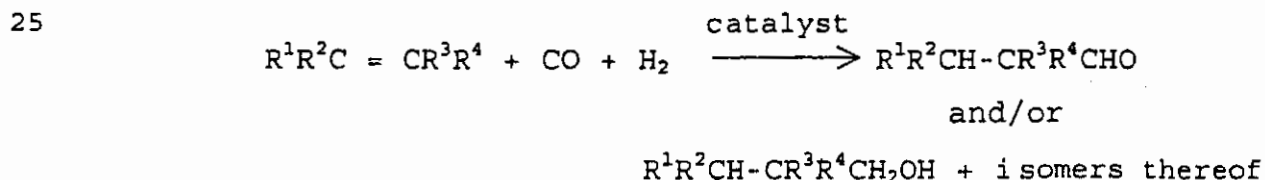


Hydroformylation Process

The present invention relates to a process for hydroformylating a compound having at least one olefinic carbon-to-carbon bond (also called an olefinic compound herein). In particular, the present invention relates to the production of aldehydes and/or alcohols by the addition of carbon monoxide and hydrogen to an olefinic compound in the presence of a cobalt catalyst.

Various processes for producing aldehyde and/or alcohol compounds by the reaction of a compound having at least one olefinic carbon-to-carbon bond with carbon monoxide and hydrogen in the presence of a catalyst are known. Typically, these reactions are performed at elevated temperatures and pressures. The aldehyde and alcohol compounds that are produced generally correspond to compounds obtained by the addition of a carbonyl or carbinol group, respectively, to an olefinically unsaturated carbon atom in the starting material with simultaneous saturation of the olefin bond. Isomerization of the olefin bond may take place to varying degrees under certain conditions with the consequent variation of the products obtained. These processes are typically known as hydroformylation reactions and involve reactions which may be shown in the general case by the following equation:



In the above equation, each group R^1 to R^4 may independently represent an organic radical, for example a hydrocarbyl group, or a suitable atom such as a hydrogen or halogen atom, or a hydroxyl group. The above reaction
5 may also be applied to a cycloaliphatic ring having an olefinic linkage, for example cyclohexene.

The catalyst employed in a hydroformylation reaction typically comprises a transition metal, such as cobalt, rhodium or ruthenium, in complex combination with carbon
10 monoxide and ligand(s) such as an organophosphine.

Representative of the earlier hydroformylation methods which use transition metal catalysts having organophosphine ligands are US 3420898, US 3501515, US
3448157, US 3440291, US 3369050 and US 3448158.

15 In attempts to improve the efficiency of a hydroformylation process, attention has typically focussed on developing novel catalysts and novel processes for recovering and re-using the catalyst. In particular, novel catalysts have been developed which may exhibit improved
20 stability at the required high reaction temperatures. Catalysts have also been developed which may permit the single-stage production of alcohols rather than a two-step procedure involving separate hydrogenation of the intermediate aldehyde. Moreover, homogeneous catalysts
25 have been developed which may permit improved reaction rates whilst providing acceptable yields of the desired products.

Although steps have been taken to develop improved catalysts, we have detected that some of these catalysts
30 suffer from problems. In particular we have detected that cobalt catalysts comprising cobalt in complex combination with carbon monoxide and a ligand may decompose during the reaction to produce cobalt carbide (a compound of cobalt

and carbon, empirical formula Co_xC , where x is 2 or 3). Cobalt carbide is catalytically inactive in hydroformylation reactions, thereby resulting in an increased rate of catalyst usage. The cobalt carbide is not only catalytically inactive in hydroformylation reactions but also has a relatively bulky, porous structure and is insoluble in the reaction medium. This represents a significant disadvantage, particularly for homogeneous cobalt catalysts, because the cobalt carbide typically tends to agglomerate and form detrimental deposits on the internal surfaces of the production facility. The deposition of cobalt carbide impedes the running of a hydroformylation production facility with optimal efficiency.

The present invention therefore seeks to solve the aforementioned problems associated with a hydroformylation process that employs a cobalt catalyst.

According to a first aspect, the present invention provides a hydroformylation process comprising reacting a compound having at least one olefinic carbon-to-carbon bond with hydrogen and carbon monoxide in the presence of a cobalt catalyst and a sulfur-containing additive, wherein the additive suppresses the formation of cobalt carbide in the reaction mixture.

The process according to the present invention addresses the aforementioned technical problems we have recognised, associated with hydroformylating a compound having an olefinic carbon-to-carbon bond in the presence of a cobalt catalyst. Suitably, the inclusion of the additive in the reaction mixture suppresses the formation of cobalt carbide compared with performing the corresponding hydroformylation reaction in the presence of the cobalt catalyst but without the additive. Suitably,

the additive reduces the formation of catalytically inactive cobalt carbide. The reduction in the formation of cobalt carbide may result in a decrease in the rate of cobalt catalyst consumption, thereby increasing the efficiency and productivity of the hydroformylation reaction. Suitably, the reduction in the formation of cobalt carbide in the process of the present invention decreases the amount of cobalt carbide deposited on the internal surfaces of the production facility.

Consequently, an increase in efficiency may be achieved.

Typically, during a hydroformylation reaction a cobalt catalyst may decompose to a minor extent to form precipitates of metallic cobalt. Although any decomposition of the cobalt catalyst represents loss of catalyst, the metallic cobalt precipitate is relatively innocuous compared with cobalt carbide formation. Typically, the metallic cobalt precipitates have a relatively small surface area compared with cobalt carbide having the same weight of cobalt and unlike cobalt carbide they typically do not agglomerate and cause the same problems of deposition on the internal surfaces of the production facility. However, although only theory, it is believed that the metallic cobalt precipitates may absorb carbon monoxide from the reaction mixture and promote the dissociation of the carbon monoxide to form cobalt carbide. It is believed that the additive used in the process of the present invention is absorbed by the metallic cobalt precipitate in preference to carbon monoxide, thereby suppressing the absorption of carbon monoxide and the formation of cobalt carbide in the reaction mixture.

The additive may be an inorganic compound which includes a sulfur atom, preferably in an anion.

A preferred inorganic sulfur-containing additive is any sulfur-containing compound that is capable of forming a sulfide anion (S^{2-}) in the reaction mixture, able to be absorbed, suitably in preference to carbon monoxide, by the metallic cobalt precipitate. Such additives may include a sulfide anion (S^{2-}) per se, for example an inorganic sulfide such as sodium sulfide. Alternatively, or additionally, such additives include those compounds which do not include a sulfide anion (S^{2-}) per se, but are capable of generating a sulfide anion during the hydroformylation reaction, for example sodium hydrogen sulfide.

Thus, preferred inorganic sulfur-containing additives include: metal sulfides, preferably of empirical formula M_xS_y where M is a metal cation and either x is 1 or 2 and y is 1, or x is 2 and y is 3; metal hydrogen sulfides, preferably of empirical formula $M(SH)_z$ where M represents a metal cation and z is 1, 2 or 3; and hydrogen sulfide. Preferably x is 1 or 2 and y is 1. Preferably z is 1 or 2. Suitably, the metal cation M is selected from alkali and alkaline earth metals; preferably from sodium, potassium, calcium, magnesium and zinc. Most preferably the metal cation is potassium, or especially, sodium.

Especially preferred inorganic sulfur-containing additives include sodium sulfide (Na_2S), hydrogen sulfide and, especially, sodium hydrogen sulfide ($NaHS$).

The additive may be an organic sulfur-containing compound. Preferred organic sulfur-containing additives include thiols, disulfides, thioethers and thiophenes. A preferred thiol is represented by the general formula R^5-SH , where R^5 represents lower alkyl or aryl as defined hereinafter. A preferred disulfide is represented by the general formula R^6-SS-R^7 , wherein R^6 and R^7 each

independently represents lower alkyl or aryl. In highly preferred disulfides both R^6 and R^7 represent lower alkyl. A preferred thioether is represented by the general formula R^6-S-R^7 wherein R^6 and R^7 each independently
5 represent lower alkyl or aryl. Highly preferred thioethers include di(lower alkyl) sulfides, especially dimethyl sulfide. A preferred thiophene is thiophene itself.

Highly preferred organic sulfur-containing additives include dimethylsulfide and thiophene.

10 An especially preferred sulfur-containing additive is sodium hydrogen sulfide which generates a sulfide anion (S^{2-}) during the hydroformylation reaction.

The term lower alkyl includes linear or branched, cyclic or acyclic, groups of up to 20 carbon atoms, which
15 may be interrupted by oxygen. Preferably no more than five oxygen atoms are present in an alkyl chain. More preferably there are no oxygen atoms present in the alkyl chain, the chain (or backbone) being made up of only carbon atoms. Optional substituents may include, for
20 example, halo, cyano, hydroxyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, (C_1-C_4 alkoxy)carbonyl, amino and mono- or di- C_1-C_4 alkylamino groups. When an alkyl group is substituted it preferably has 1-3 substituents.

Preferably, however, an alkyl group is unsubstituted.
25 Lower alkyl groups may favourably have up to 16 carbon atoms, preferably up to 10, more preferably up to 6, and most preferably up to 4. Acyclic alkyl groups are preferred. Linear groups are preferred. Preferred lower alkyl groups include the propyl and butyl groups,
30 especially n-propyl and n-butyl, and, most preferred, ethyl and, especially methyl.

The term aryl includes six to ten-membered carbocyclic aromatic groups, such as phenyl and naphthyl, which groups

are optionally substituted by one or more substituents, for example 1-3 substituents, preferably selected from halo, cyano, nitro, lower alkyl, lower haloalkyl, OR⁸, C(O)R⁸, C(O)OR⁸ where R⁸ represents a lower alkyl or aryl group. Preferred aryl groups are unsubstituted. Highly preferred aryl groups are phenyl and tolyl.

The term halo includes fluoro, chloro, bromo and iodo.

Preferably the additive provides sulfur in an amount of up to 80 ppm (parts per million), preferably up to 50 ppm, more preferably up to 30 ppm, and most preferably up to 15 ppm, by weight of the total reaction mixture.

Preferably the additive provides sulfur in an amount of at least 5 ppm, most preferably at least 10 ppm, by weight of the total reaction mixture.

Suitably, a process in accordance with the invention, including a sulfur-containing additive, produces less than 50% of the cobalt carbide, over a given time period, compared with that produced by the corresponding hydroformylation process in the absence of the additive; and preferably less than 25% (weight/weight).

Suitably, the additive does not substantially affect the activity and/or stability of the cobalt catalyst in the hydroformylation process. In other words, the rate of hydroformylation with the inclusion of the additive in the reaction mixture is substantially the same as the rate of hydroformylation without the inclusion of the additive in the reaction mixture, under identical reaction conditions. By "substantially the same" we mean that, preferably, the rate of hydroformylation with the inclusion of the additive in the reaction mixture is at least 90% of the rate of hydroformylation without the additive.

Suitably, the stability of the cobalt catalyst during the hydroformylation reaction with the inclusion of the

additive remains substantially the same as the stability of the cobalt catalyst during a corresponding hydroformylation reaction without the inclusion of the additive under identical reaction conditions. Suitably, the stability of the cobalt catalyst may be determined by methods well known to those skilled in the art, for example infra-red spectrophotometry or elemental analysis, by monitoring the amount of cobalt lost from a known concentration of a catalyst during the hydroformylation of a known concentration of an olefinic compound, at a specific reaction temperature and specific pressure of hydrogen and carbon monoxide.

Preferably the cobalt catalyst comprises cobalt in complex combination with carbon monoxide and an organophosphine. By the term "complex combination" we mean a coordination compound formed by the union of one or more carbon monoxide and organophosphine molecules with one or more cobalt atoms. In its active form the suitable cobalt catalyst contains the cobalt component in a reduced valence state.

Suitable organophosphine ligands include those having a trivalent phosphorus atom having one available or unshared pair of electrons. Any essentially organic derivative of trivalent phosphorus with the foregoing electronic configuration is a suitable ligand for the cobalt catalyst. It thus will operate as a ligand in forming the desired cobalt catalyst.

Organic radicals of any size and composition may be bonded to the phosphorus atom. For example the organophosphine ligand may comprise a trivalent phosphorus having aliphatic and/or cycloaliphatic and/or heterocyclic and/or aromatic radicals satisfying its three valences. These radicals may contain a functional group such as

carbonyl, carboxyl, nitro, amino, hydroxy, saturated or unsaturated carbon-to-carbon linkages, and saturated and unsaturated non-carbon-to-carbon linkages.

It is also suitable for an organic radical to satisfy more than one of the valences of the phosphorus atom, thereby forming a heterocyclic compound with a trivalent phosphorus atom. For example, an alkylene radical may satisfy two phosphorus valences with its two open valences and thereby form a cyclic compound. Another example would be an alkylene dioxy radical that forms a cyclic compound where the two oxygen atoms link an alkylene radical to the phosphorus atom. In these two examples, the third phosphorus valence may be satisfied by any other organic radical.

Another type of structure involving trivalent phosphorus having an available pair of electrons is one containing a plurality of such phosphorus atoms linked by organic radicals. This type of a compound is typically called a bidentate ligand when two such phosphorus atoms are present, a tridentate ligand when three such phosphorus are present, and so forth.

Suitable cobalt catalysts for use in the process of the present invention and their methods of preparation are disclosed in US Patents 3369050, 3501515, 3448158, 3448157, 3420898 and 3440291, all of which are incorporated herein by reference. Preferably, the cobalt catalyst is substantially homogeneous with the reaction mixture.

Preferred cobalt catalysts for use in the process of the present invention are those which include an organic tertiary phosphine ligand, especially a bicyclic heterocyclic tert-phosphine ligand, preferably as

disclosed in US Patent 3501515. Representative examples of such ligands include:

9-hydrocarbyl-9-phosphabicyclo[4.2.1]nonane;

9-aryl-9-phosphabicyclo[4.2.1]nonane,

5 such as 9-phenyl-9-phosphabicyclo[4.2.1]nonane;

(di)alkyl-9-aryl-9-phosphabicyclo[4.2.1]nonane,

such as 3,7-dimethyl-9-phenyl-9-phosphabicyclo[4.2.1]-

nonane and

3,8-dimethyl-9-phenyl-9-phosphabicyclo[4.2.1]nonane;

10 9-alkyl-9-phosphabicyclo[4.2.1]nonane,

such as 9-octadecyl-9-phosphabicyclo[4.2.1]nonane,

9-hexyl-9-phosphabicyclo[4.2.1]nonane,

9-eicosyl-9-phosphabicyclo[4.2.1]nonane, and

9-triacontyl-9-phosphabicyclo[4.2.1]nonane;

15 9-cycloalkyl-9-phosphabicyclo[4.2.1]nonane,

such as 9-cyclohexyl-9-phosphabicyclo[4.2.1]nonane and

9-(1-octahydropentyl)-9-phosphabicyclo[4.2.1]nonane;

9-cycloalkenyl-9-phosphabicyclo[4.2.1]nonane,

such as 9-cyclooctenyl-9-phosphabicyclo[4.2.1]nonane;

20 9-hydrocarbyl-9-phosphabicyclo[3.3.1]nonane;

9-aryl-9-phosphabicyclo[3.3.1]nonane,

such as 9-phenyl-9-phosphabicyclo[3.3.1]nonane;

9-alkyl-9-phosphabicyclo[3.3.1]nonane,

such as 9-hexyl-9-phosphabicyclo[3.3.1]nonane, and

25 9-eicosyl-9-phosphabicyclo[3.3.1]nonane.

A particularly preferred ligand includes a tricarbonyl-9-eicosyl-9-phosphabicyclo nonane compound. A particularly preferred catalyst includes a derivative thereof, believed to be a complex, with cobalt.

30 The cobalt catalysts can be prepared by a diversity of methods well known to those skilled in the art as disclosed in US Patents 3 369 500, 3 501 515, 3 448 157, 3

420 898 and 3 440 291. A convenient method is to combine a cobalt salt, organic or inorganic, with the desired phosphine ligand, for example, in liquid phase followed by reduction and carbonylation. Suitable cobalt salts
5 comprise, for example, cobalt carboxylates such as acetates, octanoates, etc. as well as cobalt salts of mineral acids such as chlorides, fluoride, sulfates, sulfonates, etc. as well as mixtures of one or more of these cobalt salts. The valence state of the cobalt may be
10 reduced and the cobalt-containing complex formed by heating the solution in an atmosphere of hydrogen and carbon monoxide. The reduction may be performed prior to the use of the catalysts or it may be accomplished simultaneously with the hydroformylation process in the
15 hydroformylation zone. Alternatively, the catalysts can be prepared from a carbon monoxide complex of cobalt. For example, it is possible to start with dicobalt octacarbonyl and, by mixing this substance with a suitable phosphine ligand, the ligand replaces one or more of the
20 carbon monoxide molecules, producing the desired catalyst.

The ratio of catalyst to the olefinic compound to be hydroformylated is generally not critical and may vary widely. It may be varied to achieve a substantially homogeneous reaction mixture. Solvents are therefore not
25 required. However, the use of solvents which are inert, or which do not interfere to any substantial degree with the desired hydroformylation reaction under the conditions employed, may be used. Saturated liquid hydrocarbons, for example, may be used as solvent in the process, as well as
30 alcohols, ethers, acetonitrile, sulfolane, and the like. Molar ratios of catalyst to the olefinic compound in the reaction zone at any given instant between about 1:1000 and about 10:1 are found to be satisfactory; a higher or

lower ratio of catalyst to olefinic compound may, however, be used, but in general it will be less than 1:1.

The ratio of hydrogen to carbon monoxide may vary widely. In general, a mole ratio of at least about 1, hydrogen to carbon monoxide, is employed. Suitably ratios of hydrogen to carbon monoxide comprise those within the range of from about 1 to 10. Higher or lower ratios may, however, be employed. The ratio of hydrogen to carbon monoxide employed will be governed to some extent by the nature of the reaction product desired. If conditions are selected that will result primarily in an aldehyde product, only one mole of hydrogen per mole of carbon monoxide enters into reaction with the olefinic compound. When an alcohol is the preferred product of the process of the present invention, two moles of hydrogen and one mole of carbon monoxide react with each mole of olefinic compound. The use of ratios of hydrogen to carbon monoxide which are somewhat lower than those defined by these values are generally preferred.

The process of the present invention may be carried out at various pressures. Consequently, hydroformylation in accordance with the process of the present invention may typically be carried out at pressures below 7×10^6 Pa, to as low as 1×10^5 Pa. The process of the present invention is, however, not limited in its applicability to the lower pressures and pressures in the broad range from 1×10^5 Pa up to about 14×10^6 Pa and in some cases up to about 20×10^6 Pa, or even higher, may be employed. Typically, the specific pressure used will be governed to some extent by the specific charge and catalyst employed. In general, pressures in the range of from about 2×10^6 Pa to 10×10^6 Pa and particularly in the range of from about 2.7×10^6 Pa to about 9×10^6 Pa are preferred.

Temperatures employed in the process of the invention will generally range from about 100°C to about 300°C and preferably about 150°C to about 210°C, a temperature of about 200°C being generally satisfactory. Somewhat higher or lower temperatures may, however, be used within the scope of the invention.

It will be appreciated by those skilled in the art that depending upon the specific charge and cobalt catalyst employed, the process of the present invention may effect the direct, single stage hydroformylation of an olefinic compound to yield a reaction product wherein the alcohols predominate over the aldehydes. By selection of reaction conditions, charge and the cobalt catalyst within the above defined ranges it is possible to obtain greater than or equal to 80% of straight chain alcohols, rather than various branched isomers from the hydroformylation of olefinic compounds. Typically, the alcohols are the desired end product. However, by varying the operating conditions as described hereinbefore the ratio of aldehydes to alcohols product may be varied.

The process of the present invention is generally applicable to the hydroformylation of any aliphatic or cycloaliphatic compound having at least one olefinic carbon-to-carbon bond. Thus, it may be applied to the hydroformylation of olefinic compounds comprising olefinically unsaturated compounds having, for example, from 2 to 19 carbons, to produce reaction mixtures predominating in aliphatic aldehydes and alcohols having one more carbon atom than the starting olefinic compound. Mono-olefinic compounds, such as ethylene, propylene, butylenes, amylenes, hexylenes, heptylenes, octylenes, nonylenes, decylenes, undecylenes, dodecylenes,

tridecylenes, tetradecylenes, pentadecylenes, hexadecylenes, heptadecylenes, octadecylenes, nonadecylenes, and their homologues, are examples of suitable unsaturated compounds which may be hydroformylated in the process of the present invention. Suitable unsaturated compounds include both branched and straight-chain compounds having one or more olefinic sites. When two or more double bonds are present these may be conjugated, as in 1,2-hexadiene. In the case of polyolefinic compounds, it is possible to hydroformylate only one of the olefinic sites or several or all of these sites. The unsaturated carbon-to-carbon olefinic linkages may be between terminal and their adjacent carbon atoms, as in 1-pentene, or between internal chain carbon atoms, as in 4-octene.

Preferably an olefinic compound used in the process is a mono-olefinic compound.

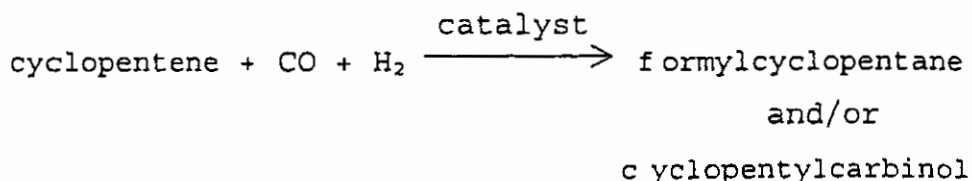
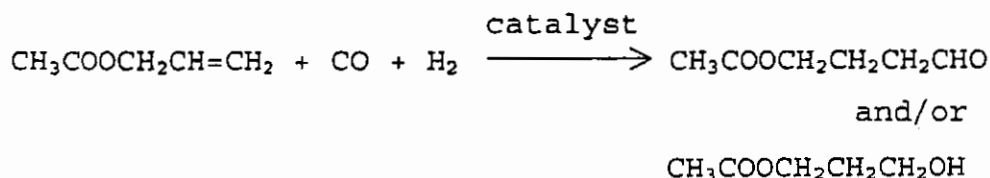
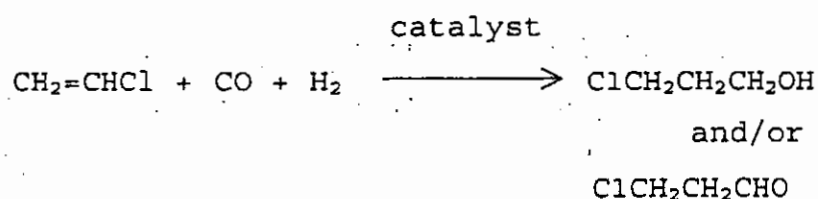
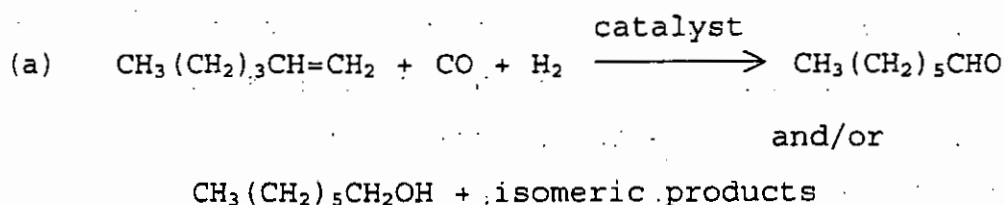
Preferably an olefinic compound used in the process has an olefinic linkage between a terminal carbon atom and its adjacent carbon atom.

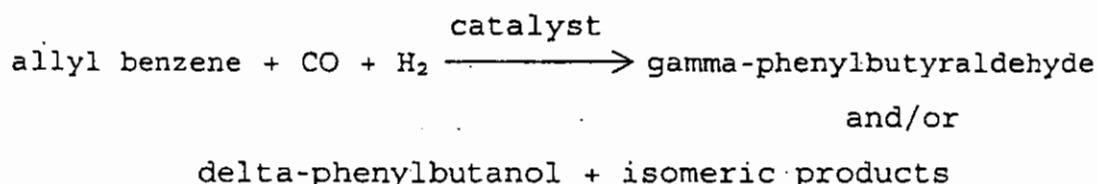
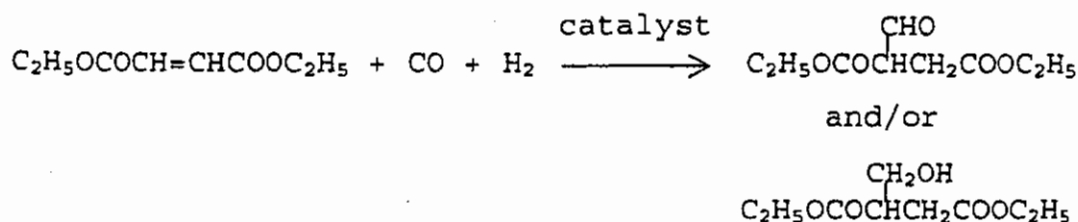
Hydroformylation of macromolecular materials involving acyclic units of the above types, such as polydiolefinic compounds, for example polybutadiene, as well as copolymers of olefinic and diolefinic compounds, for example styrene-butadiene copolymer, may also be accomplished by the process of the present invention.

Cyclic compounds are equally suitable for use in the process of the present invention. Suitable cyclic compounds include unsaturated alicyclic compounds such as the cyclic olefinic compounds containing carbon-to-carbon unsaturation, such as cyclopentene, cyclohexene, and cycloheptene. Also included in this category are the terpenes and fused-ring polycyclic olefinic compounds,

such as 2,5-bicyclo(2,2,1)heptadiene, 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene and the like.

The process of this invention is typically used to hydroformylate olefinic carbon-to-carbon linkages of hydrocarbons but may also be used for non-hydrocarbons. Thus, it is possible to hydroformylate olefinically unsaturated alcohols, epoxides, aldehydes, and acids to corresponding alcohols, aldehydes, and acids containing an aldehyde or hydroxy group on one of the carbon atoms previously involved in the olefinic bond of the starting material. The following are a few specific examples of different types of olefinic compounds that may be hydroformylated by the process of the present invention and the products obtained thereby:





The olefinic charge to the process of the invention may comprise two or more of the above-defined suitable olefinic compounds. Olefinic compounds may be hydroformylated under the conditions defined above to produce mixtures of aldehydes and alcohols in which the alcohols predominate.

The process of the present invention may thus be employed to effect the direct, single stage hydroformylation of olefinic compounds, preferably mono-olefinic compounds, and especially mono-olefins, having, for example, from 2 to 19 carbon atoms per molecule, preferably to produce predominantly terminal alcohols having 5 to 20 carbon atoms per molecule, respectively. Olefinic fractions, such as, for example, polymeric olefinic fractions, cracked wax fractions, and the like, containing substantial proportions of olefinic compounds, may be readily hydroformylated to fractions of hydroformylated products comprising mixtures of predominantly terminal aldehydes and alcohols having one more carbon than the olefinic compounds in the charge and wherein these alcohols are the predominant reaction product. Such suitable feeds consisting of olefinic

fractions include, for example C₇, C₈, C₉, C₁₀ and higher olefinic fractions as well as olefinic hydrocarbon fractions of wider boiling ranges such as C₇-C₉, C₁₀-C₁₃, C₁₄-C₁₇ olefinic hydrocarbon fractions and the like. In
5 broad terms C₈-C₁₆ olefinic compounds, in particular C₈-C₁₆ olefinic hydrocarbons, are preferred.

It will be appreciated that under the above-defined conditions, the olefinic charge may react with carbon monoxide and hydrogen to form reaction products comprising
10 aldehydes and/or alcohols having one more carbon atom per molecule than the olefin charged.

The proportions in which reactants are fed to the reaction zone may vary over relatively wide limits, for example, from about 1 to about 5 molar amounts of an
15 olefinic compound as described hereinbefore may be reacted with from about 1 to about 12 moles of hydrogen and about 1 to about 7 moles of carbon monoxide. Sufficient amounts of olefinic compound are however included in the feed to the reaction zone.

20 Admixtures of promoters, stabilizers and the like may also be included in the process of the present invention. Thus, minor amounts of phenolic stabilizers such as hydroquinone, alkaline agents such as hydroxides of alkali metals, for example NaOH and KOH, may be added to the
25 reaction zone.

The reaction mixtures obtained may be subjected to suitable catalyst and product separating means comprising one or more steps, for example, stratification, solvent extraction, distillation, fractionation, adsorption, etc.
30 The specific method of product and catalyst separation preferably employed will be governed to some extent by the specific complex and reactants charged. Catalyst or components thereof, as well as unconverted charge, and

solvent, when employed, may be recycled in part or entirety to the reaction zone.

The preformed cobalt catalyst, or separate components of the catalyst capable of producing the complex in situ in the reaction zone, may be added to material separated from the reactor which is being recycled to the reaction zone. A part of an alcoholic reaction product may, if desired, be recycled to the reaction zone to function as solvent and/or diluent and/or suspending medium for the catalyst, the catalyst components, and the like, passing to the reaction zone. A part or all of an aldehyde product may optionally be recycled to the reaction zone or may be subjected to hydroformylation conditions in a second and separate reaction zone in the presence of a cobalt catalyst. The cobalt catalyst used in the second hydroformylation step need not be the same as that used in the first step.

According to a further aspect, the present invention provides the use of an additive as defined hereinbefore for suppressing the formation of cobalt carbide in a reaction employing a cobalt complex catalyst.

The invention will be further described by way of the following non-limiting examples.

Batch and pilot plant experiments were performed to determine the stability of a cobalt/phosphine catalyst in a hydroformylation reaction and the type of catalytic decomposition products.

Example 1: Preparation of a standard cobalt catalyst solution (preliminary)

A phosphine ligand, (268g, 0.63 mol) 9-eicosyl-9-phosphabicyclononane, a commercial mixture from Shell, and hereinafter called the P-ligand, was melted at 60°C and

charged into a 1 litre glass bottle. To this was added 298g of a 10 wt% cobalt solution of cobalt octoate in 2-ethyl hexanol (equivalent to 0.48 mol of cobalt), followed by 268g of Neodol-23™, a commercial mixture of C₁₂ and C₁₃ linear detergent alcohols available from Shell. The solution was stirred for two hours at 60°C and used as stock solution for the following batch experiments. The cobalt catalyst solution was stored at ambient temperature and pressure.

10 A 1.3 wt% stock solution of potassium hydroxide in Neodol-23™ was prepared by dissolving 5g of powdered KOH in 386g of Neodol-23™ at 50°C. This solution was stored at ambient temperature and pressure.

15 Example 2: Batch experiment to determine the stability of the cobalt catalyst and the type of decomposition product without an additive (comparative)

A stainless steel autoclave, equipped with stirrer, temperature and pressure control, was charged with 100g of Neodol-23™ and 30g of the 1.3 wt% solution of KOH in Neodol-23™ of Example 1. After flushing the system with nitrogen and syngas to remove residual oxygen, the autoclave was heated to 197°C and pressurized with H₂ and CO (inlet ratio H₂/CO = 1.8) to a pressure of 6 x 10⁶ Pa. Subsequently, 30g of the cobalt catalyst solution of Example 1 was injected to start the experiment.

After 5 minutes at 197°C and 6 x 10⁶ Pa syngas pressure to allow formation of the active catalyst, a reference sample was taken and analysed by infra-red spectrophotometry to determine the composition and cobalt concentration of the catalyst.

The autoclave was kept at 197°C and 6 x 10⁶ Pa syngas pressure, while at regular intervals samples were

withdrawn to determine the cobalt concentration by infra-red spectrophotometry. After 150 hours more than 50% of the cobalt catalyst had disappeared as determined by infra-red and the autoclave was cooled to room temperature and depressurised. The liquid was decanted and the solids were collected and analysed by X-ray diffraction to determine the composition of the solid residue. The solid residue was shown to be almost pure cobalt carbide. The first-order-decay rate constant of the cobalt catalyst, determined from the decrease in cobalt concentration by infra-red spectrophotometry was 0.006 h^{-1} .

Example 3: Batch experiment to determine the stability of the cobalt catalyst and the type of decomposition product without an additive, but in the presence of added cobalt carbide (comparative)

A stainless steel autoclave, equipped with stirrer, temperature and pressure control, was charged with 100g of Neodol-23™ and 30g of the 1.3 wt% solution of KOH in Neodol-23™ of Example 1. In this particular experiment 2g of cobalt carbide in powder form was also added to the autoclave. After flushing the system with nitrogen and syngas to remove residual oxygen, the autoclave was heated to 197°C and pressurized with H_2 and CO (inlet ratio $\text{H}_2/\text{CO} = 1.8$) to a pressure of $6 \times 10^6 \text{ Pa}$. Subsequently, 30g of the standard catalyst solution of Example 1 was injected to start the experiment.

After 5 minutes at 197°C and $6 \times 10^6 \text{ Pa}$ syngas pressure to allow formation of the active catalyst, a reference sample was taken and analysed by infra-red spectrophotometry to determine the composition and cobalt concentration of the catalyst.

The autoclave was kept at 197°C and $6 \times 10^6 \text{ Pa}$ syngas pressure, while at regular time intervals samples were

withdrawn to determine the cobalt concentration by infra-red spectrophotometry. After 18 hours more than 50% of the cobalt catalyst had disappeared and the autoclave was cooled to ambient temperature and depressurised. The liquid was decanted and the solids were collected and analysed by X-ray diffraction to determine the composition of the solid residue. The solid residue was shown to be almost pure cobalt carbide. The first-order-decay rate constant of the cobalt catalyst, determined from the decrease in cobalt concentration by infra-red, was 0.062 h^{-1} .

The experiment demonstrates that the presence of cobalt carbide in the reaction mixture dramatically affects the stability of the cobalt catalyst, as the first order decay rate constant for the cobalt catalyst with added cobalt carbide in the reaction is 0.062 h^{-1} , whereas the first order decay rate constant of the catalyst without cobalt carbide is 0.006 h^{-1} (see Example 2).

Example 4: Batch experiment to determine the stability of the cobalt catalyst and the type of decomposition product in the presence of 50 ppm wt thiophene additive

A stainless steel autoclave, equipped with stirrer, temperature and pressure control, was charged with 90g of Neodol-23™ and 35g of a 1.3 wt% solution of KOH in Neodol-23™ of Example 1 and 0.022g of thiophene. After flushing the system with nitrogen and syngas to remove residual oxygen, the autoclave was heated to 192°C and pressurized with H_2 and CO (inlet ratio $\text{H}_2/\text{CO} = 1.8$) to a pressure of $6 \times 10^6 \text{ Pa}$. Subsequently 30g of the standard catalyst solution of Example 1 was injected to start the experiment.

After 5 minutes at 192°C and 6×10^6 Pa syngas pressure to allow formation of the active catalyst, a reference sample was taken and analysed by infra-red spectrophotometry to determine the composition and cobalt concentration of the catalyst.

The autoclave was kept at 192°C and 6×10^6 Pa syngas pressure, while at regular intervals samples were withdrawn to determine the cobalt concentration by infra-red. After 100 hours more than 50% of the cobalt catalyst had disappeared as determined by infra-red and the autoclave was cooled to room temperature and depressurised. The liquid was decanted and the solids were collected and analysed by X-ray diffraction to determine the composition of the solid residue. The solid residue was shown to be almost pure cobalt metal. The first order decay rate constant of the cobalt catalyst, determined from the decrease in cobalt concentration by infra-red spectrophotometry, was 0.008 h^{-1} .

This experiment shows that by addition of a sulfur-containing compound the undesired formation of cobalt carbide is prevented and the more desirable cobalt metal is formed. By comparing the first order decay rate constant of the cobalt catalyst for this Example with that of Example 2, it is evident that the sulfur-containing additive has little detrimental effect on the stability of the cobalt catalyst.

Additional batch experiments, with different additives, varying concentrations of additives, and at different temperatures, referred to as Experiments 5 to 29 in Table 1 below, were performed as described in the preceding examples to determine the efficiency of various additives at suppressing cobalt carbide formation and the effect the additives have on the stability of the cobalt

catalyst. The results are presented in Table 1 below. The symbol P-ligand/Co denotes the cobalt catalyst solution as described in Example 1. The symbol Co_xC denotes cobalt carbide, whether Co_2C or Co_3C , or both in admixture; the
5 structure/empirical formula is not significant and was not determined.

Table 1

Type	T (°C)	P-ligand/Co	K/Co	S-source	[S]ppmw	deposits	decay rate (h ⁻¹)
6	200	1.3	0.4	none		Co ₂ C	0.010
7	210	1.3	0.4	none		Co ₂ C	0.031
8	192	1.3	0.5	none		Co ₂ C	0.016
9	210	1.2	0.4	none		Co ₂ C	0.27
10	210	1.3	0.4	dimethyldisulfide	1	Co ₂ C	0.040
11	210	1.3	0.4	dimethyldisulfide	5	Co ₂ C and Co	0.055
12	210	1.3	0.4	dimethyldisulfide	10	Co ₂ C and Co	0.040
13	210	1.3	0.4	dimethyldisulfide	15	Co ₂ C and Co	0.038
14	210	1.3	0.4	dimethyldisulfide	20	Co ₂ C and Co	0.028
15	192	1.3	0.4	dimethyldisulfide	100	Co	0.9
16	210	1.3	0.5	dimethyldisulfide	50	Co	0.016
17	210	1.3	0.4	thiophene	10	Co ₂ C and Co	0.05
18	210	1.3	0.4	thiophene	25	Co ₂ C and Co	0.05
19	192	1.3	0.4	thiophene	50	Co ₂ C and Co	0.05
20	210	1.3	0.5	thiophene	50	Co	0.008
21	210	1.3	0.4	sodium sulfide	11	Co ₂ C and Co	0.027
22	210	1.3	0.4	sodium sulfide	50	Co ₂ C and Co	0.13
23	192	1.3	0.5	sodium sulfide	25	Co ₂ C and Co	0.024
24	192	1.3	0.5	sodium sulfide	50	Co	0.056
25	192	1.3	0.5	sodium hydrogen sulfide	25	Co ₂ C and Co	0.019
26	192	1.3	0.05	sodium hydrogen sulfide	50	Co	0.024
27	210	1.3	0.4	thianthrene	25	Co ₂ C and Co	0.039
28	210	1.3	0.4	thianthrene	50	Co ₂ C and Co	0.031
29	210	1.3	0.4	dibenzothiophene	25	Co ₂ C and Co	0.030
29	210	1.3	0.4	dibenzothiophene	50	Co ₂ C and Co	0.033

Experiment 30: Continuous experiment to determine the stability of the cobalt catalyst and the type of decomposition product without an additive (comparative)

A reaction zone, consisting of four autoclaves in series operated 192°C and 5×10^6 Pa syngas (inlet ratio $H_2/CO = 1.7$), is fed with a continuous feed stream of olefin NEODENE™, from Shell, catalyst components (cobalt octoate, P-ligand as for Example 1, KOH), fresh syngas and catalyst recycle stream. After depressurisation, the product alcohols, formed by hydroformylation of the olefin feed stream, and the catalyst dissolved in heavy by-products are separated via a short-path distillation. The heavy-bottom stream containing the cobalt catalyst is recycled back to the autoclaves. The experiment was operated in a continuous mode.

Feed rates of the catalyst components are adjusted to maintain the targeted steady-state catalyst concentration and composition: 0.25 wt% cobalt, P-ligand/Co = 1.3 and KOH/Co = 0.5.

Cobalt carbide 30g in powder form was placed in autoclaves 1 and 3 and the run was continued for 600 hours to determine a reference point. After 600 hours the autoclaves were cooled to ambient temperature and depressurised. The solids, both the on-purpose added carbide and the fresh deposits, were collected and analysed by X-ray diffraction. Operation at these conditions led to formation of fresh cobalt carbide depositions on the on-purpose added cobalt carbide sample material. The catalyst decomposition rate, a measure for catalyst stability, was determined to be 0.075 g Co/kg of hydroformylation products produced over the 600 hour test period.

Experiment 31: Continuous experiment to determine the stability of the cobalt catalyst and the type of decomposition product with a sulfur-containing additive

5 A reaction was carried out as described in Example 30, except that sodium sulfide was also added.

Feed rates of the catalyst components are adjusted to maintain the targeted steady-state catalyst concentration and composition: 0.25 wt% cobalt, P-ligand/Co = 1.3 and KOH/Co = 0.5.

10 Sodium sulfide was fed to the reactor on a continuous basis to maintain 10 ppm sulfur concentration in the reaction mixture.

Cobalt carbide (30g) in powder form was placed in reactors 1 and 3, and the run was continued for 600 hours
15 to determine a reference point. After 600 hours the reactors were cooled to room temperature and depressurised. The solids, both the on-purpose added carbide and the fresh deposits, were collected and analysed by X-ray diffraction. Operation at these
20 conditions led to formation of fresh cobalt metal on the on-purpose added cobalt carbide sample material. The catalyst decomposition rate was determined to be 0.106g Co/kg of hydroformylation products produced over the 600 hour test period.

25 The results of Experiment 30 and 31 demonstrate that the addition of a sulfur-containing additive suppresses the formation of cobalt carbide and results in the formation of the more desirable cobalt metal.

Examples 32-40: Continuous experiments to determine the stability of the cobalt catalyst and the type of decomposition product with a sulfur-containing additive

Additional continuous experiments with varying concentrations of sodium sulfide as additive were performed to determine their efficiency at suppressing the formation of cobalt catalyst and the effect the additive has on the stability of the cobalt catalyst. All experiments were carried out in the presence of added cobalt carbide, in powder form at 192° C, over an 1800 hour time period, and with other conditions as described in the preceding example 31. Conditions and results are summarised in Table 2 below.

Table 2

Example	S-source	[S]reactors (ppmw)	P-ligand/Co decomp. rate (g Co/kg olefin)	Deposits
32	none		0.115	Co ₂ C
33	none		0.087	Co ₂ C
33	none		0.070	Co ₂ C
35	sodium sulfide	<5	0.050	Co ₂ C
36	Sodium sulfide	10	0.106	Co
37	sodium sulfide	15	0.050	Co
38	Sodium sulfide	18	0.013	Co
39	Sodium sulfide	30	0.064	Co
40	sodium sulfide	40	0.160	Co

15

The results demonstrate that in a reaction mixture which comprises a sodium sulfide additive which provides a weight of sulfur greater than 5 parts per million of the weight of the reaction mixture then the formation of cobalt carbide is suppressed and cobalt metal is formed. Moreover, the stability of the cobalt catalyst is not significantly affected.

20

CLAIMS

1. A hydroformylation process comprising reacting a compound having at least one olefinic carbon-to-carbon bond with hydrogen and carbon monoxide in the presence of a cobalt catalyst and a sulfur-containing additive,
5 wherein the additive is an inorganic sulfur-containing additive which is capable of forming a sulfide anion (S^{2-}) in the reaction mixture or an organic sulfur-containing additive selected from thiols, disulfides, thioethers and thiophenes, wherein the additive
10 suppresses the formation of cobalt carbide in the reaction mixture, and wherein the compound having at least one olefinic carbon-to-carbon bond is an olefinic hydrocarbon.
2. A process as claimed in claim 1 wherein the inorganic
15 sulfur-containing additive is selected from a metal sulfide, a metal hydrogen sulfide and hydrogen sulfide.
3. A process as claimed in claim 2 wherein the inorganic sulfur-containing additive is selected from sodium hydrogen sulfide, sodium sulfide or hydrogen sulfide.
- 20 4. A process as claimed in claim 1 wherein the organic sulfur-containing compound comprises thiophene or dimethyldisulfide.
5. A process as claimed in any one of the preceding claims wherein the additive does not substantially affect
25 the stability and/or activity of the cobalt catalyst.
6. A process as claimed in any one of the preceding claims wherein the additive provides a sulfur amount of up to 80 parts per million by weight of the total reaction mixture.

7. A process as claimed in any one of the preceding claims wherein the additive provides a sulfur amount of at least 5 parts per million by weight of the total reaction mixture.
- 5 8. A process as claimed in any one of the preceding claims wherein the cobalt catalyst comprises cobalt in complex combination with at least one carbon monoxide molecule and at least one organophosphine ligand.
9. A process as claimed in claim 8 wherein the cobalt
10 catalyst comprises a compound of the general formula $\text{Co}(\text{CO})_3\text{PL}$ wherein L represents a bicyclic heterocyclic tertiary phosphine ligand.
10. A process as claimed in any one of the preceding claims wherein the compound having at least one olefinic
15 carbon-to-carbon bond comprises an olefinic hydrocarbon having up to 19 carbon atoms.
11. A process as claimed in any one of the preceding claims wherein the reaction is performed at a temperature greater than or equal to 100°C and at a pressure of
20 greater than 1×10^5 Pa.
12. Use of a sulfur-containing additive as defined in any one of the preceding claims, for suppressing the formation of cobalt carbide in a hydroformylation process as defined in any one of the preceding claims.