344, WO 95/06627, US 5 360 938, JP 07082281.

Examples thereof are diphenyl(phenoxy)phosphine and derivatives thereof in which the hydrogen atoms are wholly or partially replaced by alkyl or aryl radicals or halogen atoms, diphenyl(methoxy)phosphine, 5 diphenyl(ethoxy)phosphine etc.

Rhodium-catalyzed hydroformylations are generally carried out at pressures of from 1 to 300 bar, preferably at pressures from 15 to 270 bar. The 10 pressure used depends on the structure of the feed olefins, the rhodium catalyst used and the desired effect. Thus, for example, α -olefins can be converted to the corresponding aldehydes at pressures below 64 bar with high space-time yields. By contrast, in the 15 case of olefins with internal double bonds, in particular in the case of branched olefins, higher pressures are expedient.

The temperatures for rhodium-catalyzed hydroformyla- 20 tions are generally in the range from 40°C to 180°C, preferably 60°C to 135°C. Temperatures above 100°C afford the technical advantage that the waste heat from the reaction can be utilized to generate steam.

25 Following the hydroformylation, most of the synthesis gas is removed by relieving the pressure. The catalyst is removed from the liquid reaction discharge by distillation (catalyst removal e.g. 6 and 15 in Fig. 1). The catalyst and optionally added ligands, 30 stabilizers etc. remain in/as distillation residue. It is therefore advantageous to use a high-boiling (higher boiling than products and starting materials) inert solvent in which the catalyst dissolves. The catalyst dissolved in the high-boiling solvent can then be 35 returned directly to the reaction. It is particularly advantageous to use the high-boiling byproducts formed in the process as high-boiling solvent. Other suitable solvents are high-boiling esters, such as 2,2,4-

trimethylpentanediol 1,3-monoisobutyrate, which is available commercially as Texanol.

For the industrial execution of the distillative catalyst removal a variety of procedures can be used. Preference is given to removing the catalyst solution via falling-film, short-path or thin-film evaporators or combinations of these apparatuses. The advantage of such a combination can, for example, be the fact that still dissolved synthesis gas and some of the products and the still present starting olefins can be separated off in a first step (for example in a falling-film evaporator) in order then, in a second step (for example in a thin-film evaporator), to undertake the final removal of the catalyst.

Since the hydroformylation of olefins is an exothermic reaction, the heat produced has to be eliminated from the reactors in order to limit the temperature in the reactor. Temperatures which are too high generally bring about an increased formation of byproducts and deactivation of the catalyst. Often, as isothermic a course as possible is also desired because the reaction temperature can have a direct influence on the product composition (e.g. the n/i ratio).

The dissipation of heat is possible via various technical arrangements, for example via the reactor wall, integrated condenser etc. Industrially, it is advantageous to keep the expenditure for the dissipation of heat low. However, if olefin mixtures are used, the varying reaction rate can lead to the evolution of considerable heat as a result of the exothermicity, in particular in the first stage, since here the readily oxoable components react in preference. The process according to the invention then offers the possibility of keeping the evolution of heat, predominantly in the first process stage, within

limits which can be readily controlled in industry, by adapting the reaction conditions, for example by virtue of a low catalytic concentration or by adding an inert solvent.

5

Work-up of the catalyst-free hydroformylation mixtures

The reactor discharges freed from the catalyst and excess synthesis gas are, as shown in Figures 1-3, separated, separately or together, into the crude
10 aldehydes and a low-boiler fraction by distillation. Depending on the processing variant and process stage, the low-boiling components consist predominantly of unreacted olefins or paraffins formed by hydrogenation of the olefins. In addition to aldehydes and alcohols,
15 the bottom product also comprises high-boiling byproducts, such as formates, acetals, saturated and unsaturated ethers, esters, carboxylic acids and condensation products. The hydroformylation discharges freed from the catalyst can be separated into low-
20 boiling components and crude aldehyde separately in one or more distillations (variant 1) or in a common distillation (variants 2 and 3). The distillation conditions depend on the boiling points of the components and thus primarily on the molar mass of the
25 olefins and aldehydes. They are to be chosen such that relatively large amounts of byproducts are not formed during the distillation. Since these originate mainly from reactions of the aldehydes at elevated temperatures, the distillation can be carried out under
30 reduced pressure and in so doing the temperatures in the column can be kept low. It is, however, also possible to carry out the distillation at atmospheric pressure.

35 If the reaction discharges of the hydroformylation steps are carried out in separate distillations (variant 1), the low-boiling components of the first distillation are passed to the following process stage

(generally: the low-boiling components from one stage to the next), and the low-boiling components from the last distillation are removed and optionally also in part returned to the previous hydroformylation stage.

5 If the reaction discharges from different process stages are worked up together (variants 2 and 3), it is expedient to remove some of the low-boiling components prior to entry into the last process stage or by working up a partial stream of the discharge from the

10 last stage in order to keep the proportion of paraffins in the cycle to an acceptable level.

It is therefore possible to remove the paraffins, wholly or in part, from at least one low-boiler

15 fraction.

As well as these possibilities, also listed in the description of variants 1 to 3, of removing low-boiling components and, in particular, paraffins from the

20 process, others are also suitable. If removal of the catalyst and optionally also the distillation are carried out under reduced pressure, some of the low-boiling components and, however, also some of the product is removed from the process via the vacuum

25 system. After condensation, this fraction may be discarded, or if the amount is sufficient it may be worth while to return it (partially) to the process. Also, depending on the operating conditions, a fraction of low-boiling components and products is discharged

30 via the separated-off excess synthesis gas, which components and products can be separated off (for example by condensation) and optionally returned or worked up.

35 The crude aldehydes, if they are the target product, are worked up, separately according to stages or together, by distillation according to known methods to give the products.

Here, it is possible to work up or separate off, by distillation, the aldehydes of the combined bottom fractions from distillation step c) or, if distillation
5 step c) of the last process stage is omitted, the combined bottom fractions and the discharge of the last catalyst removal step b) of the process.

If, on the other hand, the alcohols are the target
10 products, the crude aldehydes are hydrogenated in the usual manner in gaseous or liquid phase.

It is possible to hydrogenate either the combined bottom fractions from the distillation stages c) or, if
15 the distillation step c) of the last process stage is omitted, the combined bottom fractions and the discharge of the last catalyst removal step b) of the process.

20 For the hydrogenation, copper/nickel, copper/ chromium, copper/chromium/nickel, zinc/chromium, nickel/molybdenum catalysts, for example, can be used. The catalysts can be support-free, or the hydrogenation-active substances or their precursors can be applied to
25 supports, such as, for example, silicon dioxide or aluminum dioxide.

Preferred catalysts over which the hydroformylation mixtures are hydrogenated comprise in each case 0.3-15%
30 by mass of copper and nickel and, as activators, 0.05-3.5% by mass of chromium and advantageously 0.01-1.6% by mass, preferably 0.02-1.2% by mass of an alkali metal component on a support material, preferably aluminum oxide and silicon dioxide. The quantitative
35 data refer to the as yet unreduced catalyst. The alkali metal component is optional.

The catalysts are advantageously used in a form in which they offer a low resistance to flow, e.g. in the form of granules, pellets or moldings, such as tablets, cylinders, extrudates or rings. They are expediently
5 activated prior to use, e.g. by heating in the hydrogen stream.

The hydrogenation, preferably a liquid-phase hydrogenation, is generally carried out under an
10 overall pressure of from 5 to 30 bar, in particular between 15 and 25 bar. A hydrogenation in the gas phase can also be carried out at relatively low pressures, using correspondingly large gas volumes. If two or more hydrogenation reactors are used, the overall pressures
15 in the individual reactor can be identical or different within said pressure limits.

During hydrogenation in liquid or gaseous phase, the reaction temperatures are generally between 120 and
20 220°C, in particular between 140 and 180°C. Examples of such hydrogenations are described in patent applications DE 198 42 369 and DE 198 42 370.

After the hydrogenation, the resulting reaction
25 mixtures are worked up by distillation. Where appropriate, separated-off olefins can be returned to the hydroformylation stage.

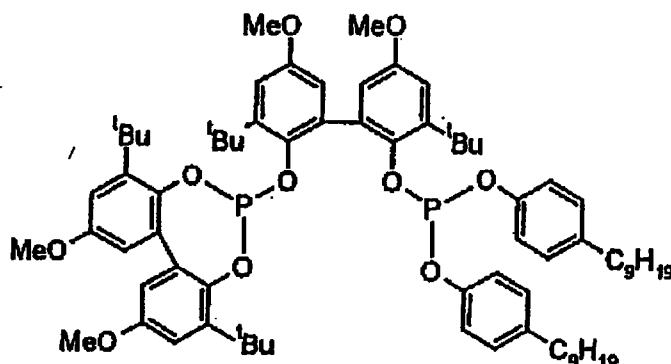
The examples below serve to illustrate the invention,
30 without limiting it in its scope of application as defined by the patent claims.

Example 1

Conversion of octene in two stages using different
35 catalyst ligands

100 g of 1-octene (> 98%, GC) were converted in a 1 l autoclave at 85°C under a synthesis gas pressure of

20 bar. The rhodium catalyst was generated in situ from rhodium octanoate and ligand 1.



Ligand 1

5 200 ml of Texanol (2,2,4-trimethylpentanediol 1,3-monoisobutyrate) were added to the reaction as inert high-boiling solvent. The rhodium concentration was adjusted to 40 ppm (based on the overall mass), and the phosphorus to rhodium ratio (P/Rh) was 20/1. The conversion of the olefin was monitored via the amount of absorbed synthesis gas. After a conversion of about 90% had been reached, virtually no more gas absorption was registered and the run was discontinued. According to GC analysis, the conversion was 91%, and the aldehyde formed consisted of 95% of nonanal. Analysis of the residual olefins produced only traces of 1-octene; main constituents were 2-octene, 3-octene and 4-octene, which had formed by isomerization of the 1-octene.

The experiment was carried out six times, and the discharges were combined and distilled. This gave 43 g of an octene mixture. These, dissolved in 100 ml of Texanol, were hydroformylated again at 120°C and a synthesis gas pressure of 50 bar in a 500 ml autoclave. The rhodium concentration was 40 ppm, and the ligand added was tris(2,4-ditert-butylphenyl) phosphite (P/Rh 20/1). During this reaction, a quantitative conversion of the olefin was achieved (GC).

The example shows that the catalyst system used in the first stage has a high n/iso selectivity, but only a low activity for the hydroformylation of octenes with an internal double bond, as are formed in the first stage by isomerization of the n-octene used (cf. P.W.N.M. van Leuwen et al., Organometallics 1996, 15, 835-847). However, these can be reacted in a second stage under different experimental conditions. Thus, on the one hand this achieves high selectivity for the desired straight-chain nonanol and, on the other hand, an improved overall yield based on the feed material.

Example 2

Hydroformylation of di-n-butene in two stages using different catalysts

A 3 l stirred autoclave was charged with about 1000 g of cobalt acetate-containing water (cobalt content about 1% by mass, calculated as metal). With stirring (1000 rpm), the mixture was placed under a synthesis gas pressure of 280 bar and the temperature was adjusted to 170°C. After 7 h, the mixture was cooled to 60°C and decompressed to 100 bar. 600 g of di-n-butene (main constituents 14% octenes, 60% 3-methylheptenes, 26% 3,4-dimethylhexenes) were then added. After stirring for 10 minutes (1000 rpm), the mixture was left to stand for 15 minutes. The aqueous phase was separated off. The di-n-butene phase contained cobalt carbonyls in a concentration of 0.019% by mass, calculated as cobalt. This solution was reacted at 170°C and a synthesis gas pressure of 280 bar. The conversion was determined via the amount of absorbed synthesis gas. At 70% conversion the reaction was stopped. After cooling to 80°C and decompression, cobalt was removed from the reaction mixture by adding 5% strength by weight aqueous acetic acid in the presence of air. The decobalted organic phase was separated by distillation into the fractions residual

olefin/small proportion of paraffin, aldehyde/alcohols and high-boiling components.

5 The residual olefin (175 g, main constituents about 4%
octenes, 52% 3-methylheptenes, 44% 3,4-dimethylhexenes)
was then reacted in a rhodium-catalyzed reaction
analogously to Example 1. The inert solvent added was
200 g of Texanol (2,2,4-trimethylpentanediol 1,3-
10 monoisobutyrate), the rhodium concentration was
adjusted to 200 ppm of Rh, and the molar ratio of
ligand (tris(2,4-di-tert-butylphenyl) phosphite) to
rhodium was 20/1. The pressure was constant at 50 bar,
and the temperature was 130°C.

15 After 6 hours, the autoclave was cooled and
decompressed, and the discharge was separated by
distillation into the fractions residual olefin/small
proportion of paraffin, aldehydes/alcohols and high-
boiling components. The combined aldehyde/alcohol
20 fractions from the two reactions were hydrogenated over
Raney nickel to give the alcohols. The yield of alcohol
over the two hydroformylation stages and hydrogenation
was 87%.

25 Thus, according to the invention, a higher yield is
achieved in a two-stage process than in a single-stage
process (Comparative Example 6).

Example 3

30 (Improving the conversion, reducing the byproducts)

The experiment was carried out in a pilot plant
consisting of bubble-column reactor, a thin-film
evaporator and a distillation device, which were
connected according to numbers 1-8 in Fig. 1. Using
35 this pilot plant, it was possible to investigate the
essential aspects of carrying out the process in two
stages in the laboratory. The olefin to be
hydroformylated was introduced into the bubble column

at the bottom, together with an excess of synthesis gas and a high-boiling solvent containing the catalyst. Unreacted synthesis gas was removed at the top of the reactor. The liquid fractions (residual olefin, aldehyde, byproducts, high-boiling solvent, catalyst) were passed to the thin-film evaporator, which was operated under reduced pressure such that here the aldehyde formed was separated, together with the unreacted olefins, from the higher-boiling components in which the catalyst was dissolved. The high-boiling solvent used was dioctyl phthalate, which was present in the reactor in a proportion of 20% by weight. The rhodium concentration in the reactor was 100 ppm of rhodium, the ligand added was tris(2,4-di-tert-butylphenyl) phosphite, and the P/Rh ratio was 20/1. The bubble column was heated to a constant temperature of 120°C externally via a twin-jacket, and the operating pressure was 50 bar of synthesis gas.

At the reaction conditions given above, an olefin feed of 2 kg/h of di-n-butene was established, and the bubble column had a volume of 2.1 liters. After a constant conversion level had become established, the material streams were balanced over a period of 100 hours. The mixture separated off by means of the thin-layer evaporator was separated by distillation into unreacted olefins and the aldehydes formed. 200 kg of di-n-butene gave 156 kg of aldehydes and 77 kg of olefin, which corresponds to an average conversion of 61.5%. At the same time, 130 g of high-boiling byproducts were formed, which became concentrated in the catalyst cycle.

The unreacted olefin in the first stage was reacted again in a second hydroformylation stage in the pilot plant. The reaction conditions corresponded to those of the first stage, except that the feed of olefin was reduced to 1 kg/h. The steady-state period chosen was

77 hours, during which exactly the 77 kg of olefin from the steady-state period of the first stage were reacted. 65 kg of aldehydes were obtained. At the same time, 310 g of high-boiling byproducts were formed.

5

If the results of the two steady-state periods are summarized, then 221 kg of aldehydes were obtained from 200 kg of di-n-butene over a total of 177 operating hours. 440 g of high-boiling byproducts were obtained
10 in the process.

Example 4

(Comparative Example, Single-stage hydroformylation)

As a comparison to Example 3, 200 kg of di-n-butene
15 were introduced into the pilot plant under otherwise identical experimental conditions over the course of 177 hours (1.13 kg(olefin)/h). A total of 198 kg of aldehyde were formed in the process. At the same time, 490 g of high-boiling byproducts were formed.

20

A comparison of Examples 3 and 4 shows that hydroformylation of the olefin in two stages over the same period using the same amount of olefin gives 23 kg more aldehydes. The result is that by dividing the
25 hydroformylation reaction into two stages better space-time yields are obtained than in the case of a single-stage reaction. It is also found that in the two-stage procedure fewer high-boiling byproducts form overall despite the higher conversion calculated over both
30 stages. This is of particular importance since the rhodium catalyst remains dissolved in the high-boiling components during the work-up of the hydroformylation mixtures. The more high-boiling components have to be removed, the more rhodium has to be replenished.

35

Example 5

Nonanols by two-stage hydroformylation of di-n-butene
1st stage

- In a 5 l high-pressure autoclave fitted with stirrer
5 and electrical heating, 2000 g of di-n-butene
(composition in Table 1, column 2) were hydroformylated
in the presence of a cobalt catalyst at 175°C and a
synthesis gas pressure of 280 bar for 2 hours. The
catalyst was prepared by treating 640 g of an aqueous
10 cobalt acetate solution containing 1% by mass of cobalt
with synthesis gas for 7 hours at 170°C and 280 bar.
After cooling and decompression, the cobalt carbonyls
formed were transferred to the organic phase by
extraction with the 2000 g of di-n-butene, and the
15 organic phase was separated off from the aqueous phase.
The concentration of the catalyst in the di-n-butene
was 0.020% by mass, based on di-n-butene and calculated
as cobalt metal.
- 20 After cooling to 80°C and decompression, the
hydroformylation mixture was freed from cobalt by
treatment with 5% strength by weight aqueous acetic
acid in the presence of air. The decobalted
hydroformylation mixture was separated off from the
25 aqueous phase.

- The process was carried out four times under the same
conditions. The decobalted hydroformylation mixtures
were combined. 9432 g of hydroformylation mixture were
30 obtained; the composition according to GC analysis is
given in Table 2, column 2. According to this, the di-
n-butene conversion was 67.2% and the product of value
selectivity was 93.8%, corresponding to a product of
value yield of 63.1%. The products of value were
35 considered here and below to be nonanals, nonanols and
formates thereof.

2nd stage

7500 g of decobalted hydroformylation mixture from the first stage were distilled over a column to recover unreacted olefins. The olefins were obtained as the top fraction, and the column bottoms contained the products of value and the high-boiling components. The isomer distribution in the recovered octene mixture is shown in Table 1, column 3. Compared with fresh di-n-butene containing 23% by mass of dimethylhexenes, the recovered olefin, containing 45% by mass of dimethylhexenes, contained considerably more of these unreactive olefins.

2000 g of recovered C₈-hydrocarbon mixture (91.75% by weight of C₈-olefins, 8.25% by weight of C₈-paraffins) were hydroformylated in the 5 l autoclave of the first stage at 185°C and a synthesis gas pressure of 280 bar for 3 hours. The cobalt catalyst was prepared as in the first stage and transferred to the olefin phase, its concentration being 0.050% by mass, based on the olefin and calculated as cobalt metal.

The hydroformylation mixture was cooled to 80°C, decompressed and decobalted as described in the first stage. This gave 2448 g of decobalted hydroformylation mixture whose composition according to GC analysis is given in Table 2, column 3. The olefin conversion was 91% and the product of value selectivity 83.7%, corresponding to a product of value yield of 76.2%.

The total olefin conversion over both stages was 97.2% at a product of value selectivity of 90.7%, corresponding to a total product of value yield of 88.2%, based on di-n-butene used.

Example 6

(Comparative example, nonanols from single-stage hydroformylation of di-n-butene)

In the 5 l high-pressure autoclave used in Example 5,
5 2000 g of di-n-butene (composition in Table 1, column 2) were hydroformylated in the presence of a cobalt catalyst at 185°C and a synthesis gas pressure of 280 bar for 3 hours. The catalyst was prepared as in Example 5. The concentration of the catalyst in the di-
10 n-butene was 0.040% by mass, based on di-n-butene and calculated as cobalt metal.

After cooling to 80°C, the hydroformylation mixture was decompressed and freed from cobalt by treatment with 5%
15 strength by weight aqueous acetic acid and air. Removal of the aqueous phase gave 2485 g of decobalted hydroformylation mixture whose composition determined by means of GC analysis is given in Table 2, column 4. According to this, a di-n-butene conversion of 92% was
20 achieved, at a product of value selectivity of 88.5%, corresponding to a product yield of 81.4%.

Compared with a single-stage process (Example 6), considerably better conversions, selectivities and
25 yields were achieved in the multistage process according to the invention (Example 5).

Table 1

Isomer distribution in the feed olefin

30

Olefins	Di-n-butene (starting material in Ex. 5, 1st stage and Ex. 6) % by mass	Octene mixture (starting material in Ex. 5, 2nd stage) % by mass
Dimethylhexenes	23	45
3-Methylheptenes	62	50
n-Octenes	15	5

Table 2

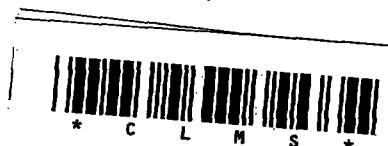
Composition of decobalted hydroformylation discharges
(calculated on an H₂O-free basis)

5

	Ex. 5, 1st stage % by mass	Ex. 5, 2nd stage % by mass	Ex. 6 % by mass
C ₈ -Olefins	27.8	6.7	6.4
C ₈ -Paraffins	2.5	10.8	3.1
C ₉ -Aldehydes	48.8	45.2	52.7
Nonyl formates	2.2	5.7	4.2
C ₉ -Alcohols	17.4	22.9	26.9
High-boiling comps.	1.3	8.7	6.7

Patent claims:

1. A process for the multistage cobalt- or rhodium-catalyzed hydroformylation of olefins having 6 to 24 carbon atoms to give alcohols and/or aldehydes, which comprises
 - a) hydroformylating the olefins in a hydroformylation step to a conversion of from 20 to 98%,
 - b) removing the catalyst from the resulting liquid reactor discharge,
 - c) separating the resulting liquid hydroformylation mixture into a low-boiler fraction comprising olefins and paraffins, and a bottoms fraction comprising aldehydes and/or alcohols,
 - d) reacting the olefins present in the low-boiler fraction in further process stages comprising the process steps a, b and c and combining the bottoms fractions of process steps c) of all process stages.
2. The process as claimed in claim 1, wherein each process stage has a hydroformylation step a), a catalyst removal step b) and a distillation step c), with the proviso that the catalyst separated off in b) is returned, directly or after work-up, to the hydroformylation step a) of the respective process stage.
3. The process as claimed in claim 1, wherein each process stage has a hydroformylation step a), a catalyst removal step b) and, apart from the last process stage, a distillation step c), with the proviso that the catalyst separated off in b) is returned, directly or after work-up, to the



hydroformylation step a) of the respective process stage.

4. The process as claimed in claim 1,
5 wherein
each process step has a hydroformylation step a),
a catalyst removal step b), and the combined
liquid hydroformylation mixtures are separated in
10 a common distillation step c) into a low-boiler
fraction and bottoms fraction, with the proviso
that the catalyst separated off in steps b) is
returned, directly or after work-up, to the
hydroformylation step a) of the respective process
stage.
- 15 5. The process as claimed in claim 1,
wherein
the combined reactor discharges of all
hydroformylation steps a) pass through only one
20 catalyst removal step b) and one distillation step
c), with the proviso that the catalyst separated
off in process step b) is divided, directly or
after work-up, and returned to the
hydroformylation steps a) of the individual
25 process stages.
6. The process as claimed in one of claims 1, 2, 4 or
5,
wherein
30 the paraffins are partially or completely removed
from at least one low-boiler fraction.
7. The process as claimed in one of claims 1, 2, 4 to
6,
35 wherein
the combined bottoms fractions from the
distillation steps c) are hydrogenated.



8. The process as claimed in claim 1, 3 or 6,
wherein
the combined bottoms fractions of distillation
steps c) and the discharge of catalyst removal
5 step b) of the last process stage are
hydrogenated.
9. The process as claimed in one of claims 1, 2, 4 to
6,
10 wherein
the aldehydes present in the combined bottoms
fractions of distillation steps c) are removed by
distillation.
- 15 10. The process as claimed in one of claims 1, 3 or 6,
wherein
the aldehydes present in the combined bottoms
fractions of distillation step c) and in the
discharge of catalyst removal step b) of the last
20 process stage are removed by distillation.
11. The process as claimed in one of claims 1 to 10,
wherein
in each hydroformylation step a) cobalt catalysts
25 are used.
12. The process as claimed in one of claims 1 to 10,
wherein
in each hydroformylation step a) rhodium catalysts
30 are used.
13. The process as claimed in one of claims 1 to 10,
wherein
in the first process stage in the hydroformylation
35 step a) a cobalt catalyst is used and in the
hydroformylation steps a) of the further process
stages a rhodium catalyst is used.



14. The process as claimed in one of claims 1 to 10,
wherein
in the first process stage in the hydroformylation
step a) a rhodium catalyst is used and in the
5 hydroformylation steps a) of the further process
stages a cobalt catalyst is used.
15. The process as claimed in one of claims 1 to 14,
wherein
10 the liquid reactor discharges of hydroformylation
steps a) are homogeneous liquid phases.
16. The process as claimed in one of claims 1 to 15,
wherein
15 the cobalt or rhodium catalyst is dissolved
homogeneously in the liquid reactor discharges of
hydroformylation steps a).
17. The process as claimed in one of claims 1 to 16,
20 wherein
the olefins in the hydroformylation steps a) of
the further process stages which follow the first
process stage are in each case hydroformylated to
a conversion of at least 50%.
- 25 18. The process as claimed in claim 17,
wherein
the olefins in the hydroformylation steps a) of
the further process stages which follow the first
30 process stage are in each case hydroformylated to
a conversion of from 55 to 98%.
19. The process as claimed in one of claims 1 to 18,
which comprises two process stages.

