

formylation processes of this invention is preferably below the threshold level that causes rapid degradation of the organopolyphosphite ligand, i.e., below the threshold for autocatalytic hydrolysis of the organopolyphosphite ligand. The concentration of phosphorus acidic compounds in the hydroformylation processes of this invention is such that the pH of said reaction product fluid is from about 4 to about 9. The phosphorus acidic compound concentration is preferably controlled by employing an aqueous buffer solution as described herein.

The hydroformylation processes of this invention are conducted for a period of time sufficient to produce the desired products. The exact reaction zone residence time employed is dependent, in part, upon factors such as temperature, nature and proportion of starting materials, and the like. The reaction zone residence time will normally be within the range of from about one-half to about 200 hours or more, and preferably from less than about one to about 10 hours. The reaction zone residence time should be such that the hydroformylation process can be operated below the threshold for autocatalytic hydrolysis of organopolyphosphite ligand and have a residence time in the reaction zone sufficient to achieve high raw material efficiencies, e.g., high conversion of olefinic unsaturated compounds.

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 sulfolane. Suitable solvents are disclosed in U.S. Pat. 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, nonadecanal, 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. Pat. No. 4,148,830 or a gas recycle procedure such as disclosed, for example, in U.S. Pat. No. 4,247,486, as well as a combination of both a liquid and gas recycle procedure if desired. The disclosures of said U.S. Pat. Nos. 4,148,830 and 4,247,486 are incorporated herein by reference thereto. The most preferred hydroformy-