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(54) Title: IMPROVED METAL-LIGAND COMPLEX CATALYZED PROCESSES

(57) Abstract

This invention relates to a process which comprises reacting one or more reactants in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, wherein said process is conducted at a carbon monoxide partial pressure such that reaction rate increases as carbon monoxide partial pressure decreases and reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

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IMPROVED METAL-LIGAND COMPLEX CATALYZED PROCESSES

Brief Summary of the Invention

Technical Field

This invention relates to an improved metal-organopolyphosphite ligand complex catalyzed hydroformylation process directed to producing aldehydes. More particularly, this invention relates to conducting the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst and one or more process parameters sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

Background of the Invention

It is well known in the art that aldehydes may be readily produced by reacting an olefinically unsaturated compound with carbon monoxide and hydrogen in the presence of a rhodium-organophosphite ligand complex catalyst and that preferred processes involve continuous hydroformylation and recycling of the catalyst solution such as disclosed, for example, in U.S. Patent Nos. 4,148,830; 4,717,775 and 4,769,498. Such aldehydes have a wide range of known utility and are useful, for example, as intermediates for hydrogenation to aliphatic alcohols, for aldol condensation to produce plasticizers, for oxidation to produce aliphatic acids, etc.

However, notwithstanding the benefits attendant with such rhodium-organophosphite ligand complex catalyzed hydroformylation processes, stabilization of the catalyst and

organophosphite ligand remains a primary concern of the art. Obviously catalyst stability is a key issue in the employment of any catalyst. Loss of catalyst or catalytic activity due to undesirable reactions of the highly expensive rhodium catalysts can be detrimental to the production of the desired aldehyde. Likewise degradation of the organophosphite ligand employed during the hydroformylation process can lead to poisoning organophosphite compounds or inhibitors or acidic byproducts that can lower the catalytic activity of the rhodium catalyst. Moreover, production costs of the aldehyde product obviously increase when productivity of the catalyst decreases.

Numerous methods have been proposed to maintain catalyst and/or organophosphite ligand stability. For instance, U.S. Patent No. 5,288,918 suggests employing a catalytic activity enhancing additive such as water and/or a weakly acidic compound; U.S. Patent No. 5,364,950 suggests adding an epoxide to stabilize the organophosphite ligand; and U.S. Patent No. 4,774,361 suggests carrying out the vaporization separation employed to recover the aldehyde product from the catalyst in the presence of an organic polymer containing polar functional groups selected from the class consisting of amide, ketone, carbamate, urea, and carbonate radicals in order to prevent and/or lessen rhodium precipitation from solution as rhodium metal or in the form of clusters of rhodium. Notwithstanding the value of the teachings of said references, the search for alternative methods and hopefully an even better and more efficient means for stabilizing the rhodium catalyst and organophosphite ligand employed remains an ongoing activity in the art.

For instance, a major cause of organophosphite ligand degradation and catalyst deactivation of rhodium-organophosphite ligand complex catalyzed hydroformylation processes is due to the hydrolytic instability of the organophosphite ligands. All organophosphites are susceptible to hydrolysis in one degree or another, the rate of hydrolysis of organophosphites in general being

dependent on the stereochemical nature of the organophosphite. In general, the bulkier the steric environment around the phosphorus atom, the slower the hydrolysis rate. For example, tertiary triorganophosphites such as triphenylphosphite are more susceptible to hydrolysis than diorganophosphites, such as disclosed in U.S. Patent No. 4,737,588, and organopolyphosphites such as disclosed in U.S. Patent Nos. 4,748,261 and 4,769,498. Moreover, all such hydrolysis reactions invariably produce phosphorus acidic compounds which catalyze the hydrolysis reactions. For example, the hydrolysis of a tertiary organophosphite produces a phosphonic acid diester, which is hydrolyzable to a phosphonic acid monoester, which in turn is hydrolyzable to H_3PO_3 acid. Moreover, hydrolysis of the ancillary products of side reactions, such as between a phosphonic acid diester and the aldehyde or between certain organophosphite ligands and an aldehyde, can lead to production of undesirable strong aldehyde acids, e.g., n-$C_3H_7CH(OH)P(O)(OH)_2$.

Indeed even highly desirable sterically-hindered organobisphosphites which are not very hydrolyzable can react with the aldehyde product to form poisoning organophosphites, e.g., organomonophosphites, which are not only catalytic inhibitors, but far more susceptible to hydrolysis and the formation of such aldehyde acid byproducts, e.g., hydroxy alkyl phosphonic acids, as shown, for example, in U.S. Patent Nos. 5,288,918 and 5,364,950. Further, the hydrolysis of organophosphite ligands may be considered as being autocatalytic in view of the production of such phosphorus acidic compounds, e.g., H_3PO_3 , aldehyde acids such as hydroxy alkyl phosphonic acids, H_3PO_4 and the like, and if left unchecked the catalyst system of the continuous liquid recycle hydroformylation process will become more and more acidic in time. Thus in time the eventual build-up of an unacceptable amount of such phosphorus acidic materials can cause the total destruction of the organophosphite present, thereby rendering the hydroformylation catalyst totally

ineffective (deactivated) and the valuable rhodium metal susceptible to loss, e.g., due to precipitation and/or depositing on the walls of the reactor.

Compounding the organophosphite stability problem is the need to continually hydrolyze a poisoning or inhibiting organomonophosphite referred to above which forms during hydroformylation catalysis with a metal-organopolyphosphite ligand complex catalyst. For example, if hydroformylation is operated under conventional conditions, a steadily declining catalyst activity is observed because of the accumulation of inhibiting organomonophosphite/organopolyphosphite ligand-metal complexes. Attempts to prevent or lessen the accumulation of such organomonophosphite/organopolyphosphite ligand-metal complexes can cause undesirable disruption of hydroformylation operating parameters, e.g., temperature, pressure, reaction rate, etc. Accordingly, a successful method for preventing and/or lessening the accumulation of such organomonophosphite/organopolyphosphite ligand-metal complexes while at the same time minimizing disruption of hydroformylation process parameters would be highly desirable to the art.

Disclosure of the Invention

It has now been discovered that deactivation of metal-organopolyphosphite ligand complex catalysts caused by an inhibiting or poisoning organomonophosphite can be reversed or at least minimized by carrying out hydroformylation processes in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and optionally at one or more of the following conditions: at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction

pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process; at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process; at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process; and at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention relates in part to a process which comprises reacting one or more reactants in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, wherein said process is conducted at a carbon monoxide partial pressure such that reaction rate increases as carbon monoxide partial pressure decreases and reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention also relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as

carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (b) at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (c) at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and (d) at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention further relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, and at a temperature

such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and at one or more of the following conditions: (a) at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (b) at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and (c) at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention yet further relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, and at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total

reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention also relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, and at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention further relates in part to an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, the improvement comprising preventing and/or lessening deactivation of the metal-organopolyphosphite ligand complex catalyst and preventing and/or lessening cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process by conducting said hydroformylation process at a carbon monoxide partial pressure such that hydroformylation

reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, (b) at a carbon monoxide conversion of less than about 90%, (c) at a hydrogen conversion of greater than about 65%, and (d) at an olefinic unsaturated compound conversion of greater than about 50%.

This invention yet further relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

This invention also relates in part to an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, wherein said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, the improvement comprising conducting said hydroformylation

process at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (b) at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (c) at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and (d) at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention further relates in part to an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product

fluid, wherein said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, the improvement comprising preventing and/or lessening coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst and preventing and/or lessening cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process by conducting said hydroformylation process at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, (b) at a carbon monoxide conversion of less than about 90%, (c) at a hydrogen conversion of greater than about 65%, and (d) at an olefinic unsaturated compound conversion of greater than about 50%.

This invention yet further relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst.

This invention relates in part to a process which comprises reacting one or more reactants in the presence of a metal-

organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, wherein said process is conducted at (a) a carbon monoxide partial pressure such that reaction rate increases as carbon monoxide partial pressure decreases and reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst and (b) a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, reaction rate and/or temperature during said process.

This invention also relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at (a) a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst and (b) a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention further relates in part to an improved hydroformylation process which comprises (i) reacting in at least one

reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, the improvement comprising preventing and/or lessening deactivation of the metal-organopolyphosphite ligand complex catalyst and preventing and/or lessening cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process by conducting said hydroformylation process at (a) a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and (b) a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C.

This invention also relates in part to an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, wherein said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, the improvement comprising conducting said hydroformylation process at (a) a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as

carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst and (b) a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

This invention further relates in part to an improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, wherein said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, the improvement comprising preventing and/or lessening coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst and preventing and/or lessening cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process by conducting said hydroformylation process at (a) a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and (b) a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C.

This invention yet further relates in part to a hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst.

Brief Description of the Drawing

Fig. 1 is a graphical representation of the relationship between hydroformylation reaction rate and carbon monoxide partial pressure.

Detailed Description

The hydroformylation processes of this invention may be asymmetric or non-asymmetric, the preferred processes being non-asymmetric, and may be conducted in any continuous or semi-continuous fashion and may involve any catalyst liquid and/or gas recycle operation desired. Thus it should be clear that the particular hydroformylation process for producing such aldehydes from an olefinic unsaturated compound, as well as the reaction conditions and ingredients of the hydroformylation process are not critical features of this invention. As used herein, the term "hydroformylation" is contemplated to include, but not limited to, all permissible asymmetric and non-asymmetric hydroformylation processes which involve converting one or more substituted or unsubstituted olefinic compounds or a reaction mixture comprising one or more substituted or

unsubstituted olefinic compounds to one or more substituted or unsubstituted aldehydes or a reaction mixture comprising one or more substituted or unsubstituted aldehydes. As used herein, the term "reaction product fluid" is contemplated to include, but not limited to, a reaction mixture containing an amount of any one or more of the following: (a) a metal-organopolyphosphite ligand complex catalyst, (b) free organopolyphosphite ligand, (c) one or more phosphorus acidic compounds formed in the reaction, (d) aldehyde product formed in the reaction, (e) unreacted reactants, and (f) an organic solubilizing agent for said metal-organopolyphosphite ligand complex catalyst and said free organopolyphosphite ligand. The reaction product fluid encompasses, but is not limited to, (a) the reaction medium in the reaction zone, (b) the reaction medium stream on its way to the separation zone, (c) the reaction medium in the separation zone, (d) the recycle stream between the separation zone and the reaction zone, (e) the reaction medium withdrawn from the reaction zone or separation zone for treatment in the acid removal zone, (f) the withdrawn reaction medium treated in the acid removal zone, (g) the treated reaction medium returned to the reaction zone or separation zone, and (h) reaction medium in external cooler.

Illustrative metal-organopolyphosphite ligand complex catalyzed hydroformylation processes which may experience such catalytic deactivation include such processes as described, for example, in U.S. Patent Nos. 4,148,830; 4,593,127; 4,769,498; 4,717,775; 4,774,361; 4,885,401; 5,264,616; 5,288,918; 5,360,938; 5,364,950; and 5,491,266; the disclosures of which are incorporated herein by reference. Accordingly, the hydroformylation processing techniques of this invention may correspond to any known processing techniques. Preferred processes are those involving catalyst liquid recycle hydroformylation processes.

In general, such catalyst liquid recycle hydroformylation processes involve the production of aldehydes by reacting an olefinic

unsaturated compound with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst in a liquid medium that also contains an organic solvent for the catalyst and ligand. Preferably free organopolyphosphite ligand is also present in the liquid hydroformylation reaction medium. By "free organopolyphosphite ligand" is meant organopolyphosphite ligand that is not complexed with (tied to or bound to) the metal, e.g., metal atom, of the complex catalyst. The recycle procedure generally involves withdrawing a portion of the liquid reaction medium containing the catalyst and aldehyde product from the hydroformylation reactor (i.e., reaction zone), either continuously or intermittently, and recovering the aldehyde product therefrom by use of a composite membrane such as disclosed in U.S. Patent No. 5,430,194 and copending U.S. Patent Application Serial No. 08/430,790, filed May 5,1995, the disclosures of which are incorporated herein by reference, or by the more conventional and preferred method of distilling it (i.e., vaporization separation) in one or more stages under normal, reduced or elevated pressure, as appropriate, in a separate distillation zone, the non-volatilized metal catalyst containing residue being recycled to the reaction zone as disclosed, for example, in U.S. Patent No. 5,288,918. Condensation of the volatilized materials, and separation and further recovery thereof, e.g., by further distillation, can be carried out in any conventional manner, the crude aldehyde product can be passed on for further purification and isomer separation, if desired, and any recovered reactants, e.g., olefinic starting material and syn gas, can be recycled in any desired manner to the hydroformylation zone (reactor). The recovered metal catalyst containing raffinate of such membrane separation or recovered non-volatilized metal catalyst containing residue of such vaporization separation can be recycled, to the hydroformylation zone (reactor) in any conventional manner desired.

In a preferred embodiment, the hydroformylation reaction product fluids employable herein includes any fluid derived from any

corresponding hydroformylation process that contains at least some amount of four different main ingredients or components, i.e., the aldehyde product, a metal-organopolyphosphite ligand complex catalyst, free organopolyphosphite ligand and an organic solubilizing agent for said catalyst and said free ligand, said ingredients corresponding to those employed and/or produced by the hydroformylation process from whence the hydroformylation reaction mixture starting material may be derived. It is to be understood that the hydroformylation reaction mixture compositions employable herein can and normally will contain minor amounts of additional ingredients such as those which have either been deliberately employed in the hydroformylation process or formed in situ during said process. Examples of such ingredients that can also be present include unreacted olefin starting material, carbon monoxide and hydrogen gases, and in situ formed type products, such as saturated hydrocarbons and/or unreacted isomerized olefins corresponding to the olefin starting materials, and high boiling liquid aldehyde condensation byproducts, as well as other inert co-solvent type materials or hydrocarbon additives, if employed.

Illustrative metal-organopolyphosphite ligand complex catalysts employable in such hydroformylation reactions encompassed by this invention as well as methods for their preparation are well known in the art and include those disclosed in the above mentioned patents. In general such catalysts may be preformed or formed in situ as described in such references and consist essentially of metal in complex combination with an organopolyphosphite ligand. It is believed that carbon monoxide is also present and complexed with the metal in the active species. The active species may also contain hydrogen directly bonded to the metal.

The catalyst useful in the hydroformylation process includes a metal-organopolyphosphite ligand complex catalyst which can be optically active or non-optically active. The permissible metals

which make up the metal-organopolyphosphite ligand complexes include Group 8, 9 and 10 metals selected from rhodium (Rh), cobalt (Co), iridium (Ir), ruthenium (Ru), iron (Fe), nickel (Ni), palladium (Pd), platinum (Pt), osmium (Os) and mixtures thereof, with the preferred metals being rhodium, cobalt, iridium and ruthenium, more preferably rhodium, cobalt and ruthenium, especially rhodium. Other permissible metals include Group 6 metals selected from chromium (Cr), molybdenum (Mo), tungsten (W) and mixtures thereof. Mixtures of metals from Groups 6, 8, 9 and 10 may also be used in this invention. The permissible organopolyphosphite ligands which make up the metal-organopolyphosphite ligand complexes and free organopolyphosphite ligand include mono-, di-, tri- and higher polyorganophosphites. Mixtures of such ligands may be employed if desired in the metal-organopolyphosphite ligand complex catalyst and/or free ligand and such mixtures may be the same or different. This invention is not intended to be limited in any manner by the permissible organopolyphosphite ligands or mixtures thereof. It is to be noted that the successful practice of this invention does not depend and is not predicated on the exact structure of the metal-organopolyphosphite ligand complex species, which may be present in their mononuclear, dinuclear and/or higher nuclearity forms. Indeed, the exact structure is not known. Although it is not intended herein to be bound to any theory or mechanistic discourse, it appears that the catalytic species may in its simplest form consist essentially of the metal in complex combination with the organopolyphosphite ligand and carbon monoxide and/or hydrogen when used.

The term "complex" as used herein and in the claims 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. For example, the organopolyphosphite ligands employable herein may possess one or

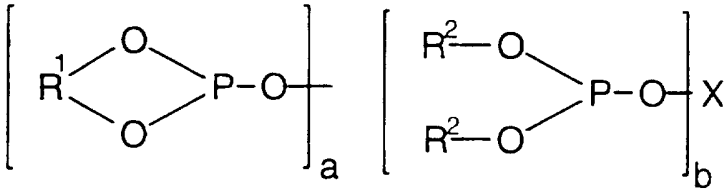
more phosphorus donor atoms, each having one available or unshared pair of electrons which are each capable of forming a coordinate covalent bond independently or possibly in concert (e.g., via chelation) with the metal. Carbon monoxide (which is also properly classified as a ligand) can also be present and complexed with the metal. The ultimate composition of the complex catalyst may also contain an additional ligand, e.g., hydrogen or an anion satisfying the coordination sites or nuclear charge of the metal. Illustrative additional ligands include, for example, halogen (Cl, Br, I), alkyl, aryl, substituted aryl, acyl, CF_3, C_2F_5, CN, $(R)_2PO$ and RP(O)(OH)O (wherein each R is the same or different and is a substituted or unsubstituted hydrocarbon radical, e.g., the alkyl or aryl), acetate, acetylacetonate, SO_4, PF_4, PF_6, NO_2, NO_3, CH_3O, $CH_2=CHCH_2$, $CH_3CH=CHCH_2$, C_6H_5CN, CH_3CN, NH_3, pyridine, $(C_2H_5)_3N$, mono-olefins, diolefins and triolefins, tetrahydrofuran, and the like. It is of course to be understood that the complex species are preferably free of any additional organic ligand or anion that might poison the catalyst or have an undue adverse effect on catalyst performance. It is preferred in the metal-organopolyphosphite ligand complex catalyzed hydroformylation reactions that the active catalysts be free of halogen and sulfur directly bonded to the metal, although such may not be absolutely necessary.

The number of available coordination sites on such metals is well known in the art. Thus the catalytic species may comprise a complex catalyst mixture, in their monomeric, dimeric or higher nuclearity forms, which are preferably characterized by at least one organopolyphosphite-containing molecule complexed per one molecule of metal, e.g., rhodium. For instance, it is considered that the catalytic species of the preferred catalyst employed in a hydroformylation reaction may be complexed with carbon monoxide and hydrogen in addition to the organopolyphosphite ligands in view of the carbon monoxide and hydrogen gas employed by the hydroformylation reaction.

The organopolyphosphites that may serve as the ligand of the metal-organopolyphosphite ligand complex catalyst and/or free ligand of the hydroformylation processes and reaction product fluids of this invention may be of the achiral (optically inactive) or chiral (optically active) type and are well known in the art. Achiral organopolyphosphites are preferred.

Among the organopolyphosphites that may serve as the ligand of the metal-organopolyphosphite ligand complex catalyst containing reaction product fluids of this invention and/or any free organopolyphosphite ligand of the hydroformylation process that might also be present in said reaction product fluids are organopolyphosphite compounds described below. Such organopolyphosphite ligands employable in this invention and/or methods for their preparation are well known in the art.

Representative organopolyphosphites contain two or more tertiary (trivalent) phosphorus atoms and may include those having the formula:



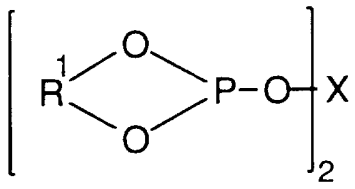
(I)

wherein X represents a substituted or unsubstituted n-valent organic bridging radical containing from 2 to 40 carbon atoms, each R^1 is the same or different and represents a divalent organic radical containing from 4 to 40 carbon atoms, each R^2 is the same or different and represents a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 24 carbon atoms, a and b can be the same or different and each have a value of 0 to 6, with the proviso that the sum of a + b is 2 to 6 and n equals a + b. Of course it is to be

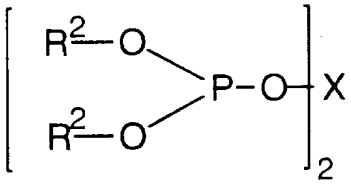
understood that when a has a value of 2 or more, each R^1 radical may be the same or different, and when b has a value of 1 or more, each R^2 radical may be the same or different.

Representative n-valent (preferably divalent) hydrocarbon bridging radicals represented by X and representative divalent organic radicals represented by R^1 above, include both acyclic radicals and aromatic radicals, such as alkylene, alkylene-Q_m-alkylene, cycloalkylene, arylene, bisarylene, arylene-alkylene, and arylene-$(CH_2)_y$-Q_m-$(CH_2)_y$-arylene radicals, and the like, wherein each y is the same or different and is a value of 0 or 1, Q represents a divalent bridging group selected from -$C(R^3)_2$-, -O-, -S-, -NR^4-, $Si(R^5)_2$- and -CO-, wherein each R^3 is the same or different and represents hydrogen, an alkyl radical having from 1 to 12 carbon atoms, phenyl, tolyl, and anisyl, R^4 represents hydrogen or a substituted or unsubstituted monovalent hydrocarbon radical, e.g., an alkyl radical having 1 to 4 carbon atoms; each R^5 is the same or different and represents hydrogen or an alkyl radical, and m is a value of 0 or 1. The more preferred acyclic radicals represented by X and R^1 above are divalent alkylene radicals, while the more preferred aromatic radicals represented by X and R^1 above are divalent arylene and bisarylene radicals, such as disclosed more fully, for example, in U.S. Patent Nos. 4,769,498; 4,774,361: 4,885,401; 5,179,055; 5,113,022; 5,202,297; 5,235,113; 5,264,616 and 5,364,950, and European Patent Application Publication No. 662,468, and the like, the disclosures of which are incorporated herein by reference. Representative preferred monovalent hydrocarbon radicals represented by each R^2 radical above include alkyl and aromatic radicals.

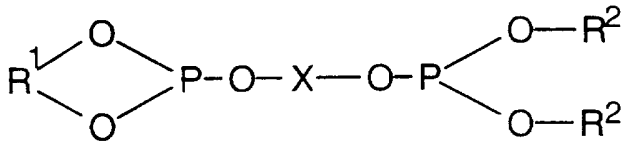
Illustrative preferred organopolyphosphites may include bisphosphites such as those of Formulas (II) to (IV) below:



(II)



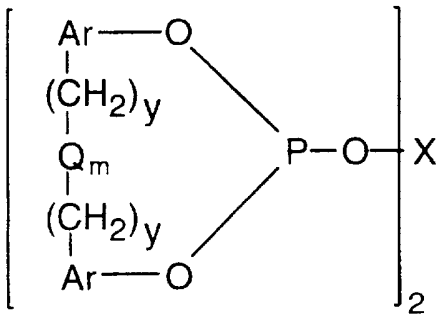
(III)



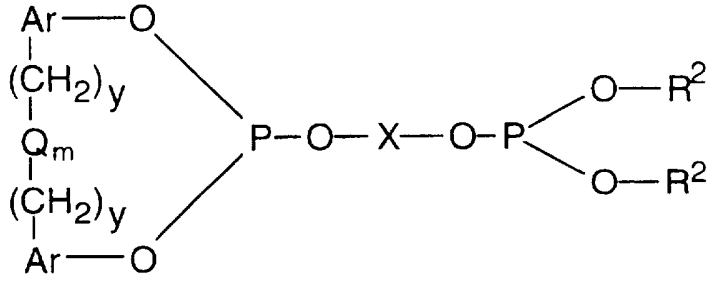
(IV)

wherein each R^1 , R^2 and X of Formulas (II) to (IV) are the same as defined above for Formula (I). Preferably each R^1 and X represents a divalent hydrocarbon radical selected from alkylene, arylene, arylene-alkylene-arylene, and bisarylene, while each R^2 radical represents a monovalent hydrocarbon radical selected from alkyl and aryl radicals. Organopolyphosphite ligands of such Formulas (II) to (IV) may be found disclosed, for example, in U.S. Patent Nos. 4,668,651; 4,748,261; 4,769,498; 4,774,361; 4,885,401; 5,113,022; 5,179,055; 5,202,297; 5,235,113; 5,254,741; 5,264,616; 5,312,996; 5,364,950; and 5,391,801; the disclosures of all of which are incorporated herein by reference.

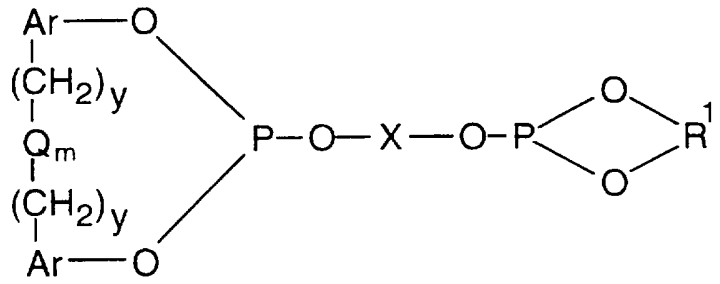
Representative of more preferred classes of organobisphosphites are those of the following Formulas (V) to (VII):



(V)



(VI)



(VII)

wherein Q, R^1, R^2, X , m, and y are as defined above, and each Ar is the same or different and represents a substituted or unsubstituted aryl radical. Most preferably X represents a divalent aryl-$(CH_2)_y$-$(Q)_m$-$(CH_2)_y$-aryl radical wherein each y individually has a value of 0 or 1; m has a value of 0 or 1 and Q is -O-, -S- or -$C(R^3)_2$ where each R^3 is the same or different and represents hydrogen or a methyl radical. More preferably each alkyl radical of the above defined R^2 groups may contain from 1 to 24 carbon atoms and each aryl radical of the above-

defined Ar, X, R^1 and R^2 groups of the above Formulas (V) to (VII) may contain from 6 to 18 carbon atoms and said radicals may be the same or different, while the preferred alkylene radicals of X may contain from 2 to 18 carbon atoms and the preferred alkylene radicals of R^1 may contain from 5 to 18 carbon atoms. In addition, preferably the divalent Ar radicals and divalent aryl radicals of X of the above formulas are phenylene radicals in which the bridging group represented by $-(CH_2)_y-(Q)_m-(CH_2)_y-$ is bonded to said phenylene radicals in positions that are ortho to the oxygen atoms of the formulas that connect the phenylene radicals to their phosphorus atom of the formulae. It is also preferred that any substituent radical when present on such phenylene radicals be bonded in the para and/or ortho position of the phenylene radicals in relation to the oxygen atom that bonds the given substituted phenylene radical to its phosphorus atom.

Moreover, if desired any given organopolyphosphite in the above Formulas (I) to (VII) may be an ionic phosphite, i.e., may contain one or more ionic moieties selected from the group consisting of:

- SO_3M wherein M represents inorganic or organic cation,
- PO_3M wherein M represents inorganic or organic cation,
- $N(R^6)_3X^1$ wherein each R^6 is the same or different and represents a hydrocarbon radical containing from 1 to 30 carbon atoms, e.g., alkyl, aryl, alkaryl, aralkyl, and cycloalkyl radicals, and X^1 represents inorganic or organic anion,
- CO_2M wherein M represents inorganic or organic cation,

as described, for example, in U.S. Patent Nos. 5,059,710; 5,113,022 5,114,473; 5,449,653; and European Patent Application Publication No. 435,084, the disclosures of which are incorporated herein by reference. Thus, if desired, such organopolyphosphite ligands may contain from 1 to 3 such ionic moieties, while it is preferred that only one such ionic moiety be substituted on any given aryl moiety in the

organopolyphosphite ligand when the ligand contains more than one such ionic moiety. As suitable counter-ions, M and X^1, for the anionic moieties of the ionic organopolyphosphites there can be mentioned hydrogen (i.e. a proton), the cations of the alkali and alkaline earth metals, e.g., lithium, sodium, potassium, cesium, rubidium, calcium, barium, magnesium and strontium, the ammonium cation and quaternary ammonium cations, phosphonium cations, arsonium cations and iminium cations. Suitable anionic atoms of radicals include, for example, sulfate, carbonate, phosphate, chloride, acetate, oxalate and the like.

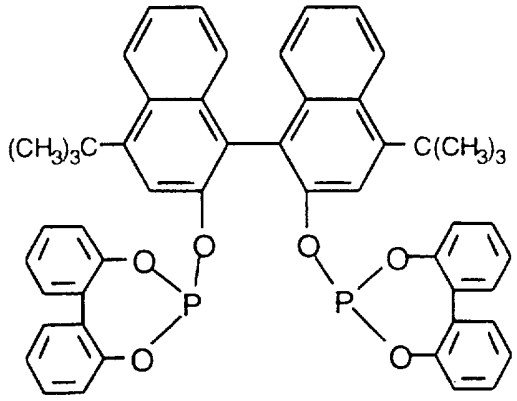
Of course any of the R^1, R^2, X, Q and Ar radicals of such non-ionic and ionic organopolyphosphites of Formulas (I) to (VII) above may be substituted if desired, with any suitable substituent containing from 1 to 30 carbon atoms that does not unduly adversely affect the desired result of the process of this invention. Substituents that may be on said radicals in addition of course to corresponding hydrocarbon radicals such as alkyl, aryl, aralkyl, alkaryl and cyclohexyl substituents, may include for example silyl radicals such as $-Si(R^7)_3$; amino radicals such as $-N(R^7)_2$; phosphine radicals such as -aryl-$P(R^7)_2$; acyl radicals such as $-C(O)R^7$ acyloxy radicals such as $-OC(O)R^7$; amido radicals such as $-CON(R^7)_2$ and $-N(R^7)COR^7$; sulfonyl radicals such as $-SO_2R^7$, alkoxy radicals such as $-OR^7$; sulfinyl radicals such as $-SOR^7$, sulfenyl radicals such as $-SR^7$, phosphonyl radicals such as $-P(O)(R^7)_2$, as well as halogen, nitro, cyano, trifluoromethyl, hydroxy radicals, and the like, wherein each R^7 radical individually represents the same or different monovalent hydrocarbon radical having from 1 to 18 carbon atoms (e.g., alkyl, aryl, aralkyl, alkaryl and cyclohexyl radicals), with the proviso that in amino substituents such as $-N(R^7)_2$ each R^7 taken together can also represent a divalent bridging group that forms a heterocyclic radical with the nitrogen atom, and in amido substituents such as $-C(O)N(R^7)_2$ and $-N(R^7)COR^7$

each R^7 bonded to N can also be hydrogen. Of course it is to be understood that any of the substituted or unsubstituted hydrocarbon radicals groups that make up a particular given organopolyphosphite may be the same or different.

More specifically illustrative substituents include primary, secondary and tertiary alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, neo-pentyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, decyl, octadecyl, and the like; aryl radicals such as phenyl, naphthyl and the like; aralkyl radicals such as benzyl, phenylethyl, triphenylmethyl, and the like; alkaryl radicals such as tolyl, xylyl, and the like; alicyclic radicals such as cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, and the like; alkoxy radicals such as methoxy, ethoxy, propoxy, t-butoxy, -$OCH_2CH_2OCH_3$, -$O(CH_2CH_2)_2OCH_3$, -$O(CH_2CH_2)_3OCH_3$, and the like; aryloxy radicals such as phenoxy and the like; as well as silyl radicals such as -$Si(CH_3)_3$, -$Si(OCH_3)_3$, -$Si(C_3H_7)_3$, and the like; amino radicals such as -NH_2, -$N(CH_3)_2$, -$NHCH_3$, -$NH(C_2H_5)$, and the like; arylphosphine radicals such as -$P(C_6H_5)_2$, and the like; acyl radicals such as -$C(O)CH_3$, -$C(O)C_2H_5$, -$C(O)C_6H_5$, and the like; carbonyloxy radicals such as -$C(O)OCH_3$ and the like; oxycarbonyl radicals such as -$O(CO)C_6H_5$, and the like; amido radicals such as -$CONH_2$, -$CON(CH_3)_2$, -$NHC(O)CH_3$, and the like; sulfonyl radicals such as -$S(O)_2C_2H_5$ and the like; sulfinyl radicals such as -$S(O)CH_3$ and the like; sulfenyl radicals such as -SCH_3, -SC_2H_5, -SC_6H_5, and the like; phosphonyl radicals such as -$P(O)(C_6H_5)_2$, -$P(O)(CH_3)_2$, -$P(O)(C_2H_5)_2$, -$P(O)(C_3H_7)_2$, -$P(O)(C_4H_9)_2$, -$P(O)(C_6H_{13})_2$, -$P(O)CH_3(C_6H_5)$, -$P(O)(H)(C_6H_5)$, and the like.

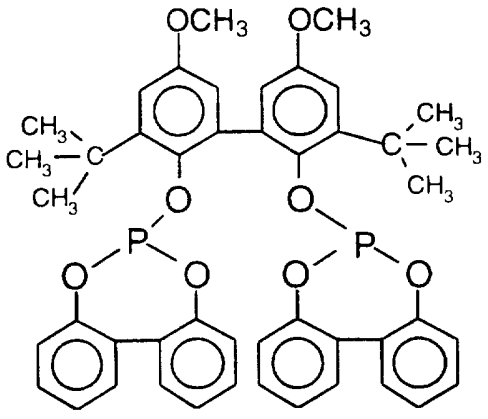
Specific illustrative examples of such organobisphosphite ligands include the following;

6,6'-[[4;4'-bis(1,1-dimethylethyl)-[1,1'-binaphthyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]-dioxaphosphepin having the formula:



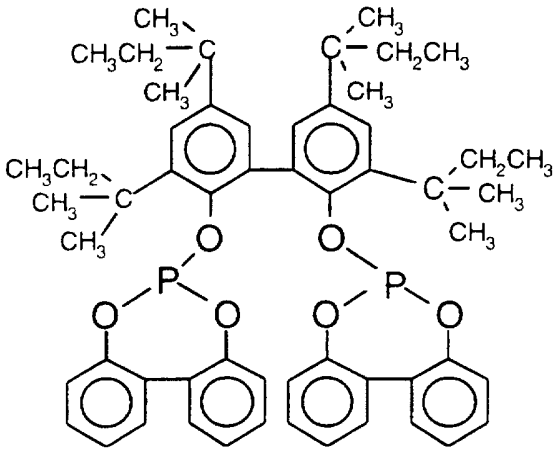
Ligand A

6,6'-[[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



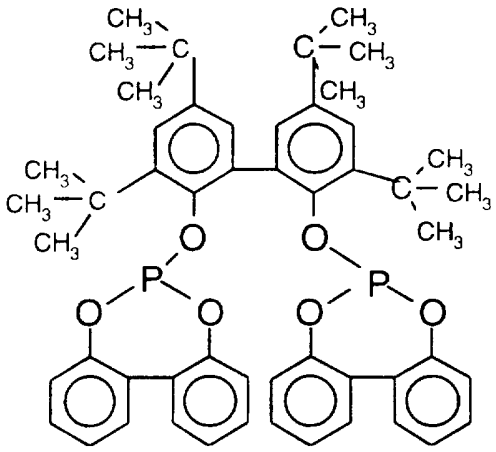
Ligand B

6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylpropyl)-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



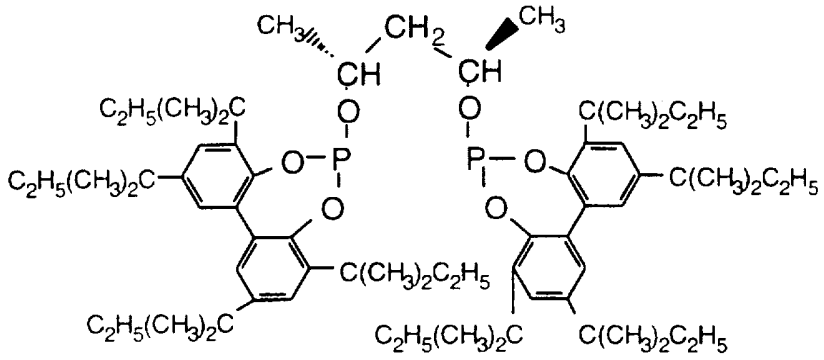
Ligand C

6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylethyl)-1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]-dioxaphosphepin having the formula:



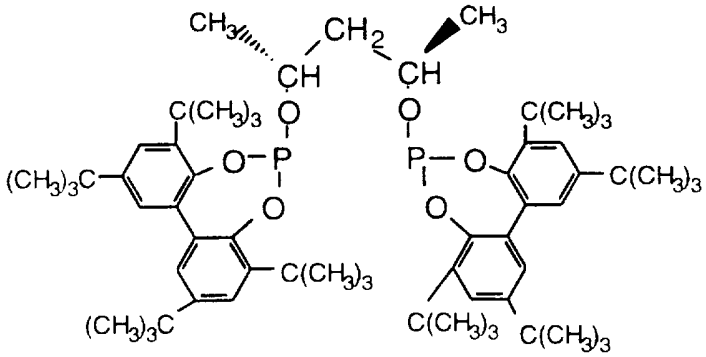
Ligand D

(2R,4R)-di[2,2'-(3,3',5,5'-tetrakis-tert-amyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



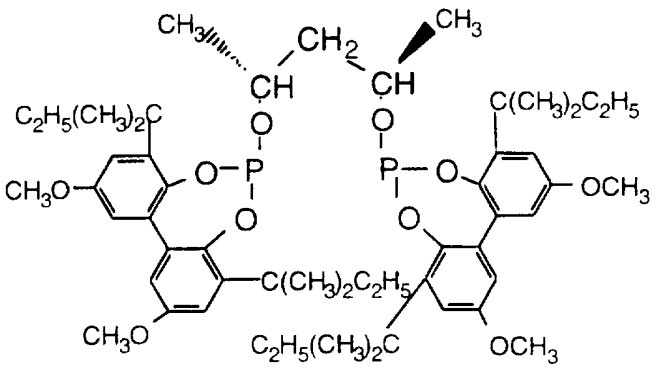
Ligand E

(2R,4R)-di[2,2'-(3,3',5,5'-tetrakis-tert-butyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



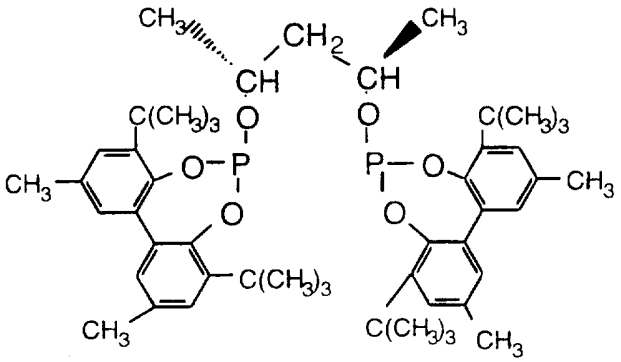
Ligand F

(2R,4R)-di[2,2'-(3,3'-di-amyl-5,5'-dimethoxy-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



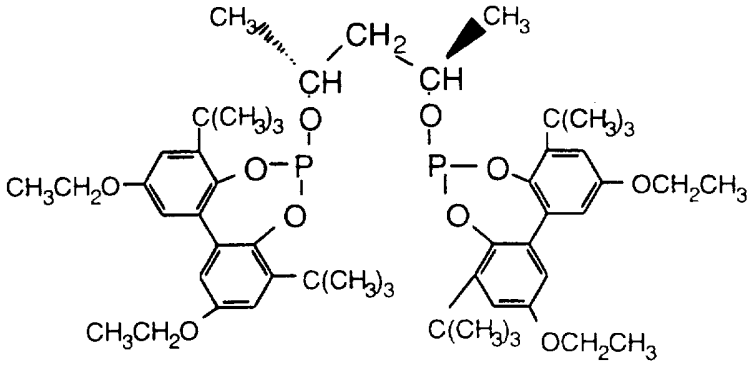
Ligand G

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-dimethyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



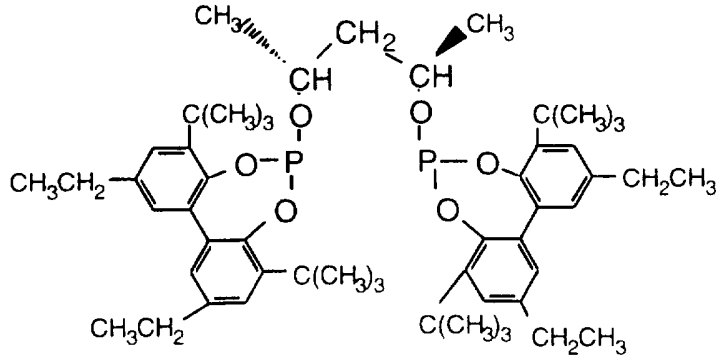
Ligand H

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-diethoxy-1,1'-biphenyl)]- 2,4-pentyldiphosphite having the formula:



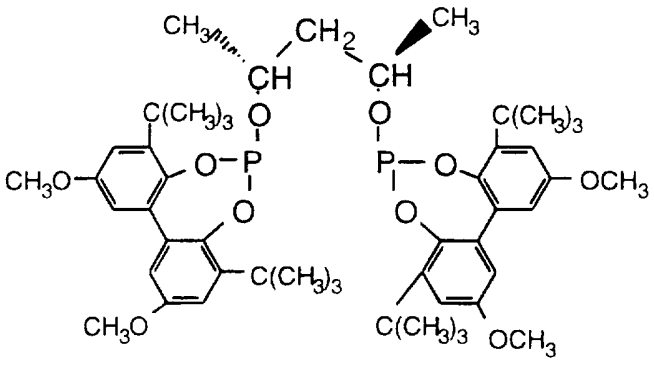
Ligand I

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-diethyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



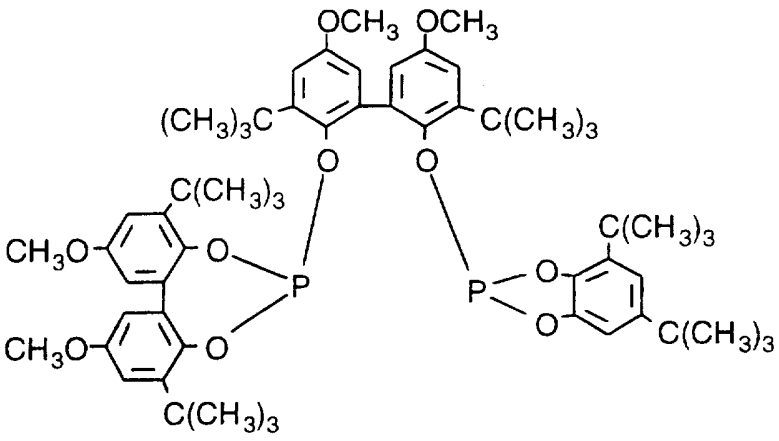
Ligand J

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-dimethoxy-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



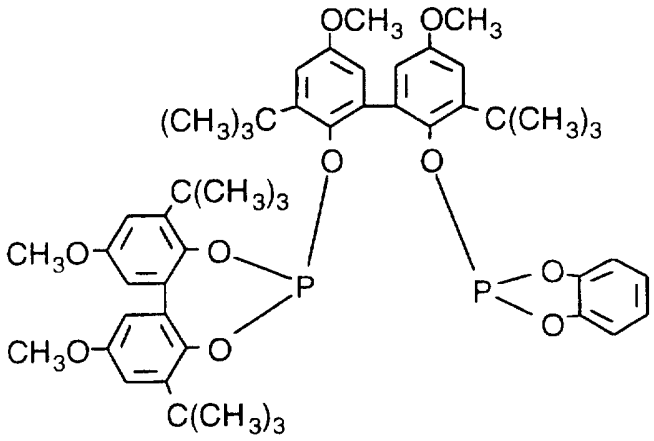
Ligand K

6-[[2'-[(4,6-bis(1,1-dimethylethyl)-1,3,2-benzodioxaphosphol-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



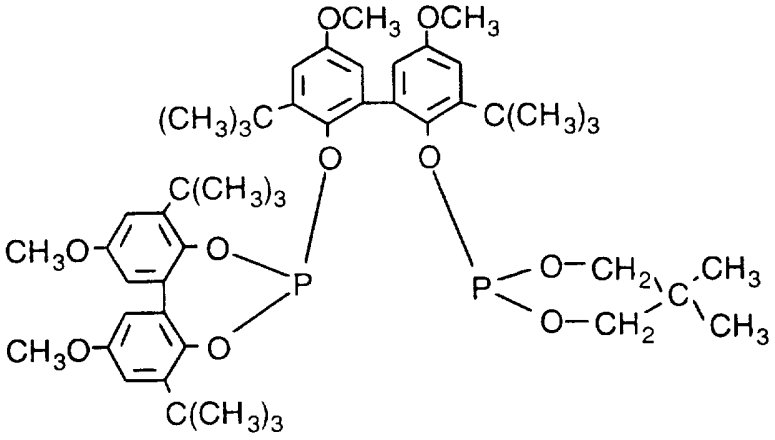
Ligand L

6-[[2'-[1,3,2-benzodioxaphosphol-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



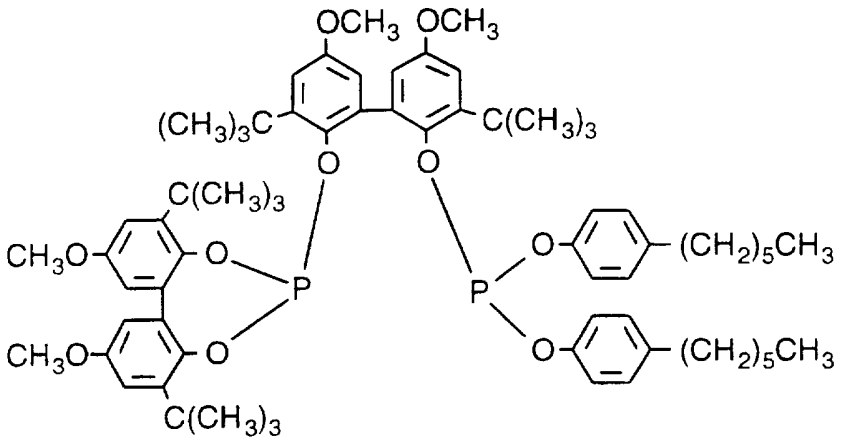
Ligand M

6-[[2'-[(5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



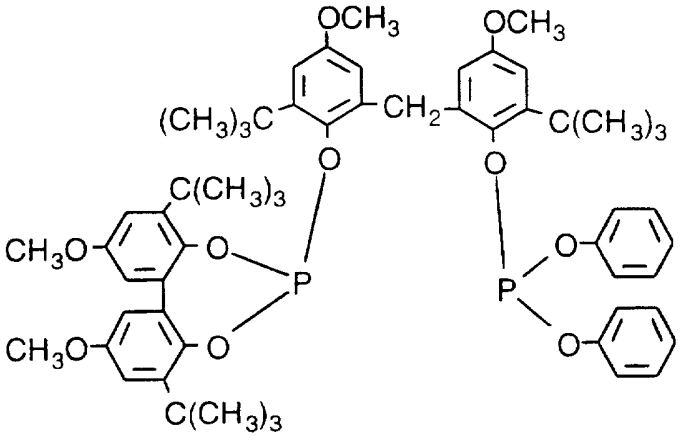
Ligand N

2'-[[4 ,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]-dioxaphosphepin-6-yl]oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'- biphenyl]-2-yl bis(4-hexylphenyl)ester of phosphorous acid having the formula:



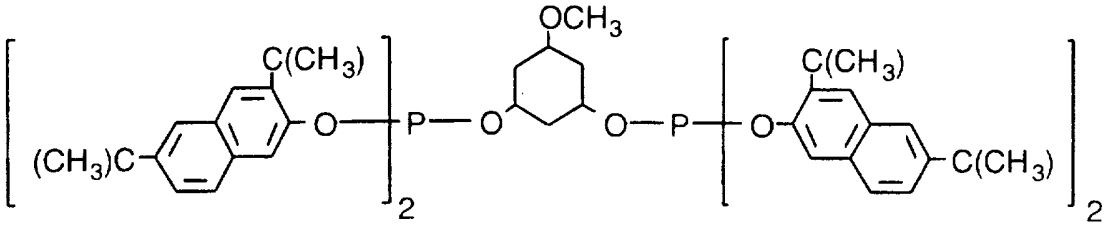
Ligand O

2-[[2-[[4,8,-bis(1,1-dimethylethyl), 2,10-dimethoxydibenzo-[d,f][1,3,2]dioxophosphepin-6-yl]oxy]-3-(1,1-dimethylethyl)-5-methoxyphenyl]methyl]-4-methoxy, 6-(1,1-dimethylethyl)phenyl diphenyl ester of phosphorous acid having the formula:



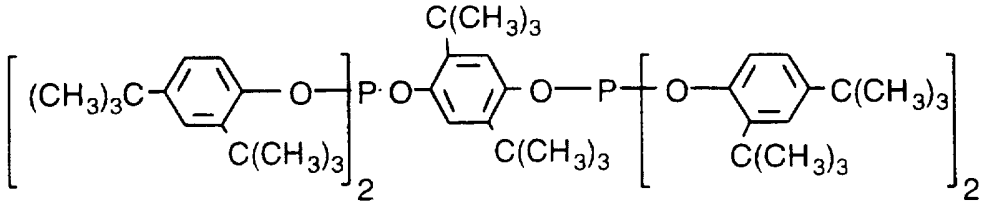
Ligand P

3-methoxy-1,3-cyclohexamethylene tetrakis[3,6-bis(1,1-dimethylethyl)-2-naphthalenyl]ester of phosphorous acid having the formula:



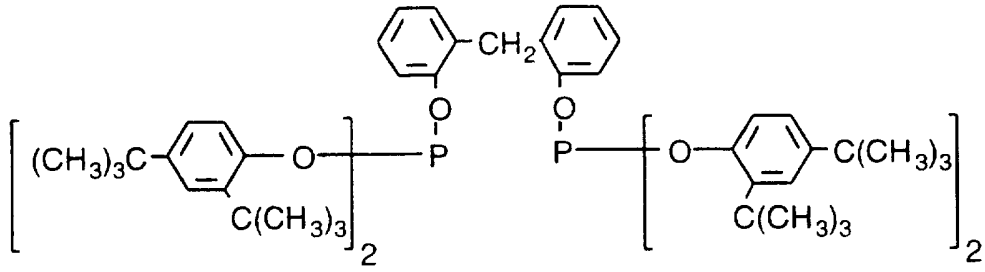
Ligand Q

2,5-bis(1,1-dimethylethyl)-1,4-phenylene tetrakis[2,4-bis(1,1-dimethylethyl)phenyl]ester of phosphorous acid having the formula:



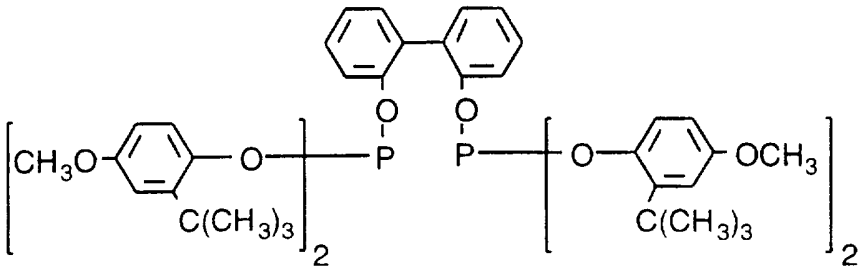
Ligand R

methylenedi-2,1-phenylene tetrakis[2,4-bis(1,1-dimethylethyl)phenyl]ester of phosphorous acid having the formula:



Ligand S

[1,1'-biphenyl]-2,2'-diyl tetrakis[2-(1,1-dimethylethyl)-4-methoxyphenyl]ester of phosphorous acid having the formula:



Ligand T

As noted above, the metal-organopolyphosphite ligand complex catalysts employable in this invention may be formed by methods known in the art. The metal-organopolyphosphite ligand complex catalysts may be in homogeneous or heterogeneous form. For instance, preformed rhodium hydrido-carbonyl-organopolyphosphite ligand catalysts may be prepared and introduced into the reaction mixture of a hydroformylation process. More preferably, the rhodium-organopolyphosphite ligand complex catalysts can be derived from a rhodium catalyst precursor which may be introduced into the reaction medium for in situ formation of the active catalyst. For example, rhodium catalyst precursors such as rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$ and the like may be introduced into the reaction mixture along with the organopolyphosphite ligand for the in situ formation of the active catalyst. In a preferred embodiment of this invention, rhodium dicarbonyl acetylacetonate is employed as a rhodium precursor and reacted in the presence of a solvent with the organopolyphosphite ligand to form a catalytic rhodium-organopolyphosphite ligand complex precursor which is introduced into the reactor along with excess (free) organopolyphosphite ligand for the in situ formation of the active catalyst. In any event, it is sufficient for the purpose of this invention that carbon monoxide, hydrogen and organopolyphosphite compound are all ligands that are capable of being complexed with the metal and that an active metal-organopolyphosphite ligand catalyst is present in

the reaction mixture under the conditions used in the hydroformylation reaction.

More particularly, a catalyst precursor composition can be formed consisting essentially of a solubilized metal-organopolyphosphite ligand complex precursor catalyst, an organic solvent and free organopolyphosphite ligand. Such precursor compositions may be prepared by forming a solution of a rhodium starting material, such as a rhodium oxide, hydride, carbonyl or salt, e.g. a nitrate, which may or may not be in complex combination with a organopolyphosphite ligand as defined herein. Any suitable rhodium starting material may be employed, e.g. rhodium dicarbonyl acetylacetonate, Rh_2O_3, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$, and organopolyphosphite ligand rhodium carbonyl hydrides. Carbonyl and organopolyphosphite ligands, if not already complexed with the initial rhodium, may be complexed to the rhodium either prior to or in situ during the hydroformylation process.

By way of illustration, the preferred catalyst precursor composition of this invention consists essentially of a solubilized rhodium carbonyl organopolyphosphite ligand complex precursor catalyst, a solvent and optionally free organopolyphosphite ligand prepared by forming a solution of rhodium dicarbonyl acetylacetonate, an organic solvent and a organopolyphosphite ligand as defined herein. The organopolyphosphite ligand readily replaces one of the carbonyl ligands of the rhodium acetylacetonate complex precursor at room temperature as witnessed by the evolution of carbon monoxide gas. This substitution reaction may be facilitated by heating the solution if desired. Any suitable organic solvent in which both the rhodium dicarbonyl acetylacetonate complex precursor and rhodium organopolyphosphite ligand complex precursor are soluble can be employed. The amounts of rhodium complex catalyst precursor, organic solvent and organopolyphosphite ligand, as well as their preferred embodiments present in such catalyst precursor compositions

may obviously correspond to those amounts employable in the hydroformylation process of this invention. Experience has shown that the acetylacetonate ligand of the precursor catalyst is replaced after the hydroformylation process has begun with a different ligand, e.g., hydrogen, carbon monoxide or organopolyphosphite ligand, to form the active complex catalyst as explained above. The acetylacetone which is freed from the precursor catalyst under hydroformylation conditions is removed from the reaction medium with the product aldehyde and thus is in no way detrimental to the hydroformylation process. The use of such preferred rhodium complex catalytic precursor compositions provides a simple economical and efficient method for handling the rhodium precursor and hydroformylation start-up.

Accordingly, the metal-organopolyphosphite ligand complex catalysts used in the process of this invention consists essentially of the metal complexed with carbon monoxide and a organopolyphosphite ligand, said ligand being bonded (complexed) to the metal in a chelated and/or non-chelated fashion. Moreover, the terminology "consists essentially of", as used herein, does not exclude, but rather includes, hydrogen complexed with the metal, in addition to carbon monoxide and the organopolyphosphite ligand. Further, such terminology does not exclude the possibility of other organic ligands and/or anions that might also be complexed with the metal. Materials in amounts which unduly adversely poison or unduly deactivate the catalyst are not desirable and so the catalyst most desirably is free of contaminants such as metal-bound halogen (e.g., chlorine, and the like) although such may not be absolutely necessary. The hydrogen and/or carbonyl ligands of an active metal-organopolyphosphite ligand complex catalyst may be present as a result of being ligands bound to a precursor catalyst and/or as a result of in situ formation, e.g., due to the hydrogen and carbon monoxide gases employed in hydroformylation process of this invention.

As noted the hydroformylation processes of this invention involve the use of a metal-organopolyphosphite ligand complex catalyst as described herein. Of course mixtures of such catalysts can also be employed if desired. The amount of metal-organopolyphosphite ligand complex catalyst present in the reaction medium of a given hydroformylation process encompassed by this invention need only be that minimum amount necessary to provide the given metal concentration desired to be employed and which will furnish the basis for at least the catalytic amount of metal necessary to catalyze the particular hydroformylation process involved such as disclosed, for example, in the above-mentioned patents. In general, metal, e.g., rhodium, concentrations in the range of from about 10 parts per million to about 1000 parts per million, calculated as free rhodium, in the hydroformylation reaction medium should be sufficient for most processes, while it is generally preferred to employ from about 10 to 500 parts per million of metal, e.g., rhodium, and more preferably from 25 to 350 parts per million of metal, e.g., rhodium.

In addition to the metal-organopolyphosphite ligand complex catalyst, free organopolyphosphite ligand (i.e., ligand that is not complexed with the metal) may also be present in the hydroformylation reaction medium. The free organopolyphosphite ligand may correspond to any of the above-defined organopolyphosphite ligands discussed above as employable herein. It is preferred that the free organopolyphosphite ligand be the same as the organopolyphosphite ligand of the metal-organopolyphosphite ligand complex catalyst employed. However, such ligands need not be the same in any given process. The hydroformylation process of this invention may involve from about 0.1 moles or less to about 100 moles or higher, of free organopolyphosphite ligand per mole of metal in the hydroformylation reaction medium. Preferably the hydroformylation process of this invention is carried out in the presence of from about 1 to about 50 moles of organopolyphosphite ligand, and more preferably

for organopolyphosphites from about 1.1 to about 4 moles of organopolyphosphite ligand, per mole of metal present in the reaction medium; said amounts of organopolyphosphite ligand being the sum of both the amount of organopolyphosphite ligand that is bound (complexed) to the metal present and the amount of free (non-complexed) organopolyphosphite ligand present. Since it is more preferred to produce non-optically active aldehydes by hydroformylating achiral olefins, the more preferred organopolyphosphite ligands are achiral type organopolyphosphite ligands, especially those encompassed by Formula (I) above, and more preferably those of Formulas (II) and (V) above. Of course, if desired, make-up or additional organopolyphosphite ligand can be supplied to the reaction medium of the hydroformylation process at any time and in any suitable manner, e.g. to maintain a predetermined level of free ligand in the reaction medium.

As indicated above, the hydroformylation catalyst may be in heterogeneous form during the reaction and/or during the product separation. Such catalysts are particularly advantageous in the hydroformylation of olefins to produce high boiling or thermally sensitive aldehydes, so that the catalyst may be separated from the products by filtration or decantation at low temperatures. For example, the rhodium catalyst may be attached to a support so that the catalyst retains its solid form during both the hydroformylation and separation stages, or is soluble in a liquid reaction medium at high temperatures and then is precipitated on cooling.

As an illustration, the rhodium catalyst may be impregnated onto any solid support, such as inorganic oxides, (i.e. alumina, silica, titania, or zirconia) carbon, or ion exchange resins. The catalyst may be supported on, or intercalated inside the pores of, a zeolite, glass or clay; the catalyst may also be dissolved in a liquid film coating the pores of said zeolite or glass. Such zeolite-supported catalysts are particularly advantageous for producing one or more

regioisomeric aldehydes in high selectivity, as determined by the pore size of the zeolite. The techniques for supporting catalysts on solids, such as incipient wetness, which will be known to those skilled in the art. The solid catalyst thus formed may still be complexed with one or more of the ligands defined above. Descriptions of such solid catalysts may be found in for example: J. Mol. Cat. 1991, 70, 363-368; Catal. Lett. 1991, 8, 209-214; J. Organomet. Chem, 1991, 403, 221-227; Nature, 1989, 339, 454-455; J. Catal. 1985, 96, 563-573; J. Mol. Cat. 1987, 39, 243-259.

The metal, e.g., rhodium, catalyst may be attached to a thin film or membrane support, such as cellulose acetate or polyphenylenesulfone, as described in for example J. Mol. Cat. 1990, 63, 213-221.

The metal, e.g., rhodium, catalyst may be attached to an insoluble polymeric support through an organophosphorus-containing ligand, such as a phosphite, incorporated into the polymer. The supported catalyst is not limited by the choice of polymer or phosphorus-containing species incorporated into it. Descriptions of polymer-supported catalysts may be found in for example: J. Mol. Cat. 1993, 83, 17-35; Chemtech 1983, 46; J. Am. Chem. Soc. 1987, 109, 7122-7127.

In the heterogeneous catalysts described above, the catalyst may remain in its heterogeneous form during the entire hydroformylation and catalyst separation process. In another embodiment of the invention, the catalyst may be supported on a polymer which, by the nature of its molecular weight, is soluble in the reaction medium at elevated temperatures, but precipitates upon cooling, thus facilitating catalyst separation from the reaction mixture. Such "soluble" polymer-supported catalysts are described in for example: Polymer, 1992, 33, 161; J. Org. Chem. 1989, 54, 2726-2730.

More preferably, the reaction is carried out in the slurry phase due to the high boiling points of the products, and to avoid

decomposition of the product aldehydes. The catalyst may then be separated from the product mixture, for example, by filtration or decantation. The reaction product fluid may contain a heterogeneous metal-organopolyphosphite ligand complex catalyst, e.g., slurry, or at least a portion of the reaction product fluid may contact a fixed heterogeneous metal-organopolyphosphite ligand complex catalyst during the hydroformylation process. In an embodiment of this invention, the metal-organopolyphosphite ligand complex catalyst may be slurried in the reaction product fluid.

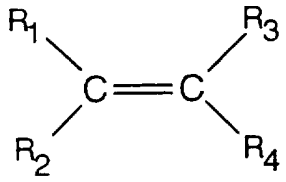
The substituted or unsubstituted olefinic unsaturated starting material reactants that may be employed in the hydroformylation processes of this invention include both optically active (prochiral and chiral) and non-optically active (achiral) olefinic unsaturated compounds containing from 2 to 40, preferably 4 to 20, carbon atoms. Such olefinic unsaturated compounds can be terminally or internally unsaturated and be of straight-chain, branched chain or cyclic structures, as well as olefin mixtures, such as obtained from the oligomerization of propene, butene, isobutene, etc. (such as so called dimeric, trimeric or tetrameric propylene and the like, as disclosed, for example, in U. S. Patent Nos. 4,518,809 and 4,528,403). Moreover, such olefin compounds may further contain one or more ethylenic unsaturated groups, and of course, mixtures of two or more different olefinic unsaturated compounds may be employed as the starting hydroformylation material if desired. For example, commercial alpha olefins containing four or more carbon atoms may contain minor amounts of corresponding internal olefins and/or their corresponding saturated hydrocarbon and that such commercial olefins need not necessarily be purified from same prior to being hydroformylated. Illustrative mixtures of olefinic starting materials that can be employed in the hydroformylation reactions include, for example, mixed butenes, e.g., Raffinate I and II. Further such olefinic unsaturated compounds and the corresponding aldehyde products

derived therefrom may also contain one or more groups or substituents which do not unduly adversely affect the hydroformylation process or the process of this invention such as described, for example, in U. S. Patent Nos. 3,527,809, 4,769,498 and the like.

Most preferably the subject invention is especially useful for the production of non-optically active aldehydes, by hydroformylating achiral alpha-olefins containing from 2 to 30, preferably 4 to 20, carbon atoms, and achiral internal olefins containing from 4 to 20 carbon atoms as well as starting material mixtures of such alpha olefins and internal olefins.

Illustrative alpha and internal olefins include, for example, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 2-butene, 2-methyl propene (isobutylene), 2-methylbutene, 2-pentene, 2-hexene, 3-hexane, 2-heptene, 2-octene, cyclohexene, propylene dimers, propylene trimers, propylene tetramers, butadiene, piperylene, isoprene, 2-ethyl-1-hexene, styrene, 4-methyl styrene, 4-isopropyl styrene, 4-tert-butyl styrene, alpha-methyl styrene, 4-tert-butyl-alpha-methyl styrene, 1,3-diisopropenylbenzene, 3-phenyl-1-propene, 1,4-hexadiene, 1,7-octadiene, 3-cyclohexyl-1-butene, and the like, as well as, 1,3-dienes, butadiene, alkyl alkenoates, e.g., methyl pentenoate, alkenyl alkanoates, alkenyl alkyl ethers, alkenols, e.g., pentenols, alkenals, e.g., pentenals, and the like, such as allyl alcohol, allyl butyrate, hex-1-en-4-ol, oct-1-en-4-ol, vinyl acetate, allyl acetate, 3-butenyl acetate, vinyl propionate, allyl propionate, methyl methacrylate, vinyl ethyl ether, vinyl methyl ether, allyl ethyl ether, n-propyl-7-octenoate, 3-butenenitrile, 5-hexenamide, eugenol, iso-eugenol, safrole, iso-safrole, anethol, 4-allylanisole, indene, limonene, beta-pinene, dicyclopentadiene, cyclooctadiene, camphene, linalool, and the like.

Prochiral and chiral olefins useful in the asymmetric hydroformylation that can be employed to produce enantiomeric aldehyde mixtures that may be encompassed by in this invention include those represented by the formula:



(VIII)

wherein R_1, R_2, R_3 and R_4 are the same or different (provided R_1 is different from R_2 or R_3 is different from R_4) and are selected from hydrogen; alkyl; substituted alkyl, said substitution being selected from dialkylamino such as benzylamino and dibenzylamino, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitro, nitrile, thio, carbonyl, carboxamide, carboxaldehyde, carboxyl, carboxylic ester; aryl including phenyl; substituted aryl including phenyl, said substitution being selected from alkyl, amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino, hydroxy, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitrile, nitro, carboxyl, carboxaldehyde, carboxylic ester, carbonyl, and thio; acyloxy such as acetoxy; alkoxy such as methoxy and ethoxy; amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino; acylamino and diacylamino such as acetylbenzylamino and diacetylamino; nitro; carbonyl; nitrile; carboxyl; carboxamide; carboxaldehyde; carboxylic ester; and alkylmercapto such as methylmercapto. It is understood that the prochiral and chiral olefins of this definition also include molecules of the above general formula where the R groups are connected to form ring compounds, e.g., 3-methyl-1-cyclohexene, and the like.

Illustrative optically active or prochiral olefinic compounds useful in asymmetric hydroformylation include, for example, p-isobutylstyrene, 2-vinyl-6-methoxy-2-naphthylene, 3-ethenylphenyl phenyl ketone, 4-ethenylphenyl-2-thienylketone, 4-ethenyl-2-fluorobiphenyl, 4-(1,3-dihydro-1-oxo-2H-isoindol-2-yl)styrene, 2-ethenyl-5-benzoylthiophene, 3-ethenylphenyl phenyl ether, propenylbenzene, isobutyl-4-propenylbenzene, phenyl vinyl ether and the like. Other olefinic compounds include substituted aryl ethylenes as described, for example, in U.S. Patent Nos. 4,329,507, 5,360,938 and 5,491,266, the disclosures of which are incorporated herein by reference.

Illustrative of suitable substituted and unsubstituted olefinic starting materials include those permissible substituted and unsubstituted olefinic compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

The reaction conditions of the hydroformylation processes encompassed by this invention may include any suitable type hydroformylation conditions heretofore employed for producing optically active and/or non-optically active aldehydes. For instance, the total gas pressure of hydrogen, carbon monoxide and olefin starting compound of the hydroformylation process may range from about 1 to about 10,000 psia. In general, however, it is preferred that the process be operated at a total gas pressure of hydrogen, carbon monoxide and olefin starting compound of less than about 2000 psia and more preferably less than about 500 psia. The minimum total pressure is limited predominately by the amount of reactants necessary to obtain a desired rate of reaction. More specifically the carbon monoxide partial pressure of the hydroformylation process of this invention is preferable from about 1 to about 1000 psia, and more preferably from about 3 to about 800 psia, while the hydrogen partial pressure is preferably about 5 to about 500 psia and more preferably from about 10 to about 300

psia. In general H_2:CO molar ratio of gaseous hydrogen to carbon monoxide may range from about 1:10 to 100:1 or higher, the more preferred hydrogen to carbon monoxide molar ratio being from about 1:10 to about 10:1. Further, the hydroformylation process may be conducted at a reaction temperature from about –25°C to about 200°C. In general hydroformylation reaction temperatures of about 50°C to about 120°C are preferred for all types of olefinic starting materials. Of course it is to be understood that when non-optically active aldehyde products are desired, achiral type olefin starting materials and organopolyphosphite ligands are employed and when optically active aldehyde products are desired prochiral or chiral type olefin starting materials and organopolyphosphite ligands are employed. Of course, it is to be also understood that the hydroformylation reaction conditions employed will be governed by the type of aldehyde product desired.

As stated above, the subject invention resides in the discovery that deactivation of such metal-organopolyphosphite ligand complex catalysts caused by an inhibiting or poisoning organomonophosphite can be reversed or at least minimized by carrying out the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and one or more of the following: at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, preferably less than about 20°C, and more preferably less than about 15°C; at a carbon monoxide conversion of less than about 90%, preferably less than about 75%, and more preferably less than about 65%; at a hydrogen conversion of greater than about 65%, preferably greater than about 85%, and more preferably greater than about 90%; and/or at an olefinic unsaturated compound conversion of greater than about 50%, preferably greater than about 60%, and more preferably greater than about 70%. When the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide, the carbon monoxide

partial pressure is sufficiently high that the inhibiting or poisoning organomonophosphite byproduct does not coordinate with and/or dissociates from the metal-organopolyphosphite ligand complex catalyst. At higher carbon monoxide partial pressures where the hydroformylation reaction rate has a negative order in carbon monoxide, carbon monoxide coordinates more effectively with respect to the metal of the metal-organopolyphosphite ligand complex catalyst greater than the inhibiting organomonophosphite and competes with the inhibiting organomonophosphite for the free coordination site on the metal, e.g., rhodium, thereby increasing the concentration of inhibiting organomonophosphite in solution. The inhibiting or poisoning organomonophosphite in solution can then be hydrolyzed with water, a weakly acidic compound, or both added water and a weakly acidic compound. See, for example, U.S. Patent No. 5,288,918.

As used herein, a hydroformylation reaction rate that is of negative or inverse order in carbon monoxide refers to a hydroformylation reaction rate in which the carbon monoxide partial pressure is such that the hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and the hydroformylation reaction rate decreases as carbon monoxide partial pressure increases. See, for example, Fig. 1 which graphically illustrates this negative or inverse relationship between hydroformylation reaction rate and carbon monoxide partial pressure.

Without wishing to be bound to any exact theory or mechanistic discourse, it appears that the structural features of certain organopolyphosphite ligands which make them such beneficially unique hydroformylation catalysts as discussed, for example, in U.S. Patent No. 4,668,651, are also a cause of the intrinsic catalyst deactivation discussed herein. The activity of the metal-organopolyphosphite ligand complex catalyst declines as inhibiting catalyst concentration builds.

For instance while metal-organopolyphosphite ligand complex catalysts of the type employable herein have been found to be highly active and selective in hydroformylation processes in converting terminal as well as internal olefins to aldehydes, it has also been observed that such catalyst systems undergo a loss in catalytic activity over time. In the course of studying such catalysts, the formation of a class of diorganophosphite byproducts have been discovered which can best be described as organomonophosphite decomposition products of the organopolyphosphite ligand employed. Such evidence is consistent with the view that the organopolyphosphite reacts with an alcohol or an alkoxy radical, such as likely to arise from the reaction of the aldehyde product and hydrogen (or hydride), to form an alkyl [1,1'-biaryl-2,2'-diyl] phosphite, i.e. an organomonophosphite byproduct, which may be further identifiable and characterizable by conventional analytical techniques, such as Phosphorus-31 nuclear magnetic resonance spectroscopy and Fast Atom Bombardment Mass Spectroscopy. The intrinsic catalyst deactivation of the preferred metal-organopolyphosphite ligand complex catalyst is thus believed to be primarily caused by such organomonophosphite byproduct which acts as a catalyst poison or inhibitor by competing for coordination sites on the metal and forming complexes that are far less catalytically reactive than the preferred metal-organopolyphosphite ligand complex catalyst employed.

A means for reversing or greatly minimizing such intrinsic catalyst deactivation has now been discovered which comprises carrying out the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and one or more of the following: at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, preferably less than about 20°C, and more preferably less than about 15°C; at a carbon monoxide conversion of less than about

90%, preferably less than about 75%, and more preferably less than about 65%; at a hydrogen conversion of greater than about 65%, preferably greater than about 85%, and more preferably greater than about 90;, and/or at an olefinic unsaturated compound conversion of greater than about 50%, preferably greater than about 60%, and more preferably greater than about 70%.

It has now been discovered that the catalyst activity of a metal-organopolyphosphite ligand complex catalyst that has become at least partially intrinsically deactivated due to the formation of organomonophosphite ligand byproduct over continuous hydroformylation, can be restored to a significant degree (i.e. catalyst reactivation) by conducting the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and one or more of the following: at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, preferably less than about 20°C, and more preferably less than about 15°C; at a carbon monoxide conversion of less than about 90%, preferably less than about 75%, and more preferably less than about 65%; at a hydrogen conversion of greater than about 65%, preferably greater than about 85%, and more preferably greater than about 90%; and/or at an olefinic unsaturated compound conversion of greater than about 50%, preferably greater than about 60%, and more preferably greater than about 70%. More preferably such intrinsic catalyst deactivation can be prevented or at least greatly minimized by conducting the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and a combination of one or more of the following: at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, preferably less than about 20°C, and more preferably less than about 15°C; at a carbon monoxide conversion of less than about

90%, preferably less than about 75%, and more preferably less than about 65%; at a hydrogen conversion of greater than about 65%, preferably greater than about 85%, and more preferably greater than about 90%; and/or at an olefinic unsaturated compound conversion of greater than about 50%, preferably greater than about 60%, and more preferably greater than about 70% prior to any significant build-up of such organomonophosphite byproducts (e.g. employing such negative or inverse order in carbon monoxide and permissible combinations from the start of the hydroformylation process).

The carbon monoxide partial pressure of the hydroformylation processes of this invention is such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases, i.e., the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide. The carbon monoxide partial pressure is sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with the metal-organopolyphosphite ligand complex catalyst. As indicated herein, the carbon monoxide partial pressure is preferably from about 1 psia to about 1000 psia, more preferably from about 3 psia to about 800 psia, and most preferably from about 5 psia to about 500 psia.

In contrast to metal-organopolyphosphite ligand complex catalyzed hydroformylation processes, carbon monoxide partial pressure is kept relatively low in the conventional triphenylphosphine-modified rhodium hydroformylation processes because higher linear to branched aldehyde ratios are obtained (J. Falbe "New Syntheses with Carbon Monoxide, Springer Verlag, Berlin Heidelberg New York, 1980. p 55.) and to minimize catalyst deactivation through the formation of relatively inactive rhodium clusters (see, for example, U.S. Patent No. 4,277,627).

Aldehyde isomer ratios produced by organopolyphosphite modified metal catalysts do not have the same sensitivity to carbon

monoxide as do triphenylphosphine-modified metal catalysts. With organopolyphosphite modified metal catalysts, very high isomer ratios can be achieved in the region where carbon monoxide is of negative reaction order. In addition, the organopolyphosphite modified metal catalysts do not undergo the type of catalyst deactivating clustering reactions characteristic of triphenylphosphine-modified metal catalysts. Thus one is not limited by considerations of isomer ratio or of metal, e.g., rhodium, clustering to operating in the lower carbon monoxide partial pressure ranges.

When the rate of hydroformylation is graphically depicted as a function of carbon monoxide partial pressure, the resulting curve passes through a maximum as set out in Fig. 1. In the rising part of the curve, hydroformylation has a positive order in carbon monoxide, on the descending part of the curve, hydroformylation has a negative order in carbon monoxide.

Where the reaction is of positive order in carbon monoxide, an increase in hydroformylation reaction rate will decrease the partial pressure of carbon monoxide. This decrease in concentration will slow the rate such that the reaction temperature and carbon monoxide and hydrogen partial pressures can be easily controlled.

Conversely, when hydroformylation has an inverse or negative order in carbon monoxide, then as carbon monoxide is consumed, that which remains is at a lower partial pressure and has a greater propensity to react. As more carbon monoxide is consumed, the hydroformylation reaction goes even faster. In addition to the rate increase from decreasing carbon monoxide partial pressure, there will also be an increase in rate from the heat of reaction since hydroformylation is an exothermic reaction. A feedback loop develops which can result in essentially complete consumption of the limiting reactant and therefore termination of the hydroformylation reaction.

The amount of inhibiting organomonophosphite free in solution can be increased by increasing carbon monoxide partial pressure. Carbon monoxide competes with the inhibiting organomonophosphite for the free coordination site on the metal, e.g., rhodium, thereby increasing the concentration of inhibiting organomonophosphite in solution.

If hydroformylation is operated under conditions of a positive order in carbon monoxide, a steadily declining catalyst activity is observed because of the accumulation of inhibiting organomonophosphite/organopolyphosphite ligand-metal complex. Alternatively, if hydroformylation is operated at higher carbon monoxide partial pressures in a region where hydroformylation has a negative order in carbon monoxide in order to dissociate inhibiting complex and/or prevent or lessen coordination of the organomonophosphite ligand with the metal-organopolyphosphite ligand complex catalyst and facilitate its hydrolysis, then the hydroformylation is operated in a reaction region where control of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature is more difficult.

Hydroformylation reaction rate may cycle during continuous operation in a continuous stirred type reactor as may carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature if one is hydroformylating under conditions where the reaction is of negative or inverse order in carbon monoxide. Cycling conditions disrupt steady operation of the unit. Uniform partial pressures and temperature are desired. As used herein, "cycling" refers to frequent periodic and extreme changes in process parameters, e.g., reaction rate, reaction temperature, total reaction pressure, carbon monoxide partial pressure and hydrogen partial pressure, during the hydroformylation process.

The cycling may be initiated when operating under conditions were the rate of hydroformylation is inverse order in carbon monoxide. These conditions are not normally encountered with conventional triphenylphosphine-modified metal catalysts since the region where carbon monoxide is of negative rate order is also a region which gives lower isomer ratios and increased catalyst deactivation. Conventional triphenylphosphine-modified metal catalysts typically operate under conditions where increasing carbon monoxide partial pressure increases reaction rate and conversely decreasing carbon monoxide partial pressure decreases rate.

Higher carbon monoxide partial pressures provide desired benefits in organopolyphosphite modified metal catalysts in that olefin efficiency losses due to hydrogenation may be reduced and the dissociation of an inhibiting organomonophosphite from the catalyst is favored. The dissociated or uncoordinated inhibiting organomonophosphite is more readily hydrolyzed and the hydrolysis fragments can be scrubbed from the solution as disclosed herein. Higher carbon monoxide partial pressures give both a higher lined out activity and lower efficiency losses to alkanes since the higher carbon monoxide partial pressure makes it a more effective competitor for a metal, e.g., rhodium, alkyl. If carbon monoxide reacts with the metal, e.g., rhodium, alkyl, the acyl precursor of the aldehyde is obtained; if hydrogen reacts with the metal, e.g., rhodium, alkyl, the corresponding alkane is obtained. However, as indicated above, operating at the higher carbon monoxide partial pressures where hydroformylation is of a negative order significantly complicates control of partial pressures.

It is normally desirable to increase the temperature difference between the reaction temperature and the reactor cooling means, e.g., coolant, so that the equipment size can be minimized. Some have disclosed running at reactor temperatures hot enough to generate useful steam from the exothermic heat of reaction. A typical

non-aqueous triphenylphosphine system will have a temperature difference of approximately 30°C between the reaction and the coolant.

Design of the heat removal equipment is an important aspect of controlling the reaction partial pressures in this invention where the process is operated in inverse or negative order in carbon monoxide. The temperature difference between the reaction product fluid temperature and the inlet coolant temperature should be small to provide to provide the necessary control. The lower the temperature difference the better the control will be. For hydroformylation in regions where the reaction is of a negative order in carbon monoxide, the difference should be below 25°C and more preferably below 20°C. Temperature difference below 15°C may be achieved using such as evaporative cooling, enhanced heat transfer or larger equipment.

Continuous stirred tank reactors used for exothermic reactions must have some means of removing the heat of reaction from the reactor. The cooling can be accomplished in a number of ways, putting a cooling jacket around the reactor, installing cooling coils in the reactor, or pumping the reactor solution through an external heat exchanger. In all cases the driving force for the heat removal is the temperature difference between the reaction product fluid and the reactor zone coolant.

Most chemical reactions are affected by temperature, and by some or all of the reactant concentrations. If a catalyst is used, its concentration also will affect the reaction rate. In most circumstances it is desirable to control the conditions in the reactor at some steady state. Changes in conditions may cause undesirable changes in selectivity, catalyst performance or other operational difficulties. Temperature has an exponential effect on the hydroformylation reaction rate. A change in reaction temperature of 10°C typically doubles the rate of reaction. If the reaction rate increases, the heat generated increases, and the extra heat must be removed to keep the temperature from continuing to increase.

Removal of heat from a system is described by the following equation:

Heat Removed = UAΔT

wherein U is a heat transfer coefficient dependent on the conditions on both the process and coolant sides of the equipment, A is the surface area available for heat transfer, and ΔT is the appropriate temperature difference between the reaction product fluid temperature and inlet coolant temperature. At steady state,

Heat Removed = Heat Generated by the reaction.

As an illustration, assume a reaction is only dependent on reaction temperature. If for some reason the reactor temperature increases by 1°C, the reaction rate will increase by approximately 10% which will in turn generate 10% more heat. If nothing is changed with the reaction zone cooler, the heat removed will depend on the new ΔT of the system. If the original ΔT was 5C°, the new ΔT will be 6°C, a 20% (i.e. 1/5) increase in heat removed which tends to drive the system back to the original set of steady conditions.

If instead of a 5°C ΔT between reaction product fluid and reaction zone coolant, e.g., heat exchanger, the ΔT was 20C°, a 1°C increase in reactor temperature will give a new temperature difference between reaction product fluid and reaction zone coolant, e.g., heat exchanger, of 21°C. Whereas the reaction rate increased by 10%, there was only a 5% (i.e. 1/20) increase in the heat removal capability. Since more heat is being generated than is being removed, the reactor would continue to warm until some action is taken to increase the heat transfer from the system or until the reactant(s) were exhausted.

When carbon monoxide is of negative order, in order to have an intrinsically stable system, a disturbance in the temperature

must produce a smaller percentage increase in reaction rate than the percentage increase in ΔT of the system. As used herein, "inlet coolant temperature" refers to the temperature of the coolant prior to entering any heat transfer means, e.g., internal coils, external jackets, shell and tube heat exchanger, plate and frame heat exchanger and the like. This invention is not intended to be limited in any manner by the permissible coolants and/or heat transfer means.

Commercial systems are more complicated in that the reaction rate depends on reactant and catalyst concentrations as well as temperature. Furthermore, the reaction rate may increase with an increase in concentration of one reactant and decrease with an increase in concentration of another reactant. When the reaction rate changes are the same sign as the concentration changes, the concentration changes help the stability of the operation. If a disturbance in the system causes the rate to increase, more reactant is consumed which in turn makes the rate slow down bringing it back toward a steady state. In contrast, systems where the reaction rate increases with a decrease in reactant concentration are more difficult to control. Rate increases consume more reactant which causes the rate to increase even consuming more of the reactant. As a result the ΔT of the heat exchanger will have to be lower to produce intrinsic stability than it would for a system where the reactants had no effect on reaction rate. These effects will vary in magnitude with the kinetic responses of the different reactants.

The effect of the feedback loop described above created by the negative or inverse order in carbon monoxide can be minimized by keeping the conversion of the carbon monoxide low in a given reaction stage. Disturbances in the carbon monoxide feed or the reaction rate are a smaller portion of the total carbon monoxide exiting the reaction stage when the conversion is low. As a result, the disturbance has a smaller feedback effect on the reaction system.

For example, given that stoichiometric amounts of olefin, hydrogen and carbon monoxide are fed to a reactor, and the total molar feed to the reactor is 3 lb. moles/hr., if the conversion in the reactor is 50%, 0.5 lb. mole of carbon monoxide will exit the reactor. If a disturbance in the carbon monoxide feed causes a momentary increase of 0.1 lb. mole, the amount of carbon monoxide will increase by no more than 0.1/0.5 or 20% immediately after the disturbance. If, however, the conversion in the reactor was 80%, the disturbance could potentially be 0.1/0.2 or 50% of the exiting carbon monoxide. The 50% response for the high conversion case would produce a more significant feedback response than the lower conversion case of 20%. Hence, the lower the carbon monoxide conversion, the more stability will be imparted to the reaction system.

In order to consume excess reactant, carbon monoxide must either be recycled back to the reaction system or the portion of the reactant that is not converted to the product in the stages with control difficulties must be converted in subsequent reaction vessels or stages. The above example uses carbon monoxide as the reactant with the hydroformylation reaction rate of a negative or inverse order in carbon monoxide. Any reactant that has a negative effect on the reaction rate will behave in a similar manner. Lower conversions of the negative order reactant will provide for more stable operation of the reaction system.

As a result of this invention, more stability will be imparted to a hydroformylation reaction vessel or stage by employing one or more of a low ΔT, low carbon monoxide conversions, high hydrogen conversions and high olefinic unsaturated compound conversions in hydroformylation processes that are conducted in reaction regions where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide. A carbon monoxide conversion of less than about 90%, preferably less than about 75%, and

more preferably less than about 65%, may be employed in the processes of this invention to produce a stable reaction system.

The hydroformylation reaction can be controlled by limiting the amount of hydrogen fed to the reaction system. If the hydroformylation reaction is consuming essentially all of the hydrogen fed to the reactor, the reaction rate cannot increase. It is limited by the availability of hydrogen.

The hydrogen partial pressure exiting the reactor should be very low to successfully control the reaction. As hydrogen feed is limited, the rate of aldehyde production will begin to be governed by mass transfer effects rather than pure kinetics. Mass transfer in a vapor liquid medium is proportional to the concentration of the reactant in the vapor. In the limit, the hydroformylation reaction rate must be zero when no hydrogen is present because it is an essential reactant. A large positive effect on rate by a reactant concentration is beneficial for controlling the conditions in the reactor. As the rate increases, the reactant is consumed which slows down the rate. If the rate slows down, the concentration of the reactant increases which tends to increase the reaction rate. This is depicted by the following equation:

Mass Transfer rate = Constant x (concentration of hydrogen in vapor)

In principle, the hydroformylation reaction could be limited by throttling any one of the reactants, olefin, carbon monoxide or hydrogen. However, limiting the olefin would mean the reaction system would have to be very large to produce commercial quantities of product. Limiting the carbon monoxide feed to the reactor would allow undesirable side reactions to occur with the ligand as described earlier. Hydrogen is the best component to use as the limiting reactant for this system.

When the hydroformylation reaction rate is limited by mass transfer, the reaction rate cannot increase significantly because it is limited by the rate which the hydrogen can be transported to the active catalyst site. Even if the rate were not limited by the rate of transport, the maximum increase in reaction rate is bound by the excess hydrogen that is exiting the reactor. If the excess of hydrogen is very small, the possible increase in rate is very small. The hydroformylation reaction rate can only increase until it consumes all, or essentially all, of the hydrogen entering the reactor.

For example, if 99.5% of the hydrogen fed to a reactor is converted to aldehyde, the possible increase in reaction rate is only 0.005 x (Feed rate of hydrogen). If the conversion of hydrogen were only 97.5%, the rate could increase by 0.025 x (Feed rate of hydrogen) producing a disturbance five times the size of the disturbance where the conversion was 99.5%. The best hydrogen conversion for operation will depend on the kinetics of the system.

As used herein, conversions refer to conversions in an individual reactive stage. Within an individual reactive stage, a liquid or gas element within that stage will have essentially the same composition as a liquid or gas element taken from some other region of the reactive stage. A separate reactive stage is said to exist when some type of barrier whether physical or mechanical allows a difference in composition between a representative element from each stage, or catalyst product fluid zone, where reactants and catalysts are present together under reaction conditions described herein. Certain "non-idealities" will occur within a single reactive stage such as near the inlet point of the reactants. This definition of a reactive stage is not meant to include such non-idealities. The definition of a reactive stage does not imply that the stages have no mixing between them. Some backmixing between the stages may occur diminishing the efficiency of a single reactive stage, but the stages are still distinct. One or more reactive stages may be present in a reactive zone.

As a result of this invention, more stability will be imparted to a hydroformylation reaction vessel or stage by employing one or more of a low ΔT, low carbon monoxide conversions, high hydrogen conversions and high olefinic unsaturated compound conversions in hydroformylation processes that are conducted in reaction regions where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide. A hydrogen conversion of greater than about 65%, preferably greater than about 85%, and more preferably greater than about 90%, may be employed in the processes of this invention to produce a stable reaction system.

The hydroformylation rate is approximately of first order with respect to the olefin partial pressure in the reaction vessel. When a disturbance in reaction conditions increases the reaction rate, the amount of olefin in the reaction vessel will decrease. A decrease in olefin concentration will slow the hydroformylation rate which tends to push the system back to the steady-state that it was at before the disturbance. Likewise, a disturbance in the reaction rate that slows the reaction will tend to increase the amount of olefin in the reaction vessel. The increase in olefin concentration has the effect of increasing the hydroformylation rate which also tends to push the system back toward the original steady-state. However, depending on the relative concentration of reactants in the vessel, the concentration of olefin may or may not change significantly. If a large excess of olefin is present in the reaction vessel such as when operating at low olefin conversions, the amount of olefin present in the reaction vessel may change little even when a relatively large disturbance in the reaction condition occurs. Another condition favorable to the olefin acting as a stabilizing influence could be when the conversion of the olefin is low, but the concentration of the olefin in the reaction system is also low. Under either of these conditions, a change in reaction rate during an upset in reaction conditions produces a similarly significant change in the olefin present in the reaction vessel. If the amount of olefin in the reaction

vessel does not change significantly, its ability to behave as a stabilizing influence is diminished. One disadvantage of keeping the olefin concentration low and the conversion low is that the equipment used to produce the same amount of product will be larger than the situation where the olefin conversion is high.

For the purposes of this invention, the conversion of the olefin should be greater than about 70%, preferably greater than about 80%, and more preferably greater than about 85%. The benefits of stabilization from the olefin can be combined with other operating conditions such as temperature difference between the process and the coolant, hydrogen conversion, and low carbon monoxide conversion (high carbon monoxide partial pressures), and high hydrogen partial pressures (low hydrogen conversion). By combining one or more of the techniques, an operable region may be found without going to an extreme in any one of the conditions.

It should also be understood that much of the necessary total conversion of the olefin could be performed in reaction vessels or compartments preceding the vessel of interest. The olefin conversion within a given compartment may be greater than about 50%, preferably greater than about 60%, and more preferably greater than about 70%. However, the olefin can still have a stabilizing influence on the reaction conditions if the olefin concentration changes significantly with a corresponding significant change in reaction conditions. This is a similar situation as described above where the olefin conversion is low, but the concentration of the olefin in the particular vessel is also low.

The reaction rate may increase with an increase in concentration of one reactant and decrease with an increase in concentration of another reactant. When the reaction rate changes are the same sign as the concentration changes, the concentration changes help the stability of the operation. If a disturbance in the system causes the rate to increase, more reactant is consumed which in turn

makes the rate slow down bringing it back toward a steady state. In contrast, systems where the reaction rate increases with a decrease in reactant concentration are more difficult to control. Rate increases consume more reactant which causes the rate to increase even consuming more of the reactant. As a result the ΔT of the heat exchanger will have to be lower to produce intrinsic stability than it would for a system where the reactants had no effect on reaction rate. These effects will vary in magnitude with the kinetic responses of the different reactants.

In addition to the stabilizing effect conversion can have on the hydroformylation reaction system, the system can also have stability imparted to it simply by the kinetic response of the system. The kinetic response of an organopolyphosphite to carbon monoxide partial pressure for a significant range of carbon monoxide pressures is negative. In other words, for a given change in carbon monoxide partial pressure, the reaction rate will respond in the opposite direction; an increase in carbon monoxide partial pressure causing a decrease in rate, or a decrease in carbon monoxide partial pressure causing an increase in rate. It is possible to represent this negative response empirically by saying the reaction rate is a function of the carbon monoxide partial pressure raised to some power "b". The kinetic response may not always behave in this manner, but it can be a very useful way of representing the reaction rate over some portion of the operating conditions. If "b" is less than zero, the rate is said to be negative order in carbon monoxide and, if "b" is less than zero, the change in reaction rate for a fixed change in carbon monoxide partial pressure will decrease as the partial pressure of carbon monoxide increases. For example if the reaction rate is proportional to the carbon monoxide partial pressure raised to the "-1" power, a change from 30 to 40 psi carbon monoxide results in a relative change in reaction rate of 1.33, whereas a change from 100 to 110 psi carbon monoxide results in a relative change in reaction rate of 1.10. This

response is due only to the conditions within the reactor, and is not dependent on the conversion of any particular reactant. All of the reactants may affect the reaction rate whether positive or negative order, but the exact responses will depend on the specific kinetic response for a particular catalyst and a particular reactant.

The subject invention may be useful in conjunction with another invention which resides in the discovery that deactivation of metal-organopolyphosphite ligand complex catalysts caused by an inhibiting or poisoning organomonophosphite can be reversed or at least minimized by carrying out hydroformylation processes in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process. Such invention is disclosed in copending U.S. Patent Application Serial No. (D-17688), filed on an even date herewith, the disclosure of which is incorporated herein by reference.

The hydroformylation processes encompassed by this invention are also conducted in the presence of an organic solvent for the metal-organopolyphosphite ligand complex catalyst and free organopolyphosphite ligand. The solvent may also contain dissolved water up to the saturation limit. Depending on the particular catalyst and reactants employed, suitable organic solvents include, for example, alcohols, alkanes, alkenes, alkynes, ethers, aldehydes, higher boiling aldehyde condensation byproducts, ketones, esters, amides, tertiary amines, aromatics and the like. Any suitable solvent which does not unduly.adversely interfere with the intended hydroformylation reaction can be employed and such solvents may include those disclosed heretofore commonly employed in known metal catalyzed

hydroformylation reactions. Mixtures of one or more different solvents may be employed if desired. In general, with regard to the production of achiral (non-optically active) aldehydes, it is preferred to employ aldehyde compounds corresponding to the aldehyde products desired to be produced and/or higher boiling aldehyde liquid condensation byproducts as the main organic solvents as is common in the art. Such aldehyde condensation byproducts can also be preformed if desired and used accordingly. Illustrative preferred solvents employable in the production of aldehydes include ketones (e.g. acetone and methylethyl ketone), esters (e.g. ethyl acetate), hydrocarbons (e.g. toluene), nitrohydrocarbons (e.g. nitrobenzene), ethers (e.g. tetrahydrofuran (THF) and glyme), 1,4-butanediols and sulfolane. Suitable solvents are disclosed in U.S. Patent No. 5,312,996. The amount of solvent employed is not critical to the subject invention and need only be that amount sufficient to solubilize the catalyst and free ligand of the hydroformylation reaction mixture to be treated. In general, the amount of solvent may range from about 5 percent by weight up to about 99 percent by weight or more based on the total weight of the hydroformylation reaction mixture starting material.

Accordingly illustrative non-optically active aldehyde products include e.g., propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, 2-methyl 1-butyraldehyde, hexanal, hydroxyhexanal, 2-methyl valeraldehyde, heptanal, 2-methyl 1-hexanal, octanal, 2-methyl 1-heptanal, nonanal, 2-methyl-1-octanal, 2-ethyl 1-heptanal, 3-propyl 1-hexanal, decanal, adipaldehyde, 2-methylglutaraldehyde, 2-methyladipaldehyde, 3-methyladipaldehyde, 3-hydroxypropionaldehyde, 6-hydroxyhexanal, alkenals, e.g., 2-, 3- and 4-pentenal, alkyl 5-formylvalerate, 2-methyl-1-nonanal, undecanal, 2-methyl 1-decanal, dodecanal, 2-methyl 1-undecanal, tridecanal, 2-methyl.1-tridecanal, 2-ethyl, 1-dodecanal, 3-propyl-1-undecanal, pentadecanal, 2-methyl-1-tetradecanal, hexadecanal, 2-methyl-1-pentadecanal, heptadecanal, 2-methyl-1-hexadecanal, octadecanal, 2-

methyl-1-heptadecanal, nonodecanal, 2-methyl-1-octadecanal, 2-ethyl 1-heptadecanal, 3-propyl-1-hexadecanal, eicosanal, 2-methyl-1-nonadecanal, heneicosanal, 2-methyl-1-eicosanal, tricosanal, 2-methyl-1-docosanal, tetracosanal, 2-methyl-1-tricosanal, pentacosanal, 2-methyl-1-tetracosanal, 2-ethyl 1-tricosanal, 3-propyl-1-docosanal, heptacosanal, 2-methyl-1-octacosanal, nonacosanal, 2-methyl-1-octacosanal, hentriacontanal, 2-methyl-1-triacontanal, and the like.

Illustrative optically active aldehyde products include (enantiomeric) aldehyde compounds prepared by the asymmetric hydroformylation process of this invention such as, e.g. S-2-(p-isobutylphenyl)-propionaldehyde, S-2-(6-methoxy-2-naphthyl)propionaldehyde, S-2-(3-benzoylphenyl)-propionaldehyde, S-2-(p-thienoylphenyl)propionaldehyde, S-2-(3-fluoro-4-phenyl)phenylpropionaldehyde, S-2-[4-(1,3-dihydro-1-oxo-2H-isoindol-2-yl)phenyl]propionaldehyde, S-2-(2-methylacetaldehyde)-5-benzoylthiophene and the like.

Illustrative of suitable substituted and unsubstituted aldehyde products include those permissible substituted and unsubstituted aldehyde compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

As indicated above, it is generally preferred to carry out the hydroformylation processes of this invention in a continuous manner. In general, continuous hydroformylation processes are well known in the art and may involve: (a) hydroformylating the olefinic starting material(s) with carbon monoxide and hydrogen in a liquid homogeneous reaction mixture comprising a solvent, the metal-organopolyphosphite ligand complex catalyst, and free organopolyphosphite ligand; (b) maintaining reaction temperature and pressure conditions favorable to the hydroformylation of the olefinic starting material(s); (c) supplying make-up quantities of the olefinic starting material(s), carbon monoxide and hydrogen to the reaction

medium as those reactants are used up; and (d) recovering the desired aldehyde hydroformylation product(s) in any manner desired. The continuous process can be carried out in a single pass mode, i.e., wherein a vaporous mixture comprising unreacted olefinic starting material(s) and vaporized aldehyde product is removed from the liquid reaction mixture from whence the aldehyde product is recovered and make-up olefinic starting material(s), carbon monoxide and hydrogen are supplied to the liquid reaction medium for the next single pass without recycling the unreacted olefinic starting material(s). Such types of recycle procedure are well known in the art and may involve the liquid recycling of the metal-organopolyphosphite complex catalyst fluid separated from the desired aldehyde reaction product(s), such as disclosed, for example, in U.S. Patent 4,148,830 or a gas recycle procedure such as disclosed, for example, in U.S. Patent 4,247,486, as well as a combination of both a liquid and gas recycle procedure if desired. The disclosures of said U.S. Patents 4,148,830 and 4,247,486 are incorporated herein by reference thereto. The most preferred hydroformylation process of this invention comprises a continuous liquid catalyst recycle process. Suitable liquid catalyst recycle procedures are disclosed, for example, in U. S. Patent Nos. 4,668,651; 4,774,361; 5,102,505 and 5,110,990.

In an embodiment of this invention, the aldehyde product mixtures may be separated from the other components of the crude reaction mixtures in which the aldehyde mixtures are produced by any suitable method. Suitable separation methods include, for example, solvent extraction, crystallization, distillation, vaporization, wiped film evaporation, falling film evaporation, phase separation, filtration and the like. It may be desired to remove the aldehyde products from the crude reaction mixture as they are formed through the use of trapping agents as described in published Patent Cooperation Treaty Patent Application WO 88/08835. A preferred method for separating the aldehyde mixtures from the other components of the crude reaction

mixtures is by membrane separation. Such membrane separation can be achieved as set out in U.S. Patent No. 5,430,194 and copending U.S. Patent Application Serial No. 08/430,790, filed May 5, 1995, referred to above.

As indicated above, at the conclusion of (or during) the process of this invention, the desired aldehydes may be recovered from the reaction mixtures used in the process of this invention. For example, the recovery techniques disclosed in U.S. Patents 4,148,830 and 4,247,486 can be used. For instance, in a continuous liquid catalyst recycle process the portion of the liquid reaction mixture (containing aldehyde product, catalyst, etc.), i.e., reaction product fluid, removed from the reaction zone can be passed to a separation zone, e.g., vaporizer/separator, wherein the desired aldehyde product can be separated via distillation, in one or more stages, under normal, reduced or elevated pressure, from the liquid reaction fluid, condensed and collected in a product receiver, and further purified if desired. The remaining non-volatilized catalyst containing liquid reaction mixture may then be recycled back to the reactor as may any other volatile materials, e.g., unreacted olefin, together with any hydrogen and carbon monoxide dissolved in the liquid reaction after separation thereof from the condensed aldehyde product, e.g., by distillation in any conventional manner. In general, it is preferred to separate the desired aldehydes from the catalyst-containing reaction mixture under reduced pressure and at low temperatures so as to avoid possible degradation of the organopolyphosphite ligand and reaction products. When an alpha-mono-olefin reactant is also employed, the aldehyde derivative thereof can also be separated by the above methods.

More particularly, distillation and separation of the desired aldehyde product from the metal-organopolyphosphite complex catalyst containing reaction product fluid may take place at any suitable temperature desired. In general, it is recommended that such distillation take place at relatively low temperatures, such as below

150°C, and more preferably at a temperature in the range of from about 50°C to about 140°C. It is also generally recommended that such aldehyde distillation take place under reduced pressure, e.g., a total gas pressure that is substantially lower than the total gas pressure employed during hydroformylation when low boiling aldehydes (e.g., C_4 to C_6) are involved or under vacuum when high boiling aldehydes (e.g. C_7 or greater) are involved. For instance, a common practice is to subject the liquid reaction product medium removed from the hydroformylation reactor to a pressure reduction so as to volatilize a substantial portion of the unreacted gases dissolved in the liquid medium which now contains a much lower synthesis gas concentration than was present in the hydroformylation reaction medium to the distillation zone, e.g. vaporizer/separator, wherein the desired aldehyde product is distilled. In general, distillation pressures ranging from vacuum pressures on up to total gas pressure of about 50 psig should be sufficient for most purposes.

As indicated above, once the inhibiting organomonophosphite byproduct is dissociated from the metal-organopolyphosphite ligand complex catalyst or otherwise in solution, treatment with water and/or weakly acidic additives causes the undesirable organomonophosphite ligand byproduct to hydrolyze at a much faster rate than the desired organopolyphosphite ligand employed. A water and/or weakly acidic additive treatment allows one to selectively remove such undesired organomonophosphite byproducts from the reaction system or more preferably prevent or minimize any undue adverse buildup of such organomonophosphite ligand byproduct within the reaction system as described below.

Weakly acidic additives which are employable herein and which are added to the hydroformylation reaction medium are well known compounds as are methods for their preparation and in general are readily commercially available. Any weakly acidic compound having a pKa value of from about 1.0 to about 12 and more preferably

from about 2.5 to about 10 may be employed herein. The slightly acidic nature of such compounds has been found to catalyze the hydrolysis of the organomonophosphite ligand byproduct, even when no additional water is deliberately added to the hydroformylation reaction medium, without unduly adversely affecting the organopolyphosphite ligand employed. For example, the acidity of the additive compound should not be so high as to also destroy the organopolyphosphite ligand by acid hydrolysis at an unacceptable rate. Such pKa values are a measure of the acidity of a compound as given in terms of the negative (decadic) logarithm of the acidic dissociation constant, i.e., $-\log_{10}Ka$ = pKa as defined in "Lange's Handbook of Chemistry", Thirteenth Edition, J. A. Dean Editor, pp 5-18 to 5-60 (1985); McGraw-Hill Book Company. Of course estimated pKa values may be obtained by making a comparison with compounds of recognizably similar character for which pKa values are known as discussed on page 5-13 of said "Lange's Handbook of Chemistry".

Among the more preferred weakly acidic compounds are aryl compounds containing from 1 to 3 substituent radicals directly bonded thereto (i.e. directly attached to the aryl ring of said aryl compounds as opposed to being bonded to some substituent of said aryl compounds), each said substituent radical being individually selected from the group consisting of hydroxy and carboxylic acid radicals. Such aryl compounds include those selected from the group consisting of phenyl, biphenyl, naphthyl and dinaphthyl compounds as well as heterocyclic type aryl compounds such as pyridine, and the like. Preferably such weakly acidic compounds contain from 1 to 2 hydroxy radicals or 1 to 2 carboxylic acid radicals or mixtures thereof. Of course, if desired such weakly acidic aryl compounds may also contain other groups or substituents which do not unduly adversely interfere with the purpose of this invention, such as alkyl, halide, trifluoromethyl, nitro, and alkoxy radicals, and the like.

When selecting a particular weakly acidic compound for use in a given process of this invention, in addition to the pKa value of the weakly acidic compound, one may also wish to consider its overall catalytic performance in conjunction with the many particulars of the hydroformylation process involved, e.g. the particular olefin to be hydroformylated, the particular aldehyde product and aldehyde product isomer ratio desired, the organopolyphosphite ligand employed, the amount of water present in the reaction medium, the amount of organomonophosphite ligand present in the reaction medium, and the like, as well as such characteristics of the weakly acidic compound additive as its solubility in the hydroformylation reaction medium and its volatility (e.g. boiling point), etc.

Of course it is to be understood that such weakly acidic compound additives may be employed individually or as mixtures of two or more different weakly acidic compounds. Moreover the amount of such weakly acidic compound additives employable in any given process of this invention need only be a catalytic amount i.e. that minimum amount necessary to catalyze the selective hydrolysis of the organomonophosphite ligand byproduct. Amounts of such weakly acidic compound additives of from 0 to about 20 weight percent or higher if desired, based on the total weight of the hydroformylation reaction medium may be employed. In general, when employed, it is preferred to employ amounts of such weakly acidic compound additives in the range of from about 0.1 to about 5.0 weight percent based on the total weight of the hydroformylation reaction medium. More preferably the hydroformylation process of this invention is carried out in the absence of any such weakly acidic compound additives.

Indeed it has been found that merely by deliberately providing the hydroformylation reaction medium with a small amount of added water one can selectively hydrolyze the undesirable organomonophosphite ligand byproduct at a suitably acceptable rate without unduly adversely hydrolyzing the desired organopolyphosphite

ligand employed. For instance, by providing the hydroformylation reaction medium of the process of this invention with a suitable amount of added water right from the start of the hydroformylation process (or at least before any undue adverse build-up of organomonophosphite ligand byproduct has taken place) one can selectively hydrolyze (without the need of any weakly acidic compound additive) the undesirable organomonophosphite ligand byproduct as it being formed in situ and thereby prevent or minimize any undue adverse build-up of said organomonophosphite ligand. Such selective hydrolysis in turn prevents or minimizes the intrinsic metal-organopolyphosphite ligand complex catalyst deactivation caused by such organomonophosphite ligand as previously discussed herein.

The term "added water" as employed herein refers to water that has been deliberately supplied to the hydroformylation reaction system (as opposed to the presence of only in situ produced water in the hydroformylation reaction medium) of the subject invention. As noted above it may not be necessary to employ any such added water in the process of the subject invention, since hydrolysis of the organomonophosphite ligand byproduct, due to the presence of only in situ produced water in the reaction medium, may be satisfactorily catalyzed by the use of a weakly acidic compound additive provided that the amount of organomonophosphite ligand present is not too great. Thus, it is preferred to carry out the hydroformylation process of the subject invention in the presence of a suitable amount of added water regardless of whether a weakly acidic compound additive is also employed.

Accordingly, the amount of such added water employable in any given process of this invention need only be that minimum amount necessary to achieve the desired selective hydrolysis of the organomonophosphite ligand byproduct. Amounts of such added water of from 0 to about 20 weight percent, or higher if desired, based on the total weight of the hydroformylation reaction medium may be

employed. Of course amounts of added water that might also lead to adversely hydrolyzing the desired organopolyphosphite ligand at an undesirable rate are to be avoided. Amounts of water that may result in a two phase (organic-aqueous) hydroformylation reaction medium as opposed to the desired and conventional single phase (organic) homogeneous hydroformylation reaction medium are preferably to be avoided. In general, when employed, it is preferred to employ amounts of such added water in the range of from about 0.05 to about 10 weight percent based on the total weight of the hydroformylation reaction medium.

The addition of the added water and/or weakly acidic compound additives to the hydroformylation reaction medium of this invention may be accomplished in any suitable manner desired and their order of addition is immaterial. For instance they may be added separately and/or simultaneously, or premixed and then added if desired. Moreover, they may be introduced into the reaction system on their own or along with any conventional reactant, e.g. along with the syn gas or olefin reactant, or via the catalyst recycle line. As noted it is preferred to employ such added water and/or weakly acidic compound additive (when indeed such is used) right from the start-up of the hydroformylation process. For example the weakly acidic compound additive may be solubilized in the metal, e.g., rhodium, catalyst precursor composition and added to the reactor along with said composition, while water may be preferably added to the reaction medium via water saturated syn gas, obtained e.g., by sparging syn gas through a container of water prior to introducing the syn gas into the reactor. Thus an additional benefit of the subject invention is that conventional metal catalyzed continuous hydroformylation reaction systems do not have to be significantly modified, if indeed they have to be modified at all, to accommodate the subject invention.

The selective hydrolysis of the undesired organomonophosphite ligand byproduct can take place in the same

hydroformylation reactor and throughout the continuous reaction system and under the same hydroformylation conditions employed to produce the desired aldehyde product from its olefinic starting material. Thus the conditions employed to effect the selective hydrolysis of the undesirable organomonophosphite ligand byproduct are not critical and include any of the same conventional continuous hydroformylation conditions heretofore employed in the art. Such desired flexibility furnishes one with wide processing latitude for controlling and balancing the degree of improvement desired in preventing or minimizing the intrinsic deactivation of the metal-organopolyphosphite ligand complex catalyst caused by the organomonophosphite ligand byproduct.

Hydrolysis of the organomonophosphite ligand byproduct in turn leads to the formation of phosphorus acidic compounds, e.g., hydroxy alkyl phosphonic acids, as outlined, for example, in U.S. Patent No. 4,737,588. Moreover such phosphorus acidic compounds, e.g., hydroxy alkyl phosphonic acids, are also undesirable in metal-organopolyphosphite ligand catalyzed hydroformylation processes as disclosed, for example, in U.S. Patent Nos. 4,737,588 and 4,769,498. However the formation of such phosphorus acidic compounds as a result of the hydrolysis of the organomonophosphite ligand byproduct via the subject invention, is none the less, preferable to the continued presence of the more undesirable organomonophosphite ligand byproduct in the hydroformylation process. Indeed it is considered that the presence of such phosphorus acidic compounds, e.g., hydroxy alkyl phosphonic acid byproducts, may be effectively controlled as described in said U.S. Patent Nos. 4,737,588 and 4,769,498 or as described herein.

Thus as pointed out herein, a noticeable decrease in the catalytic activity of heretofore conventional continuous metal-organopolyphosphite complex catalyzed continuous hydroformylation processes has been observed to occur over time. This intrinsic loss in

catalytic activity manifests itself in terms of a measurable drop in productivity and is considered to be caused by in situ formation of an organomonophosphite ligand byproduct that poisons the metal-organopolyphosphite complex catalyst as described herein. Accordingly this invention rests in the discovery that such intrinsic catalyst deactivation in such hydroformylation processes may be reversed or significantly minimized by carrying out the hydroformylation process in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C.

For example, rhodium-bisphosphite ligand complex catalysts which have become partially deactivated due to the in situ build-up of undesirable organomonophosphite ligand byproduct may have at least some of their catalytic activity restored by the practice of this invention. Alternatively, it is preferred not to allow for any significant intrinsic catalyst deactivation due to in situ build-up of such organomonophosphite ligand byproduct in the hydroformylation reaction medium, but rather to prevent or at least greatly minimize such deactivation from taking place in the first place by carrying out the hydroformylation process right from its start in a reaction region where the hydroformylation reaction rate is of a negative or inverse order in carbon monoxide and at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C. The resulting reaction product fluid is then treated with added water and/or weakly acidic compound additive, so as to hydrolyze any such undesirable organomonophosphite ligand at the rate that it is produced in situ to form phosphorus acidic compounds.

As indicated above, a means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation involves carrying out the invention described and taught in copending

U.S. Patent Application Serial Nos. (D-17245-1) and (D-17646), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using an aqueous buffer solution and optionally organic nitrogen compounds as disclosed therein.

For instance, said aqueous buffer solution invention comprises treating at least a portion of a metal-organopolyphosphite ligand complex catalyst containing reaction product fluid derived from said hydroformylation process and which also contains phosphorus acidic compounds formed during said hydroformylation process, with an aqueous buffer solution in order to neutralize and remove at least some amount of the phosphorus acidic compounds from said reaction product fluid, and then returning the treated reaction product fluid to the hydroformylation reaction zone or separation zone. Illustrative phosphorus acidic compounds include, for example, H_3PO_3, aldehyde acids such as hydroxy alkyl phosphonic acids, H_3PO_4 and the like. Said treatment of the metal-organopolyphosphite ligand complex catalyst containing reaction product fluid with the aqueous buffer solution may be conducted in any suitable manner or fashion desired that does not unduly adversely affect the basic hydroformylation process from which said reaction product fluid was derived.

Thus, for example, the aqueous buffer solution may be used to treat all or part of a reaction medium of a continuous liquid catalyst recycle hydroformylation process that has been removed from the reaction zone at any time prior to or after separation of the aldehyde product therefrom. More preferably said aqueous buffer treatment involves treating all or part of the reaction product fluid obtained after distillation of as much of the aldehyde product desired, e.g. prior to or during the recycling of said reaction product fluid to the reaction zone. For instance, a preferred mode would be to continuously pass all or part (e.g. a slip stream) of the recycled reaction product fluid that is being recycled to the reaction zone through a liquid extractor

containing the aqueous buffer solution just before said catalyst containing residue is to re-enter the reaction zone.

Thus it is to be understood that the metal-organopolyphosphite ligand complex catalyst containing reaction product fluid to be treated with the aqueous buffer solution may contain in addition to the catalyst complex and its organic solvent, aldehyde product, free phosphite ligand, unreacted olefin, and any other ingredient or additive consistent with the reaction medium of the hydroformylation process from which said reaction product fluids are derived.

Typically maximum aqueous buffer solution concentrations are only governed by practical considerations. As noted, treatment conditions such as temperature, pressure and contact time may also vary greatly and any suitable combination of such conditions may be employed herein. In general liquid temperatures ranging from about 20°C to about 80°C and preferably from about 25°C to about 60°C should be suitable for most instances, although lower or higher temperatures could be employed if desired. Normally the treatment is carried out under pressures ranging from ambient to reaction pressures and the contact time may vary from a matter of seconds or minutes to a few hours or more.

Moreover, success in removing phosphorus acidic compounds from the reaction product fluid may be determined by measuring the rate degradation (consumption) of the organopolyphosphite ligand present in the hydroformylation reaction medium. In addition as the neutralization and extraction of phosphorus acidic compounds into the aqueous buffer solution proceeds, the pH of the buffer solution will decrease and become more and more acidic. When the buffer solution reaches an unacceptable acidity level it may simply be replaced with a new buffer solution.

The aqueous buffer solutions employable in this invention may comprise any suitable buffer mixture containing salts of oxyacids,

the nature and proportions of which in the mixture, are such that the pH of their aqueous solutions may range from 3 to 9, preferably from 4 to 8 and more preferably from 4.5 to 7.5. In this context suitable buffer systems may include mixtures of anions selected from the group consisting of phosphate, carbonate, citrate and borate compounds and cations selected from the group consisting of ammonium and alkali metals, e.g. sodium, potassium and the like. Such buffer systems and/or methods for their preparation are well known in the art.

Preferred buffer systems are phosphate buffers and citrate buffers, e.g. monobasic phosphate/dibasic phosphates of an alkali metal and citrates of an alkali metal. More preferred are buffer systems consisting of mixtures of the monobasic phosphate and the dibasic phosphate of sodium or potassium.

Optionally, an organic nitrogen compound may be added to the hydroformylation reaction product fluid to scavenge the acidic hydrolysis byproducts formed upon hydrolysis of the organopolyphosphite ligand, as taught, for example, in U.S. Patent No. 4,567,306, copending U.S. Patent Application Serial Nos. (D-17245-1) and (D-17646), referred to herein. Such organic nitrogen compounds may be used to react with and to neutralize the acidic compounds by forming conversion product salts therewith, thereby preventing the rhodium from complexing with the acidic hydrolysis byproducts and thus helping to protect the activity of the metal, e.g., rhodium, catalyst while it is present in the reaction zone under hydroformylation conditions. The choice of the organic nitrogen compound for this function is, in part, dictated by the desirability of using a basic material that is soluble in the reaction medium and does not tend to catalyze the formation of aldols and other condensation products at a significant rate or to unduly react with the product aldehyde.

Such organic nitrogen compounds may contain from 2 to 30 carbon atoms, and preferably from 2 to 24 carbon atoms. Primary amines should be excluded from use as said organic nitrogen

compounds. Preferred organic nitrogen compounds should have a distribution coefficient that favors solubility in the organic phase. In general more preferred organic nitrogen compounds useful for scavenging the phosphorus acidic compounds present in the hydroformylation reaction product fluid of this invention include those having a pKa value within ± 3 of the pH of the aqueous buffer solution employed. Most preferably the pKa value of the organic nitrogen compound will be essentially about the same as the pH of the aqueous buffer solution employed. Of course it is to be understood that while it may be preferred to employ only one such organic nitrogen compound at a time in any given hydroformylation process, if desired, mixtures of two or more different organic nitrogen compounds may also be employed in any given processes.

Illustrative organic nitrogen compounds include e.g., trialkylamines, such as triethylamine, tri-n-propylamine, tri-n-butylamine, tri-iso-butylamine, tri-iso-propylamine, tri-n-hexylamine, tri-n-octylamine, dimethyl-iso-propylamine, dimethyl-hexadecylamine, methyl-di-n-octylamine, and the like, as well as substituted derivatives thereof containing one or more noninterfering substituents such as hydroxy groups, for example triethanolamine, N-methyl-di-ethanolamine, tris-(3-hydroxypropyl)-amine, and the like. Heterocyclic amines can also be used such as pyridine, picolines, lutidines, collidines, N-methylpiperidine, N-methylmorpholine, N-2'-hydroxyethylmorpholine, quinoline, iso-quinoline, quinoxaline, acridien, quinuclidine, as well as, diazoles, triazole, diazine and triazine compounds, and the like. Also suitable for possible use are aromatic tertiary amines, such as N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethyl-p-toluidine, N-methyldiphenylamine, N,N-dimethylbenzylamine, N,N-dimethyl-1-naphthylamine, and the like. Compounds containing two or more amino groups, such as N,N,N',N'-tetramethylethylene diamine and triethylene diamine (i.e. 1,4-diazabicyclo-[2,2,2]-octane) can also be mentioned.

Preferred organic nitrogen compounds useful for scavenging the phosphorus acidic compounds present in the hydroformylation reaction product fluids of the this invention are heterocyclic compounds selected from the group consisting of diazoles, triazoles, diazines and triazines, such as those disclosed and employed herein. For example, benzimidazole and benztriazole are preferred candidates for such use.

Illustrative of suitable organic nitrogen compounds useful for scavenging the phosphorus acidic compounds include those permissible organic nitrogen compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, 1996, the pertinent portions of which are incorporated herein by reference.

The amount of organic nitrogen compound that may be present in the reaction product fluid for scavenging the phosphorus acidic compounds present in the hydroformylation reaction product fluids of the this invention is typically sufficient to provide a concentration of at least about 0.0001 moles of free organic nitrogen compound per liter of reaction product fluid. In general the ratio of organic nitrogen compound to total organophosphite ligand (whether bound with rhodium or present as free organophosphite) is at least about 0.1:1 and even more preferably at least about 0.5:1. The upper limit on the amount of organic nitrogen compound employed is governed mainly by economical considerations. Organic nitrogen compound: organophosphite molar ratios of at least about 1:1 up to about 5:1 should be sufficient for most purpose.

It is to be understood the organic nitrogen compound employed to scavenge said phosphorus acidic compounds need not be the same as the heterocyclic nitrogen compound employed to protect the metal catalyst under harsh conditions such as exist in the aldehyde vaporizer-separator. However, if said organic nitrogen compound and said heterocyclic nitrogen compound are desired to be the same and perform both said functions in a given process, care should be taken to

see that there will be a sufficient amount of the heterocyclic nitrogen compound present in the reaction medium to also provide that amount of free heterocyclic nitrogen compound in the hydroformylation process, e.g., vaporizer-separator, that will allow both desired functions to be achieved.

Accordingly the aqueous buffer solution treatment of this invention will not only remove free phosphoric acidic compounds from the metal-organophosphite ligand complex catalyst containing reaction product fluids, the aqueous buffer solution also surprisingly removes the phosphorus acidic material of the conversion product salt formed by the use of the organic nitrogen compound scavenger when employed, i.e., the phosphorus acid of said conversion product salt remains behind in the aqueous buffer solution, while the treated reaction product fluid, along with the reactivated (free) organic nitrogen compound is returned to the hydroformylation reaction zone.

An alternate method of transferring acidity from the hydroformylation reaction product fluid to an aqueous fraction is through the intermediate use of a heterocyclic amine which has a fluorocarbon or silicone side chain of sufficient size that it is immiscible in both the hydroformylation reaction product fluid and in the aqueous fraction. The heterocyclic amine may first be contacted with the hydroformylation reaction product fluid where the acidity present in the reaction product fluid will be transferred to the nitrogen of the heterocyclic amine. This heterocyclic amine layer may then be decanted or otherwise separated from the reaction product fluid before contacting it with the aqueous fraction where it again would exist as a separate phase. The heterocyclic amine layer may then be returned to contact the hydroformylation reaction product fluid.

Another means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation that may be useful in this invention involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17648)

and (D-17649), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using water and optionally organic nitrogen compounds as disclosed therein.

For instance, it has been found that hydrolytic decomposition and rhodium catalyst deactivation as discussed herein can be prevented or lessened by treating at least a portion of the reaction product fluid derived from the hydroformylation process and which also contains phosphorus acidic compounds formed during the hydroformylation process with water sufficient to remove at least some amount of the phosphorus acidic compounds from the reaction product fluid. Although both water and acid are factors in the hydrolysis of organophosphite ligands, it has been surprisingly discovered that hydroformylation reaction systems are more tolerant of higher levels of water than higher levels of acid. Thus, the water can surprisingly be used to remove acid and decrease the rate of loss of organophosphite ligand by hydrolysis.

Yet another means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation that may be useful in this invention involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17652) and (D-17685), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using water in conjunction with acid removal substances and optionally organic nitrogen compounds as disclosed therein.

For instance, it has been found that hydrolytic decomposition and rhodium catalyst deactivation as discussed herein can be prevented or lessened by treating at least a portion of the reaction product fluid derived from the hydroformylation process and which also contains phosphorus acidic compounds formed during said hydroformylation process with water in conjunction with one or more acid removal substances, e.g., oxides, hydroxides, carbonates, bicarbonates and carboxylates of Group 2, 11 and 12 metals, sufficient

to remove at least some amount of the phosphorus acidic compounds from said reaction product fluid. Because metal salt contaminants, e.g., iron, zinc, calcium salts and the like, in a hydroformylation reaction product fluid undesirably promote the self condensation of aldehydes, an advantage is that one can use the acidity removing capability of certain acid removal substances with minimal transfer of metal salts to the hydroformylation reaction product fluid.

A further means for preventing or minimizing ligand degradation and catalyst deactivation and/or precipitation that may be useful in this invention involves carrying out the invention described and taught in copending U.S. Patent Application Serial Nos. (D-17650) and (D-17651), both filed on an even date herewith, the disclosures of which are incorporated herein by reference, which comprises using ion exchange resins and optionally organic nitrogen compounds as disclosed therein.

For instance, it has been found that hydrolytic decomposition and rhodium catalyst deactivation as discussed herein can be prevented or lessened by (a) treating in at least one scrubber zone at least a portion of said reaction product fluid derived from said hydroformylation process and which also contains phosphorus acidic compounds formed during said hydroformylation process with water sufficient to remove at least some amount of the phosphorus acidic compounds from said reaction product fluid and (b) treating in at least one ion exchange zone at least a portion of the water which contains phosphorus acidic compounds removed from said reaction product fluid with one or more ion exchange resins sufficient to remove at least some amount of the phosphorus acidic compounds from said water. Because passing a hydroformylation reaction product fluid directly through an ion exchange resin can cause rhodium precipitation on the ion exchange resin surface and pores, thereby causing process complications, an advantage is that one can use the acidity removing capability of ion exchange resins with essentially no loss of rhodium.

Other means for removing phosphorus acidic compounds from the reaction product fluids of this invention may be employed if desired. This invention is not intended to be limited in any manner by the permissible means for removing phosphorus acidic compounds from the reaction product fluids.

Another problem that has been observed when organopolyphosphite ligand promoted metal catalysts are employed in hydroformylation processes, e.g., continuous liquid catalyst recycle hydroformylation processes, that involve harsh conditions such as recovery of the aldehyde via a vaporizer-separator, i.e. the slow loss in catalytic activity of the catalysts is believed due at least in part to the harsh conditions such as exist in a vaporizer employed in the separation and recovery of the aldehyde product from its reaction product fluid. For instance, it has been found that when an organopolyphosphite promoted rhodium catalyst is placed under harsh conditions such as high temperature and low carbon monoxide partial pressure, that the catalyst deactivates at an accelerated pace with time, due most likely to the formation of an inactive or less active rhodium species, which may also be susceptible to precipitation under prolonged exposure to such harsh conditions. Such evidence is also consistent with the view that the active catalyst which under hydroformylation conditions is believed to comprise a complex of rhodium, organopolyphosphite, carbon monoxide and hydrogen, loses at least some of its coordinated carbon monoxide ligand during exposure to such harsh conditions as encountered in vaporization, which provides a route for the formation of catalytically inactive or less active rhodium species. The means for preventing or minimizing such catalyst deactivation and/or precipitation involves carrying out the invention described and taught in copending U.S. Patent Application Serial No. (D-17423-1), filed on an even date herewith, the disclosure of which is incorporated herein by reference, which comprises carrying out the hydroformylation process under conditions of low carbon monoxide

partial pressure in the presence of a free heterocyclic nitrogen compound as disclosed therein.

By way of further explanation it is believed the free heterocyclic nitrogen compound serves as a replacement ligand for the lost carbon monoxide ligand thereby forming a neutral intermediate metal species comprising a complex of the metal, organopolyphosphite, the heterocyclic nitrogen compound and hydrogen during such harsh conditions, e.g., vaporization separation, thereby preventing or minimizing the formation of any such above mentioned catalytic inactive or less active metal species. It is further theorized that the maintenance of catalytic activity, or the minimization of its deactivation, throughout the course of such continuous liquid recycle hydroformylation is due to regeneration of the active catalyst from said neutral intermediate metal species in the reactor (i.e. hydroformylation reaction zone) of the particular hydroformylation process involved. It is believed that under the higher syn gas pressure hydroformylation conditions in the reactor, the active catalyst complex comprising metal, e.g., rhodium, organopolyphosphite, carbon monoxide and hydrogen is regenerated as a result of some of the carbon monoxide in the reactant syn gas replacing the heterocyclic nitrogen ligand of the recycled neutral intermediate rhodium species. That is to say, carbon monoxide having a stronger ligand affinity for rhodium, replaces the more weakly bonded heterocyclic nitrogen ligand of the recycled neutral intermediate rhodium species that was formed during vaporization separation as mentioned above, thereby reforming the active catalyst in the hydroformylation reaction zone.

Thus the possibility of metal catalyst deactivation due to such harsh conditions is said to be minimized or prevented by carrying out such distillation of the desired aldehyde product from the metal-organopolyphosphite catalyst containing product fluids in the added presence of a free heterocyclic nitrogen compound having a five or six membered heterocyclic ring consisting of 2 to 5 carbon atoms and from

2 to 3 nitrogen atoms, at least one of said nitrogen atoms containing a double bond. Such free heterocyclic nitrogen compounds may be selected from the class consisting of diazole, triazole, diazine, and triazine compounds, such as, e.g., benzimidazole or benzotriazole, and the like. The term "free" as it applies to said heterocyclic nitrogen compounds is employed therein to exclude any acid salts of such heterocyclic nitrogen compounds, i.e., salt compounds formed by the reaction of any phosphorus acidic compound present in the hydroformylation reaction medium with such free heterocyclic nitrogen compounds as discussed herein above.

It is to be understood that while it may be preferred to employ only one free heterocyclic nitrogen compound at a time in any given hydroformylation process, if desired, mixtures of two or more different free heterocyclic nitrogen compounds may also be employed in any given process. Moreover the amount of such free heterocyclic nitrogen compounds present during harsh conditions, e.g., the vaporization procedure, need only be that minimum amount necessary to furnish the basis for at least some minimization of such catalyst deactivation as might be found to occur as a result of carrying out an identical metal catalyzed liquid recycle hydroformylation process under essentially the same conditions, in the absence of any free heterocyclic nitrogen compound during vaporization separation of the aldehyde product. Amounts of such free heterocyclic nitrogen compounds ranging from about 0.01 up to about 10 weight percent, or higher if desired, based on the total weight of the hydroformylation reaction product fluid to be distilled should be sufficient for most purposes.

In addition to hydroformylation processes, other processes for which this invention may be useful include those which exhibit a loss in catalytic activity of organopolyphosphite promoted metal catalysts due to harsh reaction conditions such as employed in the separation and recovery of product from its reaction product fluid. Illustrative processes include, for example, hydroacylation

(intramolecular and intermolecular), hydroamidation, hydroesterification, aminolysis, alcoholysis, carbonylation, olefin isomerization, transfer hydrogenation and the like. Preferred processes involve the reaction of organic compounds with carbon monoxide, or with carbon monoxide and a third reactant, e.g., hydrogen, or with hydrogen cyanide, in the presence of a catalytic amount of a metal-organopolyphosphite ligand complex catalyst. The most preferred processes include hydroformylation and carbonylation.

As with hydroformylation processes, these other processes may be asymmetric or non-asymmetric, the preferred processes being non-asymmetric, and may be conducted in any continuous or semi-continuous fashion and may involve any catalyst liquid and/or gas recycle operation desired. The particular processes for producing products from one or more reactants, as well as the reaction conditions and ingredients of the processes are not critical features of this invention. The processing techniques of this invention may correspond to any of the known processing techniques heretofore employed in conventional processes. For instance, the processes can be conducted in either the liquid or gaseous states and in a continuous, semi-continuous or batch fashion and involve a liquid recycle and/or gas recycle operation or a combination of such systems as desired. Likewise, the manner or order of addition of the reaction ingredients, catalyst and solvent are also not critical and may be accomplished in any conventional fashion. This invention encompasses the carrying out of known conventional syntheses in a conventional fashion employing a metal-organophosphite ligand complex catalyst.

The hydroformylation processes of this invention may be carried out using, for example, a fixed bed reactor, a fluid bed reactor, a continuous stirred tank reactor (CSTR), or a slurry reactor. The optimum size and shape of the catalysts will depend on the type of reactor used. In general, for fluid bed reactors, a small, spherical catalyst particle is preferred for easy fluidization. With fixed bed

reactors, larger catalyst particles are preferred so the back pressure within the reactor is kept reasonably low. The at least one reaction zone employed in this invention may be a single vessel or may comprise two or more discrete vessels. The at least one separation zone employed in this invention may be a single vessel or may comprise two or more discrete vessels. The at least one scrubber zone employed in this invention may be a single vessel or may comprise two or more discreet vessels. It should be understood that the reaction zone(s) and separation zone(s) employed herein may exist in the same vessel or in different vessels. For example, reactive separation techniques such as reactive distillation, reactive membrane separation and the like may occur in the reaction zone(s).

The hydroformylation processes of this invention can be conducted in a batch or continuous fashion, with recycle of unconsumed starting materials if required. The reaction can be conducted in a single reaction zone or in a plurality of reaction zones, in series or in parallel or it may be conducted batchwise or continuously in an elongated tubular zone or series of such zones. The materials of construction employed should be inert to the starting materials during the reaction and the fabrication of the equipment should be able to withstand the reaction temperatures and pressures. Means to introduce and/or adjust the quantity of starting materials or ingredients introduced batchwise or continuously into the reaction zone during the course of the reaction can be conveniently utilized in the processes especially to maintain the desired molar ratio of the starting materials. The reaction steps may be effected by the incremental addition of one of the starting materials to the other. Also, the reaction steps can be combined by the joint addition of the starting materials. When complete conversion is not desired or not obtainable, the starting materials can be separated from the product, for example by distillation, and the starting materials then recycled back into the reaction zone.

The hydroformylation processes may be conducted in either glass lined, stainless steel or similar type reaction equipment. The reaction zone may be fitted with one or more internal and/or external heat exchanger(s) in order to control undue temperature fluctuations, or to prevent any possible "runaway" reaction temperatures.

The hydroformylation processes of this invention may be conducted in one or more steps or stages. The exact number of reaction steps or stages will be governed by the best compromise between capital costs and achieving high catalyst selectivity, activity, lifetime and ease of operability, as well as the intrinsic reactivity of the starting materials in question and the stability of the starting materials and the desired reaction product to the reaction conditions.

In an embodiment, the hydroformylation processes useful in this invention may be carried out in a multistaged reactor such as described, for example, in copending U.S. Patent Application Serial No. (D-17425-1), filed on an even date herewith, the disclosure of which is incorporated herein by reference. Such multistaged reactors can be designed with internal, physical barriers that create more than one theoretical reactive stage per vessel. In effect, it is like having a number of reactors inside a single continuous stirred tank reactor vessel. Multiple reactive stages within a single vessel is a cost effective way of using the reactor vessel volume. It significantly reduces the number of vessels that otherwise would be required to achieve the same results. Fewer vessels reduces the overall capital required and maintenance concerns with separate vessels and agitators.

For purposes of this invention, the term "hydrocarbon" is contemplated to include all permissible compounds having at least one hydrogen and one carbon atom. Such permissible compounds may also have one or more heteroatoms. In a broad aspect, the permissible hydrocarbons include acyclic (with or without heteroatoms) and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and

nonaromatic organic compounds which can be substituted or unsubstituted.

As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds unless otherwise indicated. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, alkyl, alkyloxy, aryl, aryloxy, hydroxy, hydroxyalkyl, amino, aminoalkyl, halogen and the like in which the number of carbons can range from 1 to about 20 or more, preferably from 1 to about 12. The permissible substituents can be one or more and the same or different for appropriate organic compounds. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

Certain of the following examples are provided to further illustrate this invention.

Example 1

A system utilizing rhodium and Ligand F (as identified herein) as the catalyst is used to hydroformylate propylene to butyraldehyde. The concentration of the ligand is 2 weight percent at all rhodium concentrations given in Table A below. The system operates in a continuously stirred tank reactor. Catalyst dissolved in butyraldehyde and hydroformylation byproducts is fed to the reactor to maintain the catalyst concentration in the reactor at a rate of 140 grams per hour per liter of volume available for reaction. The ability of the catalyst to react feeds is represented by a factor that is dependent on the temperature and rhodium metal concentration in the reactor. Table A gives examples for the value of the factor at various conditions at which the catalyst system is operated. The difference in temperature between the reaction and the inlet temperature of the fluid to the heat transfer means to prevent cycling will be the same for comparable

values of the relative reactivity constant. The pressure of the reaction system is 250 psia. Propylene is fed to the reactor along as well as synthesis gas to provide the reactants necessary for the hydroformylation reaction. Inerts in the feeds amount to less than 5 weight percent of the total weight of the feeds. Excess gases exit the reactor from a vapor purge line. Reaction product fluid is continuously removed from the reactor at a rate that maintains the liquid level within the reactor. Several examples are given for the temperature differences between the reaction and the inlet of the coolant to the heat transfer means that prevent the system from undergoing extreme cycling during the operation of the reactor system. The feed rate of the olefin to the system is 224.4 grams per hour per liter of reaction volume. Table B summarizes results for several different feed compositions for temperature differences between the reaction and the temperature of the coolant entering the heat transfer means that prevent the system from undergoing extreme cycling.

Table A: Factor for the Reactivity of Ligand F at Various Conditions

	Temperatures, deg C				
Rh, ppm	25	45	60	100	120
10	0.01	0.03	0.08	0.53	1.19
30	0.03	0.10	0.24	1.59	3.57
60	0.06	0.20	0.47	3.18	7.14
100	0.10	0.34	0.78	5.30	11.90
150	0.15	0.51	1.18	7.94	17.84
200	0.19	0.68	1.57	10.59	23.79
250	0.24	0.85	1.96	13.24	29.74
300	0.29	1.02	2.35	15.89	35.69

Table B: Summary of Temperature Differences to Eliminate Cycling

Reactivity Factor	Propylene Conversion, %	Syn Gas Feed, g/hr/L	Hydrogen to Carbon Monoxide Ratio	Temperature Difference, deg C
2.6	75	171	1:1	7
1.13	60	133	0.85	13
1.40	65	138	0.85	24

Example 2

A system utilizing rhodium and Ligand F (as identified herein) as the catalyst is used to hydroformylate propylene to butyraldehyde. The concentration of the ligand is 2 weight percent at all rhodium concentrations given in Table C below. The system operates in a continuously stirred tank reactor. Catalyst dissolved in butyraldehyde and hydroformylation by-products is fed at a rate of 140 grams per hour per liter of volume available for reaction to the reactor to maintain the catalyst concentration in the reactor. The ability of the catalyst to react feeds is represented by a factor that is dependent on the temperature and rhodium metal concentration in the reactor. Table C gives examples for the value of the factor at various conditions at which the catalyst system is operated. The conversions and temperature difference between the reaction and the inlet coolant to the heat transfer means to prevent cycling in the system will be the same for comparable values of the relative reactivity constant. The pressure of the reaction system is 250 psia. Propylene is fed to the reactor along as well as synthesis gas to provide the reactants necessary for the hydroformylation reaction. Inert compounds in the feeds amount to less than 5 weight percent of the total weight of the feeds.. Excess gases exit the reactor from a vapor purge line. Reaction product fluid is continuously removed from the reactor at a rate that maintains the liquid level within the reactor. Several examples are

given for the operating conditions that prevent the system from undergoing extreme cycling during the operation of the reactor system. The feed rate of the olefin to the system is 224.4 grams per hour per liter of reaction volume. Table D summarizes results for several different feed compositions along with the temperature difference between the reaction and the temperature of the coolant entering the heat transfer means and conversions of different reactants that prevent the system from undergoing extreme cycling.

Table C: Factor for the Reactivity of Ligand F at Various Conditions

	Temperatures, deg C				
Rh, ppm	25	45	60	100	120
10	0.01	0.03	0.08	0.53	1.19
30	0.03	0.10	0.24	1.59	3.57
60	0.06	0.20	0.47	3.18	7.14
100	0.10	0.34	0.78	5.30	11.90
150	0.15	0.51	1.18	7.94	17.84
200	0.19	0.68	1.57	10.59	23.79
250	0.24	0.85	1.96	13.24	29.74
300	0.29	1.02	2.35	15.89	35.69

Table D: Summary of Results to Eliminate Cycling

Temperature Difference, Deg C	Propylene Conversion	Hydrogen Conversion	Carbon Monoxide Conversion	Syn Gas Feed Rate, g/hr/L	Hydrogen to Carbon Monoxide Ratio in Feed
36	60	96	87	117	0.90
18	60	69	59	171	0.85
17	60	60	60	171	1.00

Examples 3 to 7 illustrate the in situ buffering effect of nitrogen containing additives such as benzimidazole and the ability of these additives to transfer the acidity to an aqueous buffer solution.

Example 3

This control example illustrates the stability of Ligand D (as identified herein) in a solution containing 200 parts per million of rhodium, and 0.39 percent by weight of Ligand D in butyraldehyde containing aldehyde dimer and trimer in the absence of added acid or benzimidazole.

To a clean, dry 25 milliliter vial was added 12 grams of the butyraldehyde solution mentioned above. Samples were analyzed for Ligand D using High Performance Liquid Chromatography after 24 and 72 hours. The weight percent of Ligand D was determined by High Performance Liquid Chromatography relative to a calibration curve. No change in the concentration of Ligand D was observed after either 24 or 72 hours.

Example 4

This Example is similar to Example 3 except that phosphorus acid was added to simulate the type of acid that might be formed during hydrolysis of an organophosphite.

The procedure for Example 3 was repeated with the modification of adding 0.017grams of phosphorous acid (H_3PO_3) to the 12 gram solution. After 24 hours the concentration of Ligand D had decreased from 0.39 to 0.12 percent by weight; after 72 hours the concentration of Ligand D had decreased to 0.04 percent by weight. This data shows that strong acids catalyze the decomposition of Ligand D.

Example 5

This Example is similar to Example 3 except that both phosphorus acid and benzimidazole were added.

The procedure for Example 3 was repeated with the modification of adding 0.018 grams of phosphorous acid and 0.0337 grams of benzimidazole to the solution. No decomposition of Ligand D

was observed after either 24 or 72 hours. This shows that the addition of benzimidazole effectively buffers the effect of the strong acid and thereby prevents the rapid decomposition of Ligand D.

Example 6

This example shows that an aqueous buffer can recover the acidity from the nitrogen base in situ buffer and allow the nitrogen base to partition into the organic phase, where it can be recycled to the hydroformylation zone.

Solid (benzimidazole)(H_3PO_4) was prepared by placing 1.18 grams (10 mmole) of benzimidazole in a 250 milliliter beaker and dissolving the benzimidazole in 30 milliliters of tetrahydrofuran. To this solution was slowly added 0.5 grams of 86 percent by weight of phosphoric acid (H_3PO_4). Upon addition of the acid a precipitate formed. The precipitate was collected on a sintered glass frit and washed with tetrahydrofuran. The resulting solid was air-dried with the application of vacuum and used without any further purification. 0.109 grams (0.504 mmole) of the water-soluble (benzimidazole)(H_3PO_4) solid prepared in the previous step was dissolved in 10 grams of 0.1 M pH 7 sodium phosphate buffer solution. The resulting solution was extracted with 10 grams of valeraldehyde. The organic layer was then separated from the aqueous layer using a separatory funnel. The volatile components were then removed from the organic layer by distillation at 100°C to yield a solid. The solid was identical to authentic benzimidazole as shown by thin layer chromatography utilizing a 1:1 by volume mixture of chloroform and acetone as the eluent and silica as the stationary phase. Based on recovery of the solid, benzimidazole was completely transferred to the organic phase.

This data shows that an organic soluble nitrogen base which exists as a strong acid salt can be regenerated by contact with an aqueous buffer and returned to the organic phase.

Example 7

This example shows that a buffer solution is effective at neutralizing an organic soluble salt of a weak base and strong acid thus allowing the base to return to the organic phase and effectively removing the acid from the organic phase.

A butyraldehyde solution was prepared containing 1.0 percent by weight of benzotriazole. The solution was then analyzed by Gas Chromatography for benzotriazole content to serve as a reference sample. To the solution prepared in the previous step was added 0.25 mole equivalents of phosphorous acid (H_3PO_3). In a one pint glass bottle was added 50 grams of the butyraldehyde solution containing benzotriazole and 50 grams of a pH 7, 0.2 molar sodium phosphate buffer solution. The mixture was stirred for 15 minutes and then transferred to a separatory funnel. The aqueous layer was then separated from the aldehyde layer. The aqueous layer was analyzed for H_3PO_3 content by Ion Chromatography. The aldehyde layer was analyzed for benzotriazole content by Gas Chromatography and H_3PO_3 content by Ion Chromatography. The H_3PO_3 was found to be completely transferred into the aqueous layer. Complete return of benzotriazole to the butyraldehyde layer was also found.

This data shows that an organic soluble salt of a weak base and strong acid can be completely neutralized by contacting the organic phase with an aqueous buffer solution and that the free base is thereby returned to the organic phase.

Although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby; but rather, the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

Claims

1. A process which comprises reacting one or more reactants in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more products, wherein said process is conducted at a carbon monoxide partial pressure such that reaction rate increases as carbon monoxide partial pressure decreases and reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

2. A hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (b) at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total

reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (c) at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and (d) at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

3. The hydroformylation process of claim 2 which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst, and at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and at one or more of the following conditions: (a) at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process,

(b) at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and (c) at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

4. An improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, the improvement comprising preventing and/or lessening deactivation of the metal-organopolyphosphite ligand complex catalyst and preventing and/or lessening cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process by conducting said hydroformylation process at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, (b) at a carbon monoxide conversion of less than about 90%, (c) at a hydrogen conversion of greater than about 65%, and (d) at an olefinic unsaturated compound conversion of greater than about 50%.

5. A hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen deactivation of the metal-organopolyphosphite ligand complex catalyst.

6. An improved hydroformylation process which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, wherein said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, the improvement comprising conducting said hydroformylation process at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and which is sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant

temperature is sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (b) at a carbon monoxide conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, (c) at a hydrogen conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process, and (d) at an olefinic unsaturated compound conversion sufficient to prevent and/or lessen cycling of carbon monoxide partial pressure, hydrogen partial pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process.

7. The improved hydroformylation process of claim 6 which comprises (i) reacting in at least one reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes and (ii) separating in at least one separation zone or in said at least one reaction zone the one or more aldehydes from said reaction product fluid, wherein said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, the improvement comprising preventing and/or lessening coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst and preventing and/or lessening cycling of carbon monoxide partial pressure, hydrogen partial pressure, total reaction pressure, hydroformylation reaction rate and/or temperature during said hydroformylation process by conducting said

hydroformylation process at a carbon monoxide partial pressure such that hydroformylation reaction rate increases as carbon monoxide partial pressure decreases and hydroformylation reaction rate decreases as carbon monoxide partial pressure increases and at one or more of the following conditions: (a) at a temperature such that the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 25°C, (b) at a carbon monoxide conversion of less than about 90%, (c) at a hydrogen conversion of greater than about 65%, and (d) at an olefinic unsaturated compound conversion of greater than about 50%.

8. A hydroformylation process which comprises reacting one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and in which said reaction product fluid contains at least some organomonophosphite ligand formed during said hydroformylation process, wherein said hydroformylation process is conducted at a carbon monoxide partial pressure sufficient to prevent and/or lessen coordination of the organomonophosphite ligand with said metal-organopolyphosphite ligand complex catalyst.

9. The process of claim 1 which comprises a hydroformylation, hydroacylation (intramolecular and intermolecular), hydrocyanation, hydroamidation, hydroesterification, aminolysis, alcoholysis, carbonylation, isomerization or transfer hydrogenation process.

10. The processes of claims 6, 7 and 8 in which the organomonophosphite ligand is treated with water, a weakly acidic compound, or both water and a weakly acidic compound.

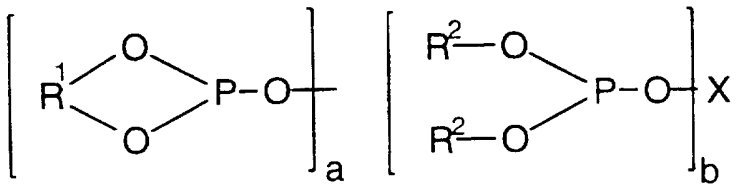
11. The processes of claim 10 wherein the organomonophosphite ligand is hydrolyzed to a phosphorus acidic compound comprising a hydroxy alkyl phosphonic acid.

12. The processes of claims 4 and 7 wherein the temperature difference between reaction product fluid temperature and inlet coolant temperature is less than about 20°C, the carbon monoxide conversion is less than about 75%, the hydrogen conversion is greater than about 85%, and the olefinic unsaturated compound conversion is greater than about 50%.

13. The processes of claims 6, 7 and 8 wherein the organomonophosphite ligand has (a) a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst less than carbon monoxide and (b) a coordination strength with respect to the metal of said metal-organopolyphosphite ligand complex catalyst less than the organopolyphosphite ligand of said metal-organopolyphosphite ligand complex catalyst.

14. The processes of claims 1, 2, 3, 4, 5, 6, 7 and 8 wherein said reaction product fluid contains a homogeneous or heterogeneous metal-organopolyphosphite ligand complex catalyst or at least a portion of said reaction product fluid contacts a fixed heterogeneous metal-organopolyphosphite ligand complex catalyst during said processes.

15. The processes of claims 1, 2, 3, 4, 5, 6, 7 and 8 wherein said metal-organopolyphosphite ligand complex catalyst comprises rhodium complexed with an organopolyphosphite ligand represented by the formula:



wherein X represents a substituted or unsubstituted n-valent organic bridging radical containing from 2 to 40 carbon atoms, each R^1 is the same or different and represents a divalent organic radical containing from 4 to 40 carbon atoms, each R^2 is the same or different and represents a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 24 carbon atoms, wherein a and b can be the same or different and each have a value of 0 to 6, with the proviso that the sum of a + b is 2 to 6 and n equals a + b.

16. The processes of claim 11 wherein phosphorus acidic compound present in the reaction product fluid of the hydroformylation process is treated with an aqueous buffer solution.

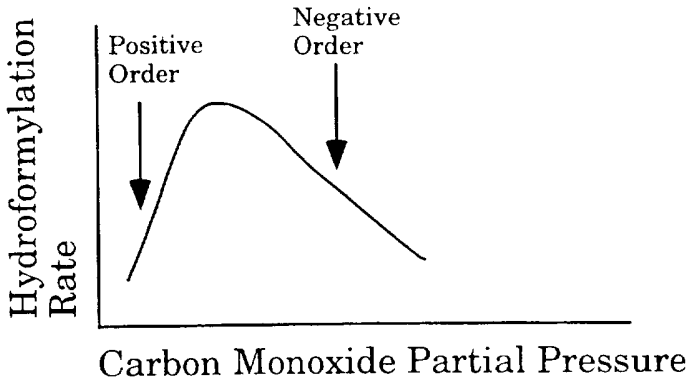
17. The processes of claim 16 wherein the aqueous buffer solution comprises a mixture of salts of oxyacids having a pH of 4 to 9.

18. The processes of claim 16 wherein phosphorus acidic compound present in the reaction product fluid is scavenged by an organic nitrogen compound that is also present in said reaction product fluid and wherein at least some amount of the phosphorus acidic compound of the conversion products of the reaction between said phosphorus acidic compound and said organic nitrogen compound are also neutralized and removed by the aqueous buffer solution treatment.

19. The processes of claim 18 wherein the organic nitrogen compound is selected from the group consisting of diazoles, triazoles, diazines and triazines.

20. The processes of claim 19 wherein the organic nitrogen compound is benzimidazole or benzotriazole.

Fig. 1


Hydroformylation Rate
Positive Order
Negative Order
Carbon Monoxide Partial Pressure

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 96/19413

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C45/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4 137 240 A (PETERSON MARVIN L) 30 January 1979 see the whole document	1,2,9,15
A	US 4 267 383 A (BOOTH FRANK B) 12 May 1981 see the whole document	1,2
A	US 3 527 809 A (PRUETT ROY L ET AL) 8 September 1970 see column 6	1,2

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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1

Date of the actual completion of the international search	Date of mailing of the international search report
11 March 1997	14. 03. 97

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Bonnevalle, E

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INTERNATIONAL SEARCH REPORT

information on patent family members

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