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# PATENT SPECIFICATION

(11) 1 599 921

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## (54) IMPROVED HYDROFORMYLATION PROCESS

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, whose registered office is 270 Park Avenue, New York, State of New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the rhodium-catalyzed hydroformylation of olefins, particularly alpha-olefins, to produce the corresponding aldehydes; and more particularly to an improved process for the hydroformylation of alpha-olefins to produce the corresponding aldehydes using rhodium catalysts whose stability is improved by the use of alkyl-diarylphosphine ligands.

Processes for forming an aldehyde by the reaction of an olefin with carbon monoxide and hydrogen have been known as hydroformylation processes or oxo processes. For many years, all commercial hydroformylation reactions employed cobalt carbonyl catalysts which required relatively high pressures (often on the order of 100 atmospheres or higher) to maintain catalyst stability.

U.S. Patent No. 3,527,809, issued September 8, 1970 to R. L. Pruett and J. A. Smith, discloses a significantly new hydroformylation process whereby alpha-olefins are hydroformylated with carbon monoxide and hydrogen to produce aldehydes in high yields at low temperatures and pressures, where the normal to iso-(or branched-chain) aldehyde isomer ratio of the product aldehydes is high. This process employs certain rhodium complex catalysts and operates under defined reaction conditions to accomplish the olefin hydroformylation. Since this new process operates at significantly lower pressures than required theretofore in the prior art, substantial advantages were realized including lower initial capital investment and lower operating costs. Further, the more desirable straight-chain aldehyde isomer could be produced in high yields.

The hydroformylation process set forth in the Pruett and Smith patent noted above includes the following essential reaction conditions:

(1) A rhodium complex catalyst which is a complex combination of rhodium with carbon monoxide and a triorganophosphorus ligand. The term "complex" means a coordination compound formed by the union of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which is also capable of independent existence. Triorganophosphorus ligands whose phosphorus atom has one available or unshared pair of electrons are capable of forming a coordinate bond with rhodium.

(2) An alpha-olefin feed of alpha-olefinic compounds characterized by a terminal ethylenic carbon-to-carbon bond such as a vinyl group  $\text{CH}_2=\text{CH}-$ . They may be straight chain or branched chain and may contain groups or substituents which do not essentially interfere with the hydroformylation reaction, and they may also contain more than one ethylenic bond. Propylene is an example of a preferred alpha-olefin.

(3) A triorganophosphorus ligand such as a triarylphosphine. Desirably each organo moiety in the ligand does not exceed 18 carbon atoms. The triarylphosphines are the preferred ligands, an example of which is triphenylphosphine.

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(4) A concentration of the triorganophosphorus ligand in the reaction mixture which is sufficient to provide at least two, and preferably at least 5, moles of free ligand per mole of rhodium metal, over and above the ligand complexed with or tied to the rhodium atom.

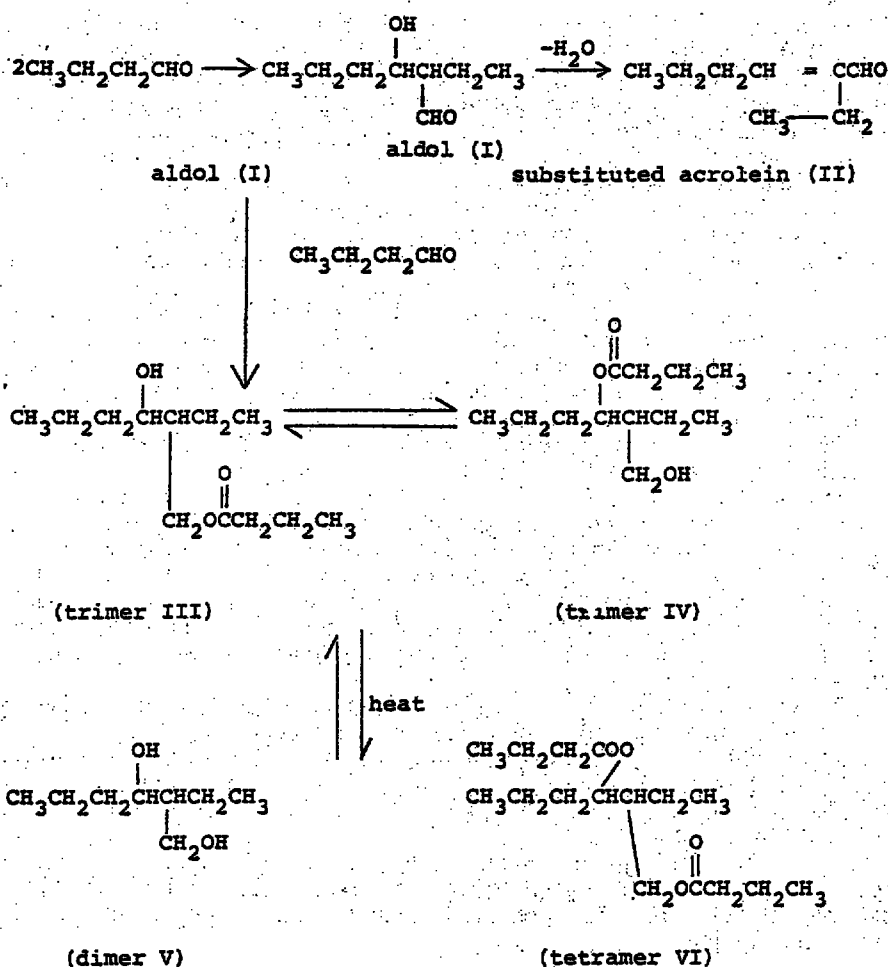
(5) A temperature of from about 50 to about 145°C, preferably from about 60 to about 125°C.

(6) A total hydrogen and carbon monoxide pressure which is less than 450 pounds per square inch absolute (psia), preferably less than 350 psia.

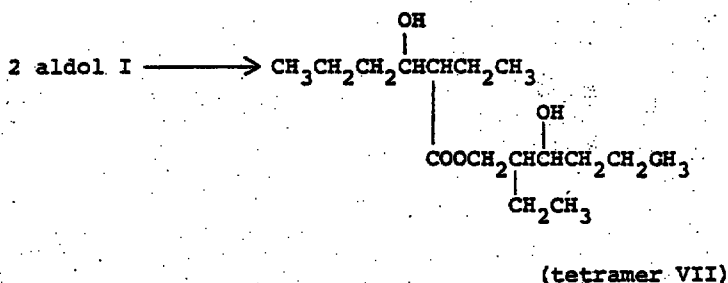
(7) A maximum partial pressure exerted by carbon monoxide no greater than about 75 percent based on the total pressure of carbon monoxide and hydrogen, preferably less than 50 percent of this total gas pressure.

It is known that, under hydroformylation conditions, some of the product aldehydes may condense to form by-product, high boiling aldehyde condensation products such as aldehyde dimers or trimers. British Patent Specification No. 1338237 discloses the use of these high boiling liquid aldehyde condensation products as a reaction solvent for the catalyst. In this process, solvent removal from the catalyst, which may cause catalyst losses, is unnecessary and, in fact, a liquid recycle containing the solvent high boiling aldehyde condensation products and catalyst is fed to the reaction zone from a product recovery zone. It may be necessary to remove a small purge stream to prevent the buildup of such aldehyde condensation products and poisons to the reaction to excessive levels of concentration.

More specifically, as pointed out in British Patent Specification No. 1338237 some of the aldehyde product is involved in various reactions as depicted below using n-butyraldehyde as an illustration:

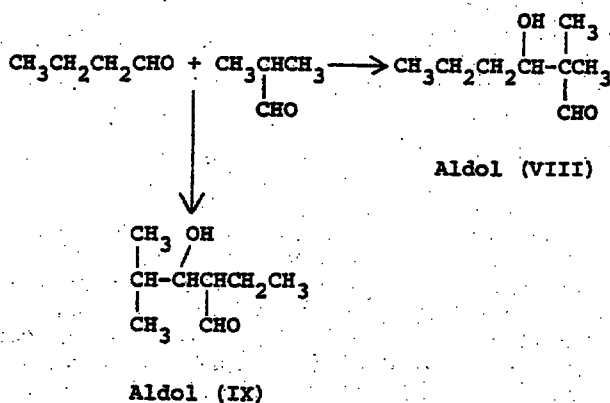


In addition, aldol I can undergo the following reaction:



The names in parentheses in the afore-illustrated equations, aldol I, substituted acrolein II, trimer III, trimer IV, dimer V, tetramer VI, and tetramer VII, are for convenience only. Aldol I is formed by an aldol condensation; trimer III and tetramer VII are formed via Tischenko reactions; trimer IV by a transesterification reaction; dimer V and tetramer VI by a dimerization reaction. Principal condensation products are trimer III, trimer IV, and tetramer VII, with lesser amounts of the other products being present. Such condensation products, therefore, contain substantial quantities of hydroxylic compounds as witnessed, for example, by trimers III and IV and tetramer VII.

Similar condensation products are produced by self-condensation of isobutyraldehyde and a further range of compounds is formed by condensation of one molecule of normal butyraldehyde with one molecule of iso-butyraldehyde. Since a molecule of normal butyraldehyde can aldolize by reaction with a molecule of isobutyraldehyde in two different ways to form two different aldols VIII and IX, a total of four possible aldols can be produced by condensation reactions of a normal/iso mixture of butyraldehydes.



Aldol I can undergo further condensation with isobutyraldehyde to form a trimer isomeric with trimer III and aldols VIII and IX and the corresponding aldol X produced by self-condensation of two molecules of isobutyraldehyde can undergo further reactions with either normal or isobutyraldehyde to form corresponding isomeric trimers. These trimers can react further analogously to trimer III so that a complex mixture of condensation products is formed.

Our copending British Patent Application No. 14742/77 (Serial No. 1,582,010) discloses a liquid phase hydroformylation reaction using a rhodium complex catalyst, wherein the aldehyde reaction products and some of their higher boiling condensation products are removed in vapor form from the catalyst containing liquid body (or solution) at the reaction temperature and pressure. The aldehyde reaction products and the condensation products are condensed out of the off gas from the reaction vessel in a product recovery zone and the unreacted starting materials (e.g., carbon monoxide, hydrogen and/or alpha-olefin) in the vapor phase from the product recovery zone are recycled to the reaction zone. Furthermore, by

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recycling gas from the product recovery zone coupled with make-up starting materials to the reaction zone in sufficient amounts, it is possible, using a C<sub>2</sub> to C<sub>5</sub> olefin as the alpha-olefin starting material, to achieve a mass balance in the liquid body in the reactor and thereby remove from the reaction zone at a rate at least as great as their rate of formation essentially all the higher boiling condensation products resulting from self-condensation of the aldehyde product.

More specifically, according to the above latter application, a process for the production of an aldehyde containing from 3 to 6 carbon atoms is disclosed which comprises passing an alpha-olefin containing from 2 to 5 carbon atoms together with hydrogen and carbon monoxide at a prescribed temperature and pressure through a reaction zone containing the rhodium complex catalyst dissolved in a liquid body, continuously removing a vapor phase from the reaction zone, passing the vapor phase to a product separation zone, separating a liquid aldehyde containing product in the product separation zone by condensation from the gaseous unreacted starting materials, and recycling the gaseous unreacted starting materials from the product separation zone to the reaction zone. Preferably, the gaseous unreacted starting materials plus make-up starting materials are recycled at a rate at least as great as that required to maintain a mass balance in the reaction zone.

It is known in the prior art that rhodium hydroformylation catalysts, such as hydrido carbonyl tris(triphenylphosphine) rhodium, are deactivated by certain extrinsic poisons which may be present in any of the gases fed to the reaction mixture. See, for example, G. Falbe, "Carbon Monoxide in Organic Synthesis", Springer-Verlag, New York, 1970. These poisons (X), termed virulent poisons, are derived from materials such as sulfur-containing compounds (e.g., H<sub>2</sub>S, COS, etc.), halogen-containing compounds (e.g., HCl, etc.), cyano-containing compounds (e.g., HCN, etc.), and the like, and can form Rh-X bonds which are not broken under mild hydroformylation conditions. If one removes such poisons from the materials fed to the reaction mixture, to below 1 part per million (ppm), one would expect therefore that no such deactivation of the catalyst would occur. However, it has been found that such is not the case. For example, when very clean gases (>1 ppm extrinsic poisons) were used in the hydroformylation of propylene and the gas recycle technique discussed above was employed, under the following conditions:

|                                        |     |
|----------------------------------------|-----|
| temperature (°C)                       | 100 |
| CO partial pressure (psia)             | 36  |
| H <sub>2</sub> partial pressure (psia) | 75  |
| olefin partial pressure (psia)         | 40  |
| ligand/rhodium mole ratio              | 94  |

the catalyst activity decreased at a rate of 3% per day (based on the original activity of the fresh catalyst). It appears therefore that even the substantially complete removal of extrinsic poisons does not prevent such catalyst deactivation.

Our Copending British Patent Application No. 2907/78 (Serial No. 1599922), (Docket D-11, 271) filed concurrently herewith, indicates that the deactivation of rhodium hydroformylation catalysts under hydroformylation conditions in the substantial absence of extrinsic poisons is due to the combination of the effects of temperature, phosphine ligand:rhodium mole ratio, and the partial pressures of hydrogen and carbon monoxide and is termed an intrinsic deactivation. It is further disclosed therein that this intrinsic deactivation can be reduced or substantially prevented by establishing and controlling and correlating the hydroformylation reaction conditions to a low temperature, low carbon monoxide partial pressure and high free triarylphosphine ligand:catalytically-active rhodium mole ratio. More specifically, this last mentioned application discloses a rhodium-catalyzed hydroformylation process for producing aldehydes from alpha-olefins containing 2 to 20 carbon atoms including the steps of reacting the olefin with hydrogen and carbon monoxide in the presence of a rhodium complex catalyst consisting essentially of rhodium complexed with carbon monoxide and triphenylphosphine, under certain defined reaction conditions, as follows:

- (1) a temperature of from 90 to 130°C;
- (2) a total gas pressure of hydrogen, carbon monoxide and alpha-olefin of less than 400 psia;
- (3) a carbon monoxide partial pressure of less than 55 psia;
- (4) a hydrogen partial pressure of less than 200 psia;
- (5) at least 100 moles of free triphenylphosphine ligand for each mole of catalytically active rhodium metal present in the rhodium complex catalyst; and

controlling and correlating the partial pressure of carbon monoxide, the temperature and the free triphenylphosphine:catalytically active rhodium mole ratio to limit the rhodium complex catalyst deactivation to a maximum determined percent loss in activity per day, based on the initial activity of the fresh catalyst. By "catalytically active rhodium" is meant the rhodium metal in the rhodium complex catalyst which has not been deactivated. The amount of rhodium in the reaction zone which is catalytically active may be determined at any given time during the reaction by comparing the conversion rate to product based on such catalyst to the conversion rate obtained using fresh catalyst.

The specific relationship between the three parameters (i.e. the carbon monoxide partial pressure, temperature and free triphenylphosphine:catalytically active rhodium mole ratio) and catalyst stability is defined by the formula:

$$F = \frac{1000}{1 + e^y}$$

where

F=stability factor

e=Napierian log base (i.e., 2.718281828)

$y = K_1 + K_2 T + K_3 P + K_4 (L/Rh)$

T=reaction temperature (°C)

P=partial pressure of CO (psia)

L/Rh=free triphenylphosphine:catalytically active rhodium mole ratio

$K_1 = -8.1126$

$K_2 = 0.07919$

$K_3 = 0.0278$

$K_4 = -0.01155$

As pointed out in our copending British Patent Application, No. 2907/78 (Serial No. 1599922), an olefin response factor must be employed to obtain the stability factor under actual hydroformylation conditions. Olefins generally enhance the stability of the catalyst and their effect on catalyst stability is more fully explained in said copending application.

The above relationship is substantially the same for other triarylphosphines, except that the constant  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  may be different. Those skilled in the art can determine the specific constants for other triarylphosphines with a minimum amount of experimentation, such as by repeating Examples 21—30 below with other triarylphosphines.

As can be understood by referring to the above formula, for given conditions of reaction temperature, carbon monoxide partial pressure and free triarylphosphine:catalytically active rhodium mole ratio, the stability factor F can be determined. The stability factor F exhibits a predictive relationship with the rate at which the rhodium complex catalyst is deactivated under hydroformylation conditions.

It has been observed that the presence of an alkyl-diarylphosphine (for example, propyldiphenylphosphine or ethyldiphenylphosphine) in the rhodium-catalyzed hydroformylation of the alpha-olefin propylene inhibits catalyst productivity; i.e., the rate at which the desired product aldehydes are formed. Specifically, the addition of small amounts of propyldiphenylphosphine or ethyldiphenylphosphine to rhodium hydroformylation solutions (i.e., 250 ppm rhodium and 12% by weight triphenylphosphine in a mixture of butyraldehydes and butyraldehyde condensation products) markedly reduced the rate of production of butyraldehydes from propylene, compared to the rate obtained in the absence of the alkyl-diarylphosphines. This is shown by the data in Table I below:

(18)

TABLE I

| Entry | TPP <sup>(1)</sup> Amount<br>(weight % of<br>solution) | PDPP <sup>(2)</sup> or<br>EDPP <sup>(3)</sup> Amount<br>(weight % of<br>solution) | PDPP or<br>EDPP/TPP<br>Ratio | Aldehyde Production Rate<br>(gram-moles/liter-hour)<br>Observed | Aldehyde Production Rate<br>Predicted <sup>(4)</sup> | Comparative<br>Rate of<br>Production (5) |
|-------|--------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------|-----------------------------------------------------------------|------------------------------------------------------|------------------------------------------|
| 1     | 4                                                      | PDPP (0)                                                                          | 0                            | 1.03                                                            | 1.02                                                 | 100                                      |
| 2     | 1.89                                                   | PDPP (2.0)                                                                        | 1.05                         | 0.36                                                            | 1.06                                                 | 34                                       |
| 3     | 3.74                                                   | PDPP (0.67)                                                                       | 0.18                         | 0.53                                                            | 1.02                                                 | 53                                       |
| 4     | 4.06                                                   | PDPP (1.33)                                                                       | 0.33                         | 0.79                                                            | 1.87                                                 | 42                                       |
| 5     | 3.61                                                   | PDPP (1.33)                                                                       | 0.37                         | 1.51                                                            | 3.51                                                 | 43                                       |
| 6     | 4.0                                                    | PDPP (0.05)                                                                       | 0.013                        | 0.62                                                            | 1.02                                                 | 60                                       |
| 7     | 9                                                      | PDPP (1.0)                                                                        | 0.11                         | 0.60                                                            | 0.69                                                 | 87                                       |
| 8     | 6                                                      | PDPP (1.0)                                                                        | 0.17                         | 0.54                                                            | 0.63                                                 | 86                                       |
| 9     | 9                                                      | PDPP (3.0)                                                                        | 0.33                         | 0.54                                                            | 0.72                                                 | 75                                       |
| 10    | 6                                                      | PDPP (3.0)                                                                        | 0.5                          | 0.47                                                            | 0.68                                                 | 68                                       |
| 11    | 9                                                      | PDPP (1.0)                                                                        | 0.11                         | 0.55                                                            | 0.69                                                 | 80                                       |
| 12    | 6                                                      | PDPP (1.0)                                                                        | 0.17                         | 0.58                                                            | 0.63                                                 | 92                                       |
| 13    | 9                                                      | PDPP (3.0)                                                                        | 0.33                         | 0.39                                                            | 0.72                                                 | 54                                       |
| 14    | 6                                                      | PDPP (3.0)                                                                        | 0.5                          | 0.52                                                            | 0.68                                                 | 77                                       |
| 15    | 9                                                      | PDPP (0)                                                                          | 0                            | 0.80                                                            | 0.60                                                 | greater than 100                         |
| 16    | 0                                                      | PDPP (9)                                                                          | ∞                            | 0.273                                                           | 0.60                                                 | 46                                       |
| 17    | 0                                                      | PDPP (4.5)                                                                        | ∞                            | 0.213                                                           | 0.47                                                 | 45                                       |
| 18    | 3.89                                                   | EDPP (0.67)                                                                       | 0.17                         | 0.42                                                            | 1.02                                                 | 42                                       |
| 19    | 3.69                                                   | EDPP (0.67)                                                                       | 0.18                         | 0.42                                                            | 1.02                                                 | 42                                       |
| 20    | 3.88                                                   | EDPP (1.33)                                                                       | 0.34                         | 0.33                                                            | 1.02                                                 | 33                                       |
| 21    | 6.95                                                   | EDPP (0.67)                                                                       | 0.10                         | 0.32                                                            | 0.82                                                 | 39                                       |
| 22    | 6.85                                                   | EDPP (1.33)                                                                       | 0.19                         | 0.24                                                            | 0.82                                                 | 29                                       |

<sup>(1)</sup>TPP=triphenylphosphine<sup>(2)</sup>PDPP=propyldiphenylphosphine<sup>(3)</sup>EDPP=ethyldiphenylphosphine<sup>(4)</sup>Predicted rate determined from a kinetic rate expression  
observed rate<sup>(5)</sup>Comparative Rate of Production =  $\frac{\text{predicted rate for same conditions with same total phosphine but all TPP}}{\text{observed rate}} \times 100$

It has therefore been suggested that the presence of alkyl diaryl phosphines in rhodium-catalyzed hydroformylation processes should be avoided since their presence does significantly reduce the catalyst productivity. It has been unexpectedly found however, that the stability of such rhodium complex catalysts can be significantly enhanced by providing an alkyl diaryl phosphine in the reaction medium. Although this reduces the productivity of the catalyst, the reaction conditions can be adjusted to be more severe in order to regain this apparent loss of catalyst productivity while retaining the enhanced catalyst stability. This is surprising especially in view of our aforementioned copending British Patent Application No. 2907/78 (Serial No. 1599922), which discloses that less severe conditions (e.g., lower temperatures) favor catalyst stability.

The present invention comprises an improved rhodium-catalyzed hydroformylation process for the production of aldehydes from alpha-olefins employing a rhodium complex catalyst, where the stability of the rhodium complex catalyst is improved by providing an amount of an alkyl diaryl phosphine ligand in the catalyst-containing reaction medium. The stability of the rhodium complex catalyst is thus significantly improved.

In its broadest aspects, the present invention is an improvement in a rhodium-catalyzed process for hydroformylating an alpha-olefin containing 2 to 20 carbon atoms to produce aldehydes having one more carbon atom than the alpha-olefin, which process includes the steps of reacting the alpha-olefin with hydrogen and carbon monoxide, in a liquid reaction medium which contains a soluble rhodium complex catalyst consisting essentially of rhodium complexed with carbon monoxide and a triorganophosphine ligand and in the presence of free triarylphosphine ligand wherein the improvement comprises improving the stability of the catalyst by charging the liquid reaction medium containing the catalyst with from 0.1 to 20 percent by weight of an alkyl diaryl phosphine ligand based on the total weight of the liquid reaction medium; and controlling the hydroformylation reaction conditions as follows:

- (1) a temperature of from 100 to 140°C;
- (2) a total gas pressure of hydrogen, carbon monoxide and alpha-olefin of less than 450 psia;
- (3) a carbon monoxide partial pressure of less than 55 psia;
- (4) a hydrogen partial pressure of less than 200 psia;
- (5) at least 75 moles of total free phosphine ligand for each mole of catalytically-active rhodium metal present in the rhodium complex catalyst.

In the process of the invention the amount of the alkyl diaryl phosphine ligand charged to the liquid reaction medium is from 0.1 to 20 percent by weight, based upon the total weight of liquid reaction medium. When a triarylphosphine ligand is employed in the hydroformylation of an alpha-olefin, some alkyl diaryl phosphine is produced *in situ*, the "alkyl" group thereof being derived from the alpha-olefin undergoing hydroformylation and the "aryl" groups thereof being the same as the aryl of the triarylphosphine. The terminology "aryl" is meant to include substituted aryl groups). Therefore, additional alkyl diaryl phosphine is formed in the reaction medium during the course of the hydroformylation reaction. The particular amount of alkyl diaryl phosphine charged to the reaction medium will depend on several factors such as the particular alpha-olefin to be reacted, the reaction conditions, and the desired rate of reaction. Generally, however, amounts falling within the aforementioned range will provide satisfactory results. Particularly advantageous results are achieved when the amount of alkyl diaryl phosphine in the liquid reaction medium is from 0.5 to 10 percent by weight, based on the total weight of the liquid reaction medium, and hence this constitutes the presently preferred embodiment.

When an alkyl diaryl phosphine ligand is present in a liquid reaction medium containing a rhodium complex catalyst consisting essentially of rhodium complexed with carbon monoxide and a triarylphosphine ligand, the resulting rhodium complex catalyst consists essentially of rhodium complexed with carbon monoxide and either one or both of the triarylphosphine ligand and the alkyl diaryl phosphine ligand. The terminology "consists essentially of" is not meant to exclude, but rather is meant to include, species containing hydrogen complexed with the rhodium, in addition to carbon monoxide and triarylphosphine and/or alkyl diaryl phosphine. However, this language is meant to exclude other materials in amounts which poison or deactivate the catalyst. Furthermore, it is not intended to limit the present invention by the above explanation as to which phosphine is tied to or complexed with the rhodium since it is sufficient for purposes of the present

invention to simply provide an amount of alkyl-diarylphosphine in the reaction medium with the triarylphosphine. We do not wish to be bound by any discussion of which phosphine is tied to the rhodium and which is free, although it has been determined that, as between triphenylphosphine and propyldiphenylphosphine, the rhodium exhibits a preference for the latter over the former as to which it is tied or bound to. This catalyst is normally soluble in the liquids which may be used as a solvent in the reaction, and the most desirable catalyst is free of contaminants such as rhodium-bound halogen such as chlorine. The total amount of triarylphosphine and alkyl-diarylphosphine present in the liquid reaction medium is sufficient to provide the above noted minimum number of moles of total free phosphine ligand per mole of catalytically active rhodium metal present in the rhodium complex catalyst. Generally, as long as the total amount of phosphine ligand is sufficient to form the rhodium complex catalyst and to provide this minimum amount of free phosphine, the particular amount of triarylphosphine ligand present in the liquid reaction medium is not particularly critical. As a general rule, the amount of triarylphosphine ligand present in the reaction medium may vary from 0.5 percent to 40 percent by weight, based on the total weight of the liquid reaction medium.

Particularly advantageous results are achieved when the amount of total free phosphine ligand in the liquid reaction medium is at least 100 moles, e.g. up to 500 moles, per mole of catalytically-active rhodium metal present in the rhodium complex catalyst. The upper limit of the amount of total free phosphine ligand is not particularly critical and would be dictated largely by commercial and economic considerations. Higher mole ratios of total free phosphine:catalytically-active rhodium metal favor the stability of the catalyst. By "total free phosphine" is meant the triarylphosphine and/or alkyl-diarylphosphine that is not tied to or complexed with the rhodium atom in the active complex catalyst. The theory of how such ligands complex with the rhodium is given in said U.S. Patent No. 3,527,809.

Illustrative triarylphosphine ligands are triphenylphosphine, tris(naphthyl)phosphine, tritolylphosphine, tri(p-biphenyl) phosphine, tri(p-methoxyphenyl) phosphine, and p-N,N-dimethylaminophenyl bis-phenylphosphine. Triphenylphosphine is the presently preferred triarylphosphine ligand.

Illustrative alkyl-diarylphosphine ligands are methyldiphenylphosphine, ethyldiphenylphosphine, propyldiphenylphosphine, butyldiphenylphosphine, ethyl-bis(p-methoxyphenyl) phosphine, ethyl-phenyl-p-biphenyl phosphine, methyl-phenyl-p(N,N-dimethylaminophenyl) phosphine, propyl-phenyl-p(N,N-dimethylaminophenyl) phosphine, ethyl-bis(tolyl) phosphine, butyl-bis(tolyl) phosphine, methyl-bis(naphthyl) phosphine, propyl-bis(naphthyl) phosphine, propyl-bis(p-methoxyphenyl) phosphine, and butyl-bis(p-methoxyphenyl) phosphine. Propyldiphenylphosphine is the presently preferred alkyl-diarylphosphine ligand.

The rhodium complex catalyst composed of rhodium complexed with hydrogen, carbon monoxide and triarylphosphine may be formed by methods known in the art. For example, a preformed stable crystalline solid of rhodium hydridocarbonyl-tris(triphenylphosphine),  $\text{RhH}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ , may be introduced into the reaction medium. This material may be formed for example, by a method disclosed in Brown, et al, *Journal of the Chemical Society*, 1970, pages 2753-2764. Alternatively, a rhodium catalyst precursor such as  $\text{Rh}_2\text{O}_3$ ,  $\text{Rh}_4(\text{CO})_{12}$ , or  $\text{Rh}_6(\text{CO})_{18}$  and the like may be introduced into the reaction medium. In a preferred embodiment rhodium carbonyl triphenylphosphine acetylacetonate or rhodium dicarbonyl acetylacetonate is employed. In either event, the active rhodium complex catalyst is formed in the reaction medium under the conditions of hydroformylation. It is also possible to preform a rhodium complex catalyst which contains both triarylphosphine and alkyl-diarylphosphine complexed with the rhodium.

The amount of catalyst present in the reaction medium should be as a minimum that amount which is necessary to catalyze the hydroformylation of the alpha-olefin to form the product aldehydes. Generally, the rhodium concentration in the reaction medium can range from about 25 ppm to about 1200 ppm, preferably about 50 ppm to about 400 ppm, of catalytically active rhodium calculated as the free metal.

The process of the present invention can be applied in the hydroformylation of alpha-olefins having up to 20 carbon atoms. The process of the present invention is particularly useful for the hydroformylation of alpha-olefins having from 2 to 5 carbon atoms, including ethylene, propylene, 1-butene and 1-pentene, and

therefore this constitutes a preferred embodiment. The process of the present invention is especially useful for the hydroformylation of propylene to form butyraldehydes having a high normal to iso ratio; i.e. the butyraldehyde which predominates in the product is the normal butyraldehyde, and hence this presently constitutes the most preferred embodiment. The alpha-olefins used in the process of the invention may be straight-chain or branched-chain and may contain groups or substituents which do not essentially interfere with the course of the hydroformylation reaction.

The amount of olefin fed to the reaction depends on several factors, such as the size of the reactor, the temperature of reaction, the total pressure, and the amount of catalyst. In general, the higher the olefin concentration is in the reaction medium, the lower usually will be the catalyst concentration that can be used to achieve a given conversion rate to aldehyde products in a given size of reactor. Since partial pressures and concentration are related, the use of higher olefin partial pressure leads to an increased proportion of the olefin in the product stream leaving the reaction mixture. Further, since some amount of saturated hydrocarbon may be formed by hydrogenation of the olefin, it may be necessary to purge part of the product gas stream in order to remove this saturated product before any recycle to the reaction zone, and this would be a source of loss for the unreacted olefin contained in the product gas stream. Hence, it is necessary to balance the economic value of the olefin lost in such a purge stream against the economic savings associated with lower catalyst concentration.

The temperature of reaction, as noted above, may vary from 100 to 140°C, with the lower temperatures favoring catalyst stability and the higher temperatures favoring higher rates of reaction. The particular temperature employed in the reaction will of course depend upon the desired stability and rate of reaction, but generally, by controlling the temperature within this range, the advantages of the present invention can be attained.

A substantial advantage of the process disclosed in U.S. Patent No. 3,527,809 is the low total pressure of hydrogen and carbon monoxide required to conduct the hydroformylation reaction. The process of the present invention operates at a low total pressure of hydrogen, carbon monoxide and alpha-olefin of less than 450 psia, preferably less than 350 psia. The minimum total pressure of these gases is not particularly critical and is limited predominantly only by the amount of reaction gases necessary to obtain the desired rate of reaction.

The make-up gases fed to the reaction medium would include the olefin, carbon monoxide and hydrogen, usually. As pointed out previously, extrinsic poisons such as sulfur and sulfur-containing compounds, as well as halogens and halogen-containing compounds, should be excluded from the make-up gases, since it is known that such materials poison the catalyst and can deactivate the catalyst rather rapidly. Hence, it is desirable to reduce the amount of such poisons in all gases fed to the reaction. Of course, the amount of such poisons that can be tolerated is determined by the maximum acceptable rate of loss of activity of the catalyst. If it is possible to permit some small amount of such poisons and still obtain a catalyst of desired stability, then such small amounts can be tolerated. It is generally desirable to reduce the amounts of such poisons in the make-up gases to below one part per million. This can be accomplished by methods known in the art.

Hydrogen does have some effect on catalyst deactivation. According to the process of the invention, the partial pressure of hydrogen should be less than 200 psia, and preferably it should range from 20 to 200 psia. Of course, the particular value will be determined depending upon the desired stability and rate of reaction and the relationship of the hydrogen partial pressure to the carbon monoxide partial pressure, as discussed below.

The partial pressure of carbon monoxide has a significant effect on the stability of the catalyst, and should be less than 55 psia. Of course, the particular partial pressure employed will depend upon the desired stability and rate of reaction. As a general rule, lower carbon monoxide partial pressures provide more stable catalysts. It is preferred according to the process of the invention that the partial pressure of carbon monoxide be from 1 psia to 50 psia. The minimum partial pressure of carbon monoxide is not critical in that it is limited predominantly only by the desired rate of reaction and the possibility of olefin hydrogenation occurring.

It is disclosed in U.S. Patent No. 3,527,809 that the normal to iso aldehyde isomer ratio of the aldehyde products decreases as the partial pressure of carbon monoxide increases relative to the hydrogen partial pressure. Similarly, in the

process of the present invention, the partial pressure of carbon monoxide relative to the partial pressure of hydrogen has an effect on the isomer ratio of the product aldehydes. Generally, to obtain the more desirable normal aldehyde isomer, the ratio of partial pressures of hydrogen:carbon monoxide should be at least 2:1, preferably at least 8:1. As long as the partial pressures of each of carbon monoxide and hydrogen are controlled within the limits described above, there is no critical ratio of the hydrogen:carbon monoxide partial pressures.

The time of reaction, or residence period of the olefin in the reaction zone, is that time which is sufficient to hydroformylate the alpha-ethylenic bond of the alpha-olefin. As a general rule, the residence period in the reaction zone can vary from about several minutes to several hours in duration and as is apparent, this variable will be influenced, to a certain extent, by the reaction temperature, the choice of alpha-olefin and catalyst, the concentration of total free phosphine ligand, the total pressure, the partial pressure exerted by carbon monoxide and hydrogen, the conversion rate and other factors. As a general rule, it is desirable to achieve the highest possible conversion rate for the smallest amount of catalyst employed. Of course, the ultimate determination of a conversion rate is influenced by many factors including the economics of the process. A substantial advantage of the present invention is that catalyst stability is greatly improved while obtaining excellent conversion rates over prolonged periods of time.

It is preferred to effect the process of the invention in a liquid phase in the reaction zone which contains the rhodium complex catalyst and, as a solvent therefore, the higher boiling liquid aldehyde condensation products.

By the term "higher boiling liquid aldehyde condensation products" as used herein is meant the complex mixture of high boiling liquid products which result from the condensation reactions of some of the aldehyde products of the process of the invention as illustrated hereinabove. Such condensation products can be preformed or produced *in situ* in the present process. The rhodium complex catalyst is soluble in these relatively high boiling liquid aldehyde condensation products while exhibiting excellent stability over extended periods of continuous hydroformylation. In a preferred form of the process of the invention the higher boiling liquid aldehyde condensation products to be used as solvents are preformed prior to introduction into the reaction zone and the start-up of the process. It is also preferred to maintain the condensation products illustrated by acrolein II above, and its isomers, at low concentrations in the reaction medium, such as below about 5 weight percent based on the total weight of the reaction medium.

These higher boiling liquid aldehyde condensation products are more fully described, and methods for preparing the same are more fully described, in British Patent Specification No 1,338,237 and reference can be made to this patent specification for a more detailed description.

It is also preferred according to the process of the invention to employ the gas recycle technique described in our copending British Patent Application No. 14742/77 (Serial No. 1582010). This gas recycle process is broadly described above. If the aforementioned higher boiling liquid aldehyde condensation products are employed as the reaction solvent, the liquid body in the reaction zone will comprise a homogeneous mixture containing the soluble catalyst, free phosphine ligand, the solvent, the product aldehydes and the reactants, alpha-olefin, carbon monoxide and hydrogen.

The relative proportion of each reaction product in solution is controlled by the amount of gas passing through the solution. Increasing this amount decreases the equilibrium aldehyde concentration and increases the rate of by-product removal from solution. The by-products include the higher boiling liquid aldehyde condensation products. The decreased aldehyde concentration leads to a reduction in the rate of formation of the by-products.

The dual effect of increased removal rate and decreased formation rate means that the mass balance in by-products in the reactor is very sensitive to the amount of gas passing through the liquid body. The gas cycle typically includes make-up quantities of hydrogen, carbon monoxide and alpha-olefin. However, the most meaningful factor is the amount of recycle gas returned to the liquid body since this determines the degree of reaction, the amount of product formed and the amount of by-product (as a consequence) removed.

Operation of the hydroformylation reaction with a given flow rate of olefin and synthesis gas (i.e., carbon monoxide and hydrogen) and with a total low amount of gas recycle less than a critical threshold rate results in a high equilibrium aldehyde concentration in solution and hence, in high by-product formation rates.

The rate of removal of by-products in the vapor phase effluent from the reaction zone (liquid body) under such conditions will be low because the low vapor phase effluent flow rate from the reaction zone can only result in a relatively low rate of carry-over of by-products. The net effect is a build-up of by-products in the liquid body solution causing an increase in the solution volume with a consequent loss of catalyst productivity. A purge must therefore be taken from the solution when the hydroformylation process is operated under such low gas flow rate conditions in order to remove by-products and hence maintain a mass balance over the reaction zone.

If however, the gas flow rate through the reaction zone is increased by increasing the gas recycle rate the solution aldehyde content falls, the by-product formation rate is decreased and by-product removal rate in the vapor phase effluent from the reaction zone is increased. The net effect of this change is to increase the proportion of the by-products removed with vapor phase effluent from the reaction zone. Increasing the gas flow rate through the reaction zone still further by a further increase in the gas recycle rate leads to a situation in which by-products are removed in the vapor phase effluent from the reaction zone at the same rate as they are formed, thus establishing a mass balance over the reaction zone. This is the critical threshold gas recycle rate which is the preferred minimum gas recycle rate used in the process of the invention. If the process is operated with a gas recycle rate higher than this threshold gas recycle rate the volume of the liquid body in the reaction zone will tend to decrease and so, at gas recycle rates above the threshold rate, some of the crude aldehyde by-product mixture should be returned to the reaction zone from the product separation zone in order to keep constant the volume of the liquid phase in the reaction zone.

The critical threshold gas recycle flow rate can be found by a process of trial and error for a given olefin and synthesis gas (the mixture of carbon monoxide and hydrogen) feed rate. Operating at recycle rates below the critical threshold rates will increase the volume of the liquid phase with time. Operating at the threshold rate keeps the volume constant. Operating above the threshold rate decreases the volume. The critical threshold gas recycle rate can be calculated from the vapor pressures at the reaction temperature of the aldehyde or aldehydes and of each of the by-products present.

With the process operating at a gas recycle rate at or greater than the threshold rate, by-products are removed in the gaseous vapors removed from the reaction zone containing the liquid body at the same rate as or faster than they are formed, and thus do not accumulate in the liquid phase in the reaction zone. Under such circumstances, it is unnecessary to purge the liquid body containing the catalyst from the reaction zone in order to remove by-products.

A by-product of the hydroformylation process is the alkane formed by hydrogenation of the alpha-olefin. Thus, for example, in the hydroformylation of propylene a by-product is propane. A purge stream may be taken from the gas recycle stream from the product recovery zone in order to remove propane and prevent its build-up within the reaction system. This purge stream will contain, in addition to unwanted propane, unreacted propylene, any inert gases introduced in the feedstock and a mixture of carbon monoxide and hydrogen. The purge stream can, if desired, be submitted to conventional gas separation techniques, e.g. cryogenic techniques, in order to recover the propylene, or it may be used as a fuel. The composition of the recycle gas is principally hydrogen and propylene. However, if the carbon monoxide is not all consumed in the reaction, the excess carbon monoxide will also be part of the recycle gas. Usually the recycle gas will contain alkane even with purging before recycle.

The preferred gas recycle is further illustrated with reference to the accompanying drawing which schematically shows a diagrammatic flowsheet suitable in practising the preferred recycle process of the invention.

Referring to the drawing, a stainless steel reactor 1 is provided with one or more disc impellers 6 having perpendicularly mounted blades and rotated by means of shaft 7, by a suitable motor (not shown). Located below the impeller 6 is a circular tubular sparger 5 for feeding the alpha-olefin, and synthesis gas plus the recycle gas. The sparger 5 contains a plurality of holes of sufficient size to provide sufficient gas flow into the liquid body at about the impeller 6 to provide the desired amount of the reactants in the liquid body. The reactor is also provided with a steam jacket (not shown) by means of which the contents of the vessel can be brought up to reaction temperature at start-up and internal cooling coils (not shown).

Vaporous product effluent from the reactor 1 is removed via line 10 to separator 11 where they are passed through a demisting pad 11a therein to return some aldehyde and condensation product and to prevent potential carry-over of catalyst. The reaction effluent is passed by line 13 to a condenser 14 and then through line 15 to catchpot 16 in which the aldehyde product and any by-product can be condensed out of the off gases (effluent). Condensed aldehyde and by-products are removed from the catchpot 16 by line 17. Gaseous materials are passed via line 18 to separator 19 containing a demisting pad and recycle line 20. Recycle gases are removed by line 21 to line 8 from which a purge through line 22 is pulled to control saturated hydrocarbon content and maintain desirable system pressure. The remaining and major proportion of the gases can be recycled via line 8 to line 4 into which is fed make-up reactant feeds through lines 2 and 3. The combined total of reactants are fed to the reactor 1. Compressor 26 aids in transporting the recycle gases.

Fresh catalyst solution can be added to the reactor 1 by line 9. The single reactor 1 can, of course, be replaced by a plurality of reactors.

The crude aldehyde product of line 17 can be treated by conventional distillation to separate the various aldehydes and the condensation products. A portion of the crude can be recycled to reactor 1 through line 23 and fed as indicated by broken-line 25 to a point above impeller 6 for the purpose of maintaining the liquid level in reactor 1 if such is required.

As pointed out above, the most preferred embodiment of the present invention is the hydroformylation of the alpha-olefin propylene to produce butyraldehydes which are predominantly normal. The stability of the rhodium complex catalyst is enhanced by the techniques of the invention, and in the case of propylene, the reaction is controlled within the following conditions:

temperature: 100 to 140°C

total gas pressure of hydrogen, carbon monoxide and propylene: less than 450 psia

carbon monoxide partial pressure: 1 to 40 psia

hydrogen partial pressure: 20 to 200 psia

total free phosphine: catalytically-active rhodium mole ratio: 75 to 500

triarylphosphine:triphenylphosphine

alkyldiarylphosphine:propyldiphenylphosphine.

#### EXAMPLES 1—30

The procedure employed in all of these Examples was the same, and was as follows. Into a stainless steel reactor was charged a rhodium hydroformylation solution of an amount of rhodium as rhodium carbonyl triphenylphosphine acetylacetonate and the amounts of triphenylphosphine and propyldiphenylphosphine shown in Table II below, in a mixture of butyraldehyde and butyraldehyde trimers (predominantly, 3 - hydroxy - 2,2,4 - trimethyl - pentylisobutyrate). An equimolar mixture of propylene, carbon monoxide and hydrogen was charged to the reactor at a standard total pressure of less than 450 pounds per square inch absolute, and the rate ( $r_1$ ) of butyraldehyde formation at 100°C was determined by measuring the time required for a given pressure drop in the reactor.

Following reaction, the gases were removed from the reactor and replaced with a mixture of hydrogen and carbon monoxide at the partial pressures indicated in Table II in order to cause deactivation of the catalyst. The reactor containing the same was heated for about 3 hours at the temperature indicated in Table II. The gases were vented and an equimolar mixture of propylene, carbon monoxide and hydrogen was again charged to the reactor and a second hydroformylation run was conducted at the same temperature as the first run. A second rate ( $r_2$ ) of butyraldehyde production was determined in the same manner as above. The results are shown in Table II below.

Examples 1—20 are within the scope of the present invention and illustrate the improved stability obtained by the provision of an alkyldiarylphosphine in the reaction medium. Examples 21—30 are for purposes of comparison since no alkyldiarylphosphine was employed.

TABLE II

| Example | Reaction Temperature (°C) | Partial Pressures (psia) |                | Amount of Rh as free metal (ppm) | Total Amount of Ligand (% by weight) |                     | L/Rh <sup>(3)</sup> | Activity (%) <sup>(4)</sup> |          |
|---------|---------------------------|--------------------------|----------------|----------------------------------|--------------------------------------|---------------------|---------------------|-----------------------------|----------|
|         |                           |                          |                |                                  |                                      |                     |                     |                             |          |
|         |                           | CO                       | H <sub>2</sub> |                                  | TPP <sup>(1)</sup>                   | PDPP <sup>(2)</sup> |                     | Predicted                   | Observed |
| 1       | 115                       | 60                       | 90             | 150                              | 5                                    | 2                   | 191                 | 39                          | 77.2     |
| 2       | 115                       | 40                       | 90             | 200                              | 7.5                                  | 4                   | 238                 | 66                          | 87.9     |
| 3       | 115                       | 40                       | 90             | 150                              | 5                                    | 4                   | 251                 | 69                          | 99.3     |
| 4       | 115                       | 60                       | 90             | 200                              | 7.5                                  | 2                   | 192                 | 39                          | 90.9     |
| 5       | 125                       | 60                       | 70             | 150                              | 7.5                                  | 2                   | 258                 | 38                          | 73.1     |
| 6       | 125                       | 40                       | 70             | 200                              | 5.0                                  | 4                   | 180                 | 30                          | 94.1     |
| 7       | 125                       | 40                       | 70             | 150                              | 7.5                                  | 4                   | 316                 | 68                          | 90.2     |
| 8       | 125                       | 60                       | 70             | 200                              | 5                                    | 2                   | 143                 | 14                          | 77       |
| 9       | 115                       | 40                       | 90             | 150                              | 5                                    | 4                   | 251                 | 69                          | 99       |
| 10      | 120                       | 60                       | 80             | 175                              | 6                                    | 3                   | 212                 | 62                          | 83.6     |
| 11      | 120                       | 60                       | 80             | 150                              | 6                                    | 2                   | 217                 | 63                          | 85.9     |
| 12      | 125                       | 50                       | 70             | 175                              | 5.0                                  | 3                   | 190                 | 53                          | 74.6     |
| 13      | 130                       | 45                       | 97.5           | 266                              | 9.0                                  | 1.0                 | 150                 | 35                          | 53.3     |
| 14      | 130                       | 65                       | 97.5           | 187                              | 6.0                                  | 1.0                 | 150                 | 24                          | 37.9     |
| 15      | 130                       | 65                       | 97.5           | 326                              | 9.0                                  | 3                   | 150                 | 24                          | 31.0     |
| 16      | 130                       | 45                       | 97.5           | 248                              | 6.0                                  | 3                   | 156                 | 35.5                        | 48.6     |
| 17      | 120                       | 65                       | 97.5           | 266                              | 9.0                                  | 1.0                 | 150                 | 41                          | 81.4     |
| 18      | 120                       | 45                       | 97.5           | 187                              | 6.0                                  | 1.0                 | 150                 | 55                          | 75.5     |
| 19      | 120                       | 45                       | 97.9           | 326                              | 9.0                                  | 3.0                 | 150                 | 55                          | 82.7     |
| 20      | 120                       | 65                       | 97.5           | 248                              | 6.0                                  | 3.0                 | 150                 | 41.0                        | 76.3     |
| 21      | 130                       | 40                       | 160            | 389                              | 2.5                                  | 0                   | 25                  | 13.0                        | 14.2     |
| 22      | 130                       | 40                       | 160            | 275                              | 2.5                                  | 0                   | 36                  | 14.5                        | 14.6     |
| 23      | 110                       | 40                       | 160            | 275                              | 0.3                                  | 0                   | 8                   | 37                          | 2.3      |
| 24      | 100                       | 40                       | 160            | 250                              | 5.0                                  | 0                   | 78                  | 75                          | 72.8     |
| 25      | 100                       | 20                       | 160            | 250                              | 5.0                                  | 0                   | 78                  | 84                          | 78.5     |
| 26      | 90                        | 10                       | 80             | 158                              | 1.0                                  | 0                   | 25                  | 89                          | 91       |
| 27      | 120                       | 10                       | 80             | 628                              | 4.0                                  | 0                   | 25                  | 43                          | 40.7     |
| 28      | 90                        | 55                       | 80             | 622                              | 4.0                                  | 0                   | 25                  | 70                          | 75.4     |
| 29      | 90                        | 10                       | 160            | 78                               | 2.0                                  | 0                   | 100                 | 95                          | 89.3     |
| 30      | 120                       | 35                       | 70             | 78                               | 2.0                                  | 0                   | 100                 | 47                          | 44.9     |

<sup>(1)</sup> TPP=triphenylphosphine<sup>(2)</sup> PDPP=propyldiphenylphosphine<sup>(3)</sup> L/Rh=total phosphine/rhodium metal mole ratio<sup>(4)</sup> % Activity=( $r_2/r_1$ ) $\times 100$

The predicted activity values given in Table II were derived using the stability formula given above which is disclosed in our copending British Patent Application No 2906/78 (Serial No. 1599922), filed concurrently herewith. The data in Table II indicate a marked improvement in catalyst stability when propyldiphenylphosphine is present, as can be seen by comparing the higher observed percent activity values in comparison to the predicted percent activities for each Example.

#### EXAMPLES 31-37

The procedure for each of these Examples was substantially the same and was as follows. A hydroformylation reaction was conducted in a stainless steel reactor using various alkylidiphenylphosphines in the same manner as in Examples 1-30. The initial partial pressures of the reactants propylene, carbon monoxide and hydrogen were the same in each Example. The rate of butyraldehyde formation was determined at several times during the reaction, and the results are shown in Table III below.

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TABLE III

| Example | TPP/Rh <sup>(1)</sup> | R <sup>(2)</sup> | Rate of Butyraldehyde Formation<br>(gram-moles/liter-hour) |  |  | End of Reaction<br>at | RDPP/Rh <sup>(3)</sup> | Maximum | End of Reaction<br>at | (% Activity) <sup>(4)</sup> | % Activity<br>Extrapolation<br>to 60 min |
|---------|-----------------------|------------------|------------------------------------------------------------|--|--|-----------------------|------------------------|---------|-----------------------|-----------------------------|------------------------------------------|
|         |                       |                  |                                                            |  |  |                       |                        |         |                       |                             |                                          |
| 31      | 20                    | —                |                                                            |  |  | 1.73                  | 0                      | 3.73    |                       | 46                          | 35.3                                     |
| 32      | 15                    | Methyl           |                                                            |  |  | .47                   | 5                      | .58     |                       | 80                          | 82                                       |
| 33      | 15                    | Ethyl            |                                                            |  |  | .93                   | 5                      | 1.31    |                       | 71                          | 66                                       |
| 34      | 15                    | Propyl           |                                                            |  |  | 1.06                  | 5                      | 1.35    |                       | 79                          | 74                                       |
| 35      | 15                    | Butyl            |                                                            |  |  | 1.04                  | 5                      | 1.52    |                       | 68                          | 64                                       |
| 36      | 24                    | Propyl           |                                                            |  |  | .834                  | 8                      | .836    |                       | 99                          | 94 or higher                             |
| 37      | 30                    | Propyl           |                                                            |  |  | .845                  | 5                      | .848    |                       | 98                          | 94 or higher                             |

<sup>(1)</sup> TPP/Rh = total triphenylphosphine/rhodium metal mole ratio<sup>(2)</sup> R = alkyl of alkylidiphenylphosphine<sup>(3)</sup> RDPP/Rh = total alkylidiphenylphosphine/rhodium metal mole ratio<sup>(4)</sup> % Activity =  $(r_2/r_1) \times 100$ , where  $r_1$  and  $r_2$  are the rates of butyraldehyde formation at the beginning and end of reaction, respectively.

As can be seen from Table III, particularly by comparing Examples 32—37 with Example 31, the provision of an alkylidiphenylphosphine ligand in the reaction medium enhances the stability of the catalyst.

#### EXAMPLES 38—45

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These examples were conducted in the same manner as Examples 31—37 except that the ligand used was an alkylidiphenylphosphine only in Examples 38—42 and 45 and a triarylphosphine only in Examples 43 and 44. The present invention is not intended to include the use of each of these ligands alone. The results are shown in Table IV below:

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TABLE IV

Rate of Butyraldehyde Formation  
(gram-moles/liter-hour)

| Example | R <sup>(1)</sup> | L/Rh <sup>(2)</sup> | Amount of<br>rhodium as<br>free metal<br>(ppm) | Reaction<br>Temperature<br>(°C) | Maximum<br>Rate | Rate at<br>1 hour | % <sup>(3)</sup> |
|---------|------------------|---------------------|------------------------------------------------|---------------------------------|-----------------|-------------------|------------------|
| 38      | Methyl           | 10.1                | 250                                            | 125                             | 1.43            | 1.26              | 88               |
| 39      | Ethyl            | 10                  | 250                                            | 100                             | 0.87            | 0.85              | 98               |
| 40      | n-Propyl         | 10                  | 250                                            | 100                             | 0.95            | 0.88              | 93               |
| 41      | iso-Propyl       | 9.9                 | 250                                            | 100                             | 3.24            | 1.85              | 57               |
| 42      | n-Butyl          | 10.6                | 250                                            | 100                             | 0.63            | 0.56              | 89               |
| 43      | Phenyl           | 10                  | 250                                            | 80                              | 1.71            | 0.97              | 56               |
| 44      | Phenyl           | 15                  | 150                                            | 80                              | .95             | .68               | 72               |
| 45      | Methyl           | 10                  | 250                                            | 120                             | .84             | .83               | 99               |

<sup>(1)</sup>R=same as in Table II<sup>(2)</sup>L/Rh=same as in Table II<sup>(3)</sup>%=(rate at 1 hour/maximum rate)×100

## WHAT WE CLAIM IS:—

1. In a process for hydroformylating an alpha-olefin containing 2 to 20 carbon atoms to produce aldehydes having one more carbon atom than the alpha-olefin by reacting the alpha-olefin with hydrogen and carbon monoxide in a liquid reaction medium which contains a soluble rhodium complex catalyst consisting essentially of rhodium complexed with carbon monoxide and a triorganophosphine ligand, and in the presence of free triarylphosphine, the improvement comprising improving the stability of the catalyst by charging the liquid reaction medium containing the catalyst with from 0.1 to 20 percent by weight of an alkyl-diarylphosphine ligand based on the total weight of the liquid reaction medium, and controlling the reaction conditions to a temperature of from 100 to 140°C, a total gas pressure of hydrogen, carbon monoxide and alpha-olefin of less than 450 pounds per square inch absolute, a carbon monoxide partial pressure of less than 55 pounds per square inch absolute, a hydrogen partial pressure of less than 200 pounds per square inch absolute, and at least 75 moles of total free phosphine ligand for each mole of catalytically-active rhodium metal present in the rhodium complex catalyst which consists essentially of rhodium complexed with carbon monoxide and one or both of said triarylphosphine and said alkyl-diarylphosphine.

2. The process of Claim 1 wherein the amount of alkyl-diarylphosphine charged to the liquid reaction medium is from 0.5 to 10 percent by weight, based on the total weight of the liquid reaction medium.

3. The process of Claim 1 or Claim 2 wherein said alpha-olefin has from 2 to 5 carbon atoms.

4. The process of any one of Claims 1 to 3, wherein said alpha-olefin is propylene.

5. The process of any one of Claims 1 to 3, wherein said alpha-olefin is ethylene.

6. The process of any one of Claims 1 to 3, wherein said alpha-olefin is 1-butene.

7. The process of any one of Claims 1 to 6, wherein said triarylphosphine is triphenylphosphine.

8. The process of any one of Claims 1 to 7, wherein the partial pressure of carbon monoxide is from 1 to 50 pounds per square inch absolute.

9. The process of any one of Claims 1 to 8, wherein the total free phosphine:catalytically-active rhodium metal mole ratio is at least 100.

10. The process of any one of Claims 1 to 9, wherein the total gas pressure of hydrogen, carbon monoxide and alpha-olefin is less than 350 pounds per square inch absolute.

11. The process of any one of Claims 1 to 10, wherein the partial pressure of hydrogen is from 20 to 200 pounds per square inch absolute.

12. The process of any one of Claims 1 to 11, wherein the ratio of the partial pressures of hydrogen:carbon monoxide is at least 2:1.

13. The process of any one of claims 1 to 12 wherein the ratio of the partial pressures of hydrogen:carbon monoxide is at least 8:1.

14. The process of any one of claims 1 to 13 wherein said catalyst is dissolved in a solvent which comprises the high boiling liquid condensation products of said aldehydes.

15. The process of claim 1 conducted substantially as herein described and exemplified.

16. Aldehydes whenever made by a process according to any one of the preceding claims.

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