

Nov. 3, 1953

D. E. BURNEY ET AL

2,658,083

SELECTIVE HYDROGENATION OF OXO-PROCESS ALDEHYDES

Filed April 26, 1951

2 Sheets-Sheet 1

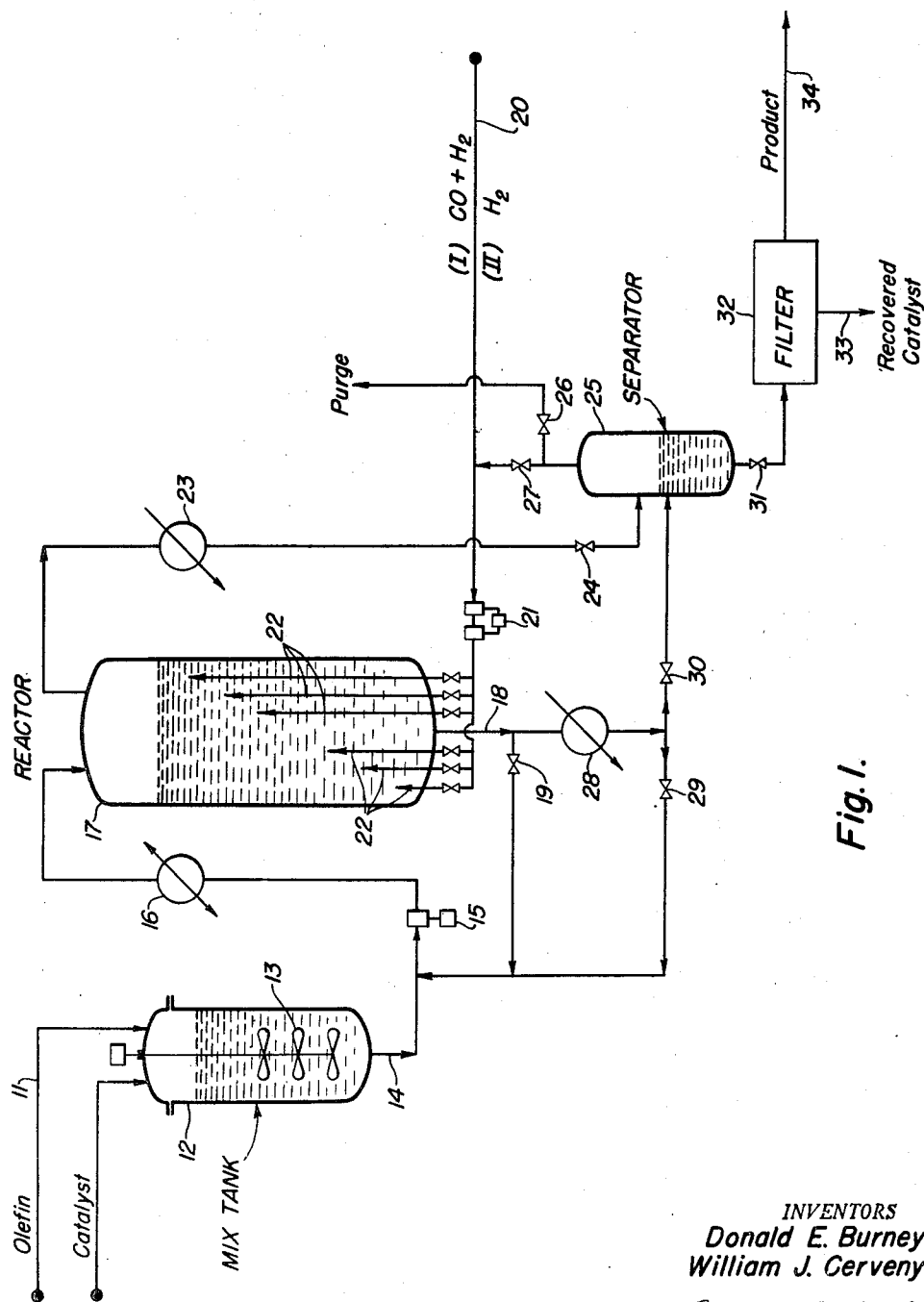


Fig. 1.

INVENTORS
 Donald E. Burney
 William J. Cervený
 BY: *Everett J. Smith*
 ATTORNEY

Nov. 3, 1953

D. E. BURNEY ET AL

2,658,083

SELECTIVE HYDROGENATION OF OXO-PROCESS ALDEHYDES

Filed April 26, 1951

2 Sheets-Sheet 2

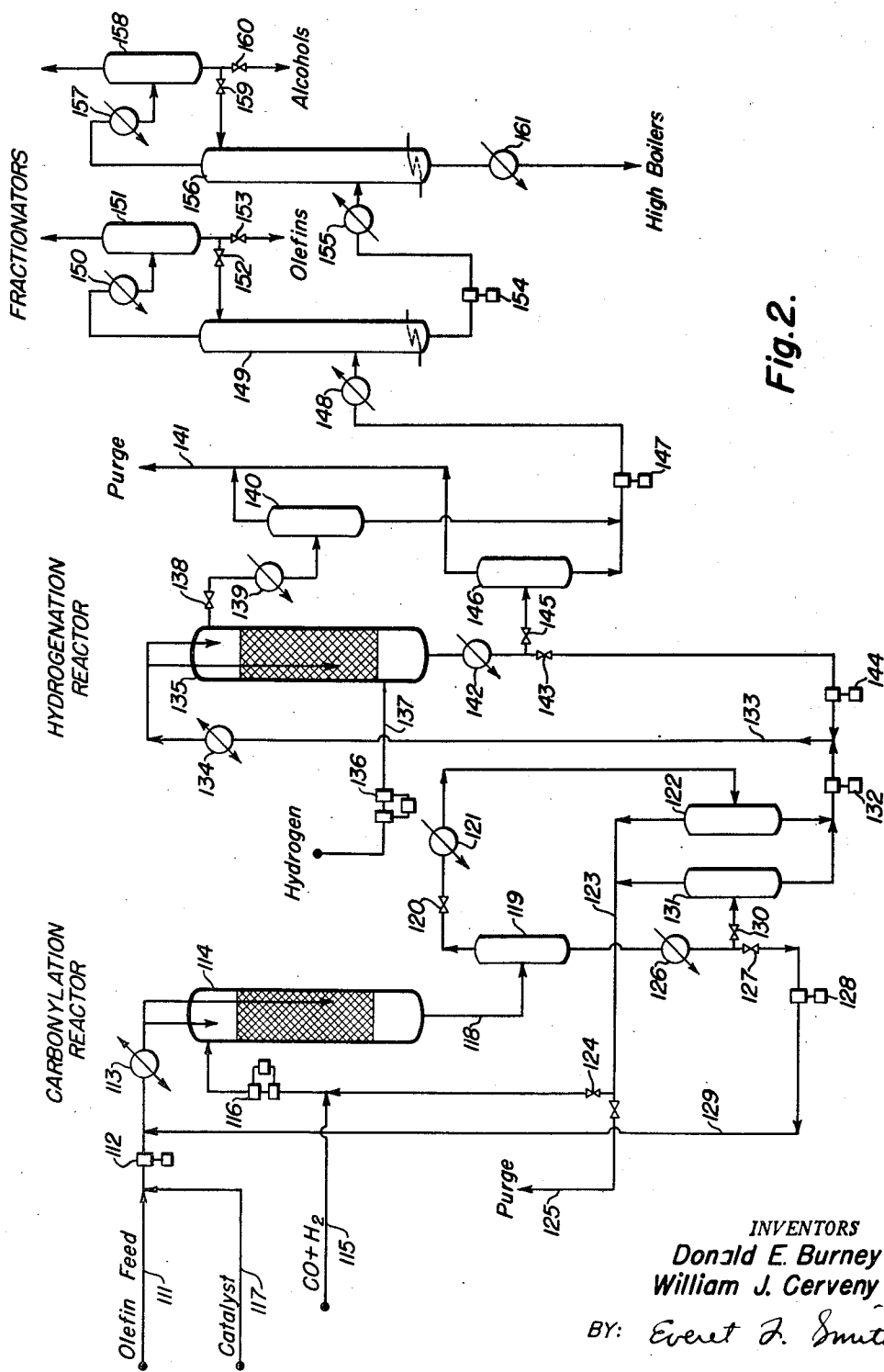


Fig. 2.

INVENTORS
Donald E. Burney
William J. Cervený

BY: *Everett J. Smith*

ATTORNEY

UNITED STATES PATENT OFFICE

2,658,083

SELECTIVE HYDROGENATION OF OXO-
PROCESS ALDEHYDES

Donald E. Burney, Griffith, Ind., and William J. Cerveny, Lansing, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application April 26, 1951, Serial No. 223,124

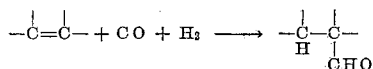
10 Claims. (Cl. 260—638)

1

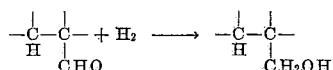
Our invention relates to the selective hydrogenation of carbonyl groups in the presence of olefinic double bonds. More particularly, it relates to the conversion of carbonyl compounds into alcohols in the presence of olefinic compounds without simultaneously effecting the saturation of the olefinic linkages in said olefinic compounds.

Numerous attempts have been made in the past to convert organic compounds containing carbonyl groups into the corresponding alcohols by hydrogenation, without simultaneously saturating olefinic double bonds present in the charging stock, either in the same compound with the carbonyl groups, or in different compounds. For example, Adkins ("Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937) failed in attempting to selectively hydrogenate the carbonyl group of aldehydes and ketones which also contained olefinic double bonds. Now, however, we have discovered an effective technique for the selective hydrogenation of carbonyl groups in certain carbonyl-olefin combinations.

In one embodiment of our invention, we have succeeded in preparing alcohols and higher-molecular weight olefins from a mixture of secondary olefins and tertiary olefins, by a combination process including an acid-copolymerization step, a treatment with carbon monoxide and hydrogen according to the so-called "Oxo" process, and our selective hydrogenation technique. A mixture of n-butylene and isobutylene, for example, may be copolymerized with sulfuric acid to give a mixture of isooctenes, the isooctenes are then reacted with carbon monoxide and hydrogen by means of the "carbonylation" step of the Oxo process,



to give a mixture of nonyl aldehydes and isooctenes, and the resulting mixture is then contacted with hydrogen in the presence of a cobalt catalyst at elevated temperature and pressure, the aldehydes being thereby converted into the corresponding nonyl alcohols,



and the isooctenes remaining unaffected. The selective hydrogenation step of our invention offers the important advantage that it avoids the necessity of isolating the aldehydes from the

2

carbonylation product of the Oxo process, an operation that is known to result in large losses of aldehydes through aldol condensation and other undesired reactions. Our selective hydrogenation step also avoids the heat effects that would be produced if the olefins were reduced to paraffins in the same operation, and the problem of temperature control within the reactor is thereby made less difficult. Our selective hydrogenation step has the additional important advantage that it permits the recovery and utilization or recycling of non-carbonylated olefins, which would be converted to paraffins in the conventional hydrogenation procedure.

One object of our invention is to provide a means for converting carbonyl compounds into alcohols in the presence of olefinic double bonds, without simultaneously saturating the double bonds. Another object of our invention is to provide a means for hydrogenating carbonyl compounds resulting from the carbonylation step of the Oxo reaction, while simultaneously leaving non-carbonylated olefinic constituents unaffected, so that the latter may be recycled to the carbonylation step. Other objects of our invention, and its advantages over the prior art, will be apparent from the following description and examples.

Our process is especially suitable for the selective hydrogenation of the products resulting from the carbonylation of secondary olefin-tertiary olefin copolymers, such as copolymers of mixtures containing at least one olefin from the group comprising propylene, 1-butene, 2-butene, and secondary amylene, and at least one olefin from the group comprising isobutylene, 2-methyl-1-butene, and 2-methyl-2-butene. Thus, our process is suitable for treating the mixture of nonyl aldehydes and isooctenes obtained from n-butylene-isobutylene codimer, the mixture of octyl aldehydes and isooctenes obtained from propylene-isobutylene copolymer, the mixture of nonyl aldehydes and isooctenes obtained from propylene and 2-methylbutenes, the mixture of decyl aldehydes and isononenes obtained from secondary amylene and isobutylene, the mixture of undecyl aldehydes and isodecenes obtained from secondary amylene and a 2-methylbutene, and similar mixtures of aldehydes and olefins.

The copolymerization of olefin mixtures may be effected by various processes, most of which employ acidic catalysts, such as sulfuric acid, phosphoric acid, or hydrogen fluoride; or potentially acidic catalysts such as copper pyrophosphate or boron fluoride; or solid catalysts such

as silica-alumina or acid-treated bentonite. Hot sulfuric acid, for example, absorbs both secondary and tertiary olefins at temperatures around 140–194° F. and converts them into copolymers, comprising chiefly the various isomeric dimers. In a particularly successful copolymerization process, secondary butylenes and isobutylene are passed over a solid granular catalyst, comprising phosphoric acid adsorbed on clay or other inert material, at 350–500° F. and around 40 atmospheres. Under these conditions, when the charge stream contains 30% of secondary butylenes and 15% of isobutylene, approximately 67% of the olefins are converted into a product, of which 85% is dimer and 15% is trimer. Fractional distillation of the crude product yields a dimer fraction having properties and composition as in the following illustrative example:

Butylene-Isobutylene Codimer: Properties and Composition

Mean molecular weight.....	112.2.
Specific gravity, 60/60° F.....	0.735.
Refractive index, n_D^{20}	1.4200.
True boiling range, ° F.....	212–240.
ASTM distillation, ° F:	
Initial.....	210.
10%.....	216.
50%.....	230.
90%.....	231.
End.....	252.
Freezing point, ° F.....	Below –76.
Flash point (Tag), ° F.....	32.
Color (Saybolt).....	30.
Olefin content, percent.....	Over 99.
Total isooctene content, percent....	Over 98.
Distribution of isooctenes, percent by weight:	
2,2,3-trimethylpentenes.....	21.
2,2,4-trimethylpentenes.....	10.
2,3,3-trimethylpentenes.....	11.
2,3,4-trimethylpentenes.....	47.
Dimethylhexenes.....	10.

The resulting mixture may be subjected to carbonylation by contact with a mixture of hydrogen and carbon monoxide having a molar ratio between about 0.5:1 and 5:1 at a temperature between about 200 and 500° F., a pressure between about 50 and 300 atmospheres, and a liquid space velocity between about 0.05 and 10 per hour, in the presence of a catalyst comprising cobalt or iron, as disclosed in the copending joint application of Donald E. Burney and Bernard H. Shoemaker, Serial No. 788,845, filed November 29, 1947, now U. S. Patent No. 2,628,981. Under these conditions, between 20 and 60 percent of the n-butylene-isobutylene codimer is converted into nonyl aldehydes, plus a minor proportion of nonyl alcohols, in a reaction time between about 30 and 120 minutes.

We have now found that mixtures of aldehydes and olefins, such as those produced by the reaction of secondary olefin-tertiary olefin copolymers with carbon monoxide and hydrogen in the Oxo process, may be selectively hydrogenated over a cobalt catalyst at an elevated pressure, suitably above about 500 pounds per square inch and preferably below about 4000 pounds per square inch, a temperature between about 150 and 700° F., and a liquid space velocity between about 0.1 and 5.0 volumes of charging stock per volume of reaction zone per hour, the aldehydes being thereby converted into the corresponding alcohols, without the simultaneous saturation of any substantial proportion of the olefinic compounds in the charging stock. The hydrogenation

may be carried out in conventional batch-type autoclaves; or the liquid charging stock may be passed upward concurrently with hydrogen through a continuous reactor in contact with the catalyst, suitably at a temperature between about 350 and 600° F.; or the liquid charging stock may be passed as a continuous phase downward through a reactor countercurrent to the hydrogen. In the preferred form of our invention, the mixture of olefin and carbonyl compound is trickled downward over a granular or pelleted catalyst in a continuous atmosphere of hydrogen at a temperature between about 350 and 600° F., a pressure between about 500 and 1500 pounds per square inch, and a liquid space velocity between about 0.2 and 2.0 per hour.

Catalysts comprising cobalt as the active constituent are suitable for the selective hydrogenation reaction of our invention. Pure cobalt may be used as the catalyst in finely divided form, or in the form of granules, fragments, or shaped masses having finely divided surfaces; or the metal may be supported on powdered, pelleted, or granular inert carriers, such as silica, bonded silica (for example, "Filtros"), pumice, alumina, Carborundum, glass kieselguhr, and the like; and it may be combined with various promoters, such as thoria, magnesia, and the like. We prefer to use supported catalysts containing between about 5 and 15 per cent cobalt, but the proportion of cobalt is not a critical variable in our process.

Freshly prepared cobalt catalysts, when first used in our process, may sometimes exhibit a tendency to hydrogenate both the carbonyl groups and the olefinic double bonds of our charging stock. However, in such cases, we have found that the activity of the catalyst toward olefinic double bonds is lost very rapidly during exposure to the charging stock and operating conditions of our process.

Prior to the hydrogenation step, the liquid product from the carbonylation step of the Oxo process should preferably be treated to remove substantially all cobalt carbonyl and carbon monoxide therefrom, since it is known that carbon monoxide tends to retard the hydrogenation. The purification may be accomplished, for example, by purging the liquid with hydrogen or an inert gas, or by washing the liquid successively with an acid and with water.

For the same reason, the hydrogen that is supplied to the hydrogenation reactor should preferably contain less than about 2 percent of carbon monoxide, and should be substantially free from catalyst poisons such as hydrogen sulfide and the like.

After the selective hydrogenation has been completed, the reaction product contains alcohols, olefins, and a small proportion of saturated hydrocarbons. This mixture may be separated by techniques that are well known in the art. For example, the alcohols will ordinarily be substantially higher-boiling than the hydrocarbon constituents; the hydrocarbons may therefore be distilled out, and may be recycled to the carbonylation step in whole or in part, if desired; and the remaining alcohols may then be subjected to further purification by fractional distillation. Alternatively, the alcohols may be selectively extracted from the reaction product, suitably by use of an extractant medium comprising a glycol, a lower aliphatic alcohol, or a hydroxy ether. Or, the reaction product may be subjected to extractive distillation with a suitable solvent such as a member selected from the groups named

above, the hydrocarbon constituents being thereby removed as an overhead fraction. As a further alternative, the reaction mixtures may be subjected to an esterification procedure, suitably with boric acid, phthalic anhydride, or the like, in order to convert the alcohols therein to the corresponding esters, and the hydrocarbon constituents may then be conveniently distilled out. The esters may afterwards be separated and used as such, or may be hydrolyzed to regenerate the alcohols. These constitute particularly advantageously embodiments of our invention, since the selective-hydrogenation step permits the recycle of unreacted olefins to the carbonylation step, whereas in the usual hydrogenation procedure they would become saturated and unsuitable for recycling. As a still further alternative, the entire reaction product may be subjected to dehydration, suitably in the vapor phase at around 700–900° F. and one atmosphere over an alumina catalyst, in order to reconvert the alcohols therein to olefins having one more carbon atom than the olefins in the charging stock prior to the carbonylation reaction.

Prior to either the carbonylation step or the selective hydrogenation step, we may optionally add to the liquid charging stock an inert liquid as a diluent and as a mutual solvent for the reactants and reaction products. As illustrations of such liquids, the following may be cited: aliphatic, aromatic, and naphthenic hydrocarbons; ethers; and alcohols, in particular the lower aliphatic alcohols, benzyl alcohol, tetrahydrofurfuryl alcohol, and the like.

Figure 1 illustrates an embodiment of our invention employing batch-type equipment. An olefin copolymer charging stock is supplied through line 11 to mixing and metering tank 12 equipped with agitator 13, wherein a quantity of powdered catalyst, suitably 3 to 5% of cobalt on kieselguhr, is suspended in the liquid. The suspension is withdrawn through line 14 by pump 15 and delivered through heat exchanger 16 into reactor 17. A flow of gases is maintained through the reactor during the filling operation at a rate sufficient to maintain the solid catalyst in suspension, and the liquid charge may be recirculated from the bottom of reactor 17 through heat exchanger 16 by way of line 18, valve 19, and pump 15 in order to bring the charge up to reaction temperature, optimally around 350° F. When the desired liquid level is reached in the reactor, the vessel is closed and a mixture of carbon monoxide and hydrogen in approximately 1:1 molar ratio is introduced through line 20, compressor 21, and sparger lines 22 until the pressure reaches approximately 200 atmospheres. From the top of the reactor, gas emerges through cooler 23 and is expanded through valve 24 into separator 25, from which a portion is purged through valve 26 as required to prevent excessive build-up of non-reactive gases, and the remainder is recycled through valve 27 and compressor 21 to the reactor. The recycle and makeup gases ordinarily have a temperature below about 100° F., and are distributed to various points in the reactor, as indicated in the drawing, to maintain an approximately uniform temperature.

After the reactive components of the olefin copolymer have reacted to the desired extent with carbon monoxide and hydrogen, the supply of gas to compressor 21 is stopped, and the gas remaining in the system is released through purge valve 26. The reactor contents are adjusted to a temperature between about 375 and

425° F. by withdrawing a stream of the reaction mixture through cooler 28 and recycling it through valve 29, pump 15, and heat exchanger 16. Hydrogen, substantially free from carbon monoxide, is then introduced into the reactor through line 20 and compressor 21, and is purged through valve 26 until the system contains little or no carbon monoxide. The hydrogen pressure is then raised to between about 500 and 1500 pounds per square inch, and hydrogen is recycled through cooler 23, valve 24, separator 25, valve 27, compressor 21, and sparger lines 22 to the reactor to maintain the catalyst in suspension and to help in controlling the reaction temperature. Under the described conditions, the reduction of aldehydes to alcohols takes place readily, with little or no reduction of olefins that failed to react with carbon monoxide and hydrogen in the carbonylation step. When the hydrogenation has been completed, the supply of hydrogen is stopped, the pressure is released through valve 26 to approximately 5 or 10 atmospheres, and the reactor charge is forced by the residual pressure through cooler 28, valve 30, separator 25, valve 31, and filter 32, where the suspended catalyst is removed. The recovered catalyst may be washed from the filter through line 33, suitably with filtered product, and subsequently reused. The filtered product is withdrawn through line 34 and subjected to further process steps, such as fractional distillation (apparatus not illustrated) to separate the various components thereof.

Figure 2 illustrates a continuous process for carrying out our invention.

An olefin charging stock, supplied through line 111, is introduced by pump 112 through heat exchanger 113 into the top of carbonylation reactor 114, where it is contacted at a pressure between about 100 and 300 atmospheres, preferably about 200 atmospheres, and a temperature between about 200 and 500° F., preferably between about 325 and 375° F., with an equimolar mixture of carbon monoxide and hydrogen, introduced through line 115 and compressor 116. The rate of injection of copolymer is suitably between about 0.05 and 10 volumes per hour per unit volume of reaction zone, and preferably between about 0.5 and 2 per hour. The reactor is packed with a suitable carbonylation catalyst, such as metallic cobalt supported on an inert siliceous material, arranged in such manner that efficient contact is obtained between the liquid hydrocarbon and the reactant gases. Makeup catalyst, suitably metal carbonyls, such as cobalt or iron carbonyl, or oil-soluble organic-acid salts, such as iron or cobalt stearate or naphthenate, may be added through line 117 to the olefin stream in line 111, in order to compensate for any loss of catalyst from the reactor as dissolved carbonyl or entrained solids in the product stream. Alternatively, solid catalyst may be omitted from the reactor altogether, and the total catalyst requirements may be supplied with the charging stock in the form of metal carbonyls (suitably between about 0.1 and 2 percent by weight) or metal salts of organic acids (suitably between about 0.1 and 10 percent by weight). The processed liquid stream and the unreacted gases are withdrawn from the base of the reactor through line 118 to high-pressure separator 119.

The gas stream from separator 119 flows through valve 120 and cooler 121 into low-pressure separator 122, where condensed liquids are removed. The gas stream emerging from sep-

arator 122 through line 123 is divided, part of it flowing through valve 124 to compressor 116, from which it is recycled to reactor 114, and the remainder being purged through line 125, or sent to suitable gas reprocessing equipment.

The liquid stream from separator 119 flows into cooler 126, and is divided into two streams. One stream is recycled through valve 127, pump 128, line 129, and heat exchanger 113 to reactor 114, where it serves to regulate the temperature of the exothermic reaction between the olefin stream, hydrogen, and carbon monoxide. The rate of recycle may be adjusted to maintain the desired temperature, the cooling liquid being introduced at the top of the reactor or at such points within it as may be required to control localized heating. The remainder of the liquid stream from cooler 126 flows through valve 130 to low-pressure separator 131, where the liquid is freed of dissolved gases. The gases are combined in line 123 with the gases from separator 122.

The liquid streams from separators 122 and 131 are combined and transferred by pump 132 through line 133 and heat exchanger 134 into selective hydrogenation reactor 135. This liquid comprises a mixture of aldehydes and unreacted olefins, together with minor proportions of alcohols and saturated hydrocarbons, and it ordinarily contains minor proportions of the catalyst from the carbonylation reaction, in the form of the metal carbonyl, oil-soluble metal salts, or suspended solids. The catalyst may be removed, if desired, before the liquid is introduced into reactor 135. For example, the liquid stream may be treated with hydrogen or other inert gases at elevated temperatures, suitably above about 150° F., in order to destroy metal carbonyl and to strip out the liberated carbon monoxide, and the precipitated metal may then be removed by filtration or centrifugation; or the liquid stream may be scrubbed with a dilute acid, such as sulfuric acid, and then with water (apparatus not shown). The hydrogenation reactor 135 contains a selective hydrogenation catalyst comprising cobalt as the active component, preferably on an inert support, such as Filtros (a bonded silica), or pumice. Hydrogen, preferably containing not more than about 2 percent of carbon monoxide is supplied by compressor 136 through line 137 into the bottom of reactor 135. The hydrogen passes upward through the downward-flowing liquid stream, the pressure within the reactor being maintained around 800 pounds per square inch, and the temperature around 550° F. Under these conditions, the aldehydes are converted into alcohols, while the olefins are substantially unaffected. Excess hydrogen is withdrawn at the top of reactor 135 through valve 138 and cooler 139 into low-pressure separator 140, from which the gas phase is withdrawn and purged through line 141 to prevent the accumulation of inert constituents within the reactor; or the gas phase may be recycled wholly or in part to gas processing equipment, not shown.

From the bottom of reactor 135, the selectively hydrogenated liquid is withdrawn through cooler 142, and the stream is then divided, part of it being recycled through valve 143, pump 144, line 133, and heat exchanger 134 to reactor 135 for use in regulating the reaction temperature therein at the desired level, while the remainder of the liquid stream from cooler 142 is reduced in pressure to around one atmosphere through valve 145 and allowed to flow into low-pressure separator 146, from which the dissolved gases are removed and purged or recycled as desired.

rator 146, from which the dissolved gases are removed and purged or recycled as desired.

The liquid streams from separators 140 and 146 are combined and transferred to a fractionation system, where the hydrocarbons and alcohols may be segregated and purified. For this purpose, Figure 2 illustrates a two-stage fractionation method:

The liquid streams from separators 140 and 146 are transferred by pump 147 through heater 148 into fractionating column 149 at an intermediate point. The hydrocarbon constituents, being lower boiling than the alcohols, are fractionally distilled overhead through condenser 150 into separator 151, from which a portion is refluxed through valve 152 to the top of column 149, and the remainder is withdrawn through valve 153 to storage, or to further purification. The hydrocarbon stream, comprising mainly olefins, may be recycled to reactor 114, either with or without an intermediate purification stage. In the event that recycling is employed, a small proportion of the recycle stock is preferably withdrawn from the process in order to prevent the accumulation therein of saturated constituents and other constituents which will not undergo the carbonylation reaction.

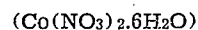
The bottoms stream from column 149 is transferred by pump 154 through heater 155 into fractionator column 156 at an intermediate point. The alcohols are fractionally distilled overhead through condenser 157 into separator 158, from which a portion is refluxed through valve 159 to the top of column 156, and the remainder is withdrawn through valve 160 to storage or further purification. A small quantity of higher-boiling material is withdrawn from the bottom of fractionator 156 through cooler 161.

It will be noted that reactor 114 is shown with liquid and gas flowing concurrently downward, whereas in reactor 135 the liquid stream flows downward countercurrent to the gas stream. It is intended that either of these flow systems may be used in either reactor. Moreover, a third modification, in which the liquid and gas flow upward in parallel, may also be used in either reactor.

The following specific examples will more fully illustrate our invention.

Example I

A solution of cobalt nitrate was prepared by mixing 120 grams of the hexahydrate



with 50 milliliters of water and heating nearly to boiling. To the hot solution were added 185 grams of 4-8 mesh "Filtros" (a bonded silica), and the mixture was stirred continuously and heated until substantially all of the water had evaporated. In this way, the cobalt nitrate was deposited uniformly on the Filtros. The heating was then continued, and the cobalt nitrate was decomposed into cobalt oxide, as evidenced by the evolution of red fumes of nitrogen peroxide. After the evolution of red fumes had ceased, the material was cooled and screened to remove the fines. The oxide was then reduced with hydrogen at atmospheric pressure and 700° F. for five hours. A yield of 192 grams of catalyst containing 5.4 percent cobalt was obtained. After reduction, the catalyst was handled under an inert atmosphere.

A charging stock was prepared by contacting a n-butylene-isobutylene codimer with carbon

monoxide and hydrogen according to the carbonylation step of the Oxo process. The resulting product, containing 34 percent by volume of nonyl aldehydes, 8 percent nonyl alcohols, 56 percent isooctenes, and 2 percent high-boiling materials, was trickled downward at the rate of 200 ml. per hour through a reactor having an inside diameter of 1.5 inches and a catalyst zone packed with cobalt catalyst, prepared as described above, to a depth of 2.5 feet. A temperature of 380–400° F. and a hydrogen pressure of 750–850 pounds per square inch were maintained in the reactor. After two passes over the catalyst (equivalent to a space velocity of 0.115/hr.), the product consisted of 35 percent by volume nonyl alcohols, 3.5 percent nonyl aldehydes, 50 percent hydrocarbons having a bromine number of 134, corresponding to an unsaturation of over 90 percent, and the remainder high-boiling materials.

Example II

A hydrogenation reactor having an inside diameter of 1.5 inches and a reaction zone 25 inches in length was charged with 645 milliliters of unreduced cobalt oxide catalyst, prepared as described in Example I, and the catalyst was reduced in place with hydrogen at around 800° F. for six hours.

A n-butylene-isobutylene codimer having a bromine number of 137 was subjected to carbonylation under Oxo process conditions, and a product was obtained consisting of 21 percent by volume of nonyl aldehydes, 7 percent nonyl alcohols, 65 percent isooctenes, and 7 percent high-boiling materials. The carbonylation product was fed into the top of the hydrogenation reactor at a rate of 198 milliliters per hour and contacted with hydrogen and cobalt catalyst at about 415° F. and 800 pounds per square inch. The reactor effluent was cooled, flashed to atmospheric pressure, and fractionally distilled under reduced pressure. The product consisted of 27 percent by volume of nonyl alcohols, 2 percent nonyl aldehydes, 63 percent hydrocarbons having a bromine number of 137, corresponding to 100 percent unsaturation, and 8 percent high-boiling materials. Thus, 90.5 percent of the aldehydes had been reduced to the

Example III

An Oxo-process carbonylation-step reaction product, prepared from a n-butylene-isobutylene codimer, and containing 24 percent by volume of nonyl aldehydes, 7 percent nonyl alcohols, 55 percent isooctenes, and 9 percent high boilers, was trickled downward over 645 milliliters of 4–8 mesh Filtros, impregnated with approximately 4.9 percent of reduced cobalt according to the general procedure outlined in Example I. The reaction conditions were as follows:

Temperature, catalyst mid-section_ 600° F.
Hydrogen pressure_____ 800 lb./in².
Feed rate_____ 492 ml./hr.
Space velocity, liquid_____ 0.8/hr.

On fractional distillation, the product was found to contain 34 percent nonyl alcohols, corresponding to 88 percent conversion of the aldehydes originally present, 3 percent nonyl aldehydes, 47 percent hydrocarbons having a bromine number of 132 corresponding to 96 percent unsaturation, and 6 percent high boilers.

Example IV

A series of selective hydrogenation experiments was carried out on a charging stock containing 21 percent by volume of nonyl aldehydes, 7 percent nonyl alcohols, 60 percent isooctenes, 7 percent high boilers, and 0.6 mg. soluble cobalt compounds per milliliter, that had been prepared by contacting a n-butylene-isobutylene codimer with carbon monoxide and hydrogen under Oxo-process carbonylation-step conditions. The carbonylation product was trickled downward over 645 milliliters of 4–8 mesh Filtros, impregnated with approximately 4.9 percent of reduced cobalt according to the general procedure outlined in Example I, and contained in a zone measuring 25 inches in length in a hydrogen-filled reactor having an inside diameter of 1.5 inches.

The experiments were continued for one hour at each set of reaction conditions before the product was collected for evaluation. Analysis of the liquid products was by fractional distillation. The reaction conditions and results were as follows:

Hydrogen pressure, lb./in. ²	Temp., ° F.	Feed rate, ml./hr.	Space velocity, liquid hr. ⁻¹	Product composition				Conversion, aldehydes to alcohols, percent
				Alcohols, vol. percent	Aldehydes, vol. percent	Hydrocarbons, vol. percent	High boilers, vol. percent	
800.....	415	198	0.3	27	2	58	8	91
800.....	405	363	0.6	27	5	60	5	76
800.....	402	540	0.8	19	11	63	4	48
800.....	505	510	0.8	30	2	60	2	91
800.....	557	500	0.8	29	2	60	5	91

corresponding alcohols, while the olefins were unchanged.

When a similar n-butylene-isobutylene codimer which had not been subjected to carbonylation was fed at a rate of 192 milliliters per hour into the same reactor, containing the same catalyst, and contacted with hydrogen at 800 pounds per square inch and an average temperature of 396° F., the product was 100 percent C₈ hydrocarbons having a bromine number of 5, which indicated that 96 percent of the olefins originally present in the codimer had been hydrogenated to the corresponding paraffins.

Bromine titration of the hydrocarbon fractions of the products indicated that all of them were between 96 and 100 percent olefinic.

Example V

An Oxo-process carbonylation-step reaction product, prepared from an n-butylene-isobutylene codimer, and containing 17 percent by volume of nonyl aldehydes, 7 percent nonyl alcohols, 71 percent isooctene, and 5 percent high boilers, was passed upward through 645 milliliters of 4–8 mesh Filtros, impregnated with 4.9 weight percent of reduced cobalt, in a reactor

having an inside diameter of 1.5 inches and a catalyst bed 25 inches in length. The reaction conditions were as follows:

Temperature, catalyst mid-section..	550° F.
Hydrogen pressure.....	800 lb./in ² .
Excess hydrogen rate.....	1.0 ft. ³ /hr.
Feed rate.....	323 ml./hr.
Space velocity, liquid.....	0.5/hr.

The resulting product contained 24 percent nonyl alcohols and 3 percent nonyl aldehydes, corresponding to an 82 percent conversion of the aldehydes originally present. The hydrocarbon fraction of the product had a bromine number of 137, corresponding to 100 percent unsaturation.

Example VI

A propylene-butylene copolymer was fractionally distilled, and from it was separated a C₇ fraction having a bromine number of 158. The C₇ fraction was mixed with 0.1 percent by weight of cobalt in the form of cobalt tallate, and the resulting solution was subjected to carbonylation by contact with a 1:1 mixture of carbon monoxide and hydrogen at 325 to 250° F., 3000 pounds per square inch, a liquid space velocity of 0.5/hour, and an excess gas rate of 200 percent of the theoretical quantity necessary for complete carbonylation. The conversion was 52 percent, molar basis, of the C₇ olefins, yielding a product having the following composition:

	Mole-percent
C ₇ hydrocarbons (Br No., 130.4)	48
C ₈ aldehydes	36
C ₈ alcohols	12
Bottoms	4

The total product liquid was washed at 30° F. with 25 percent by volume of aqueous 5% sulfuric acid, then twice with the same proportion of water. The washed product liquid was steam-distilled, and all of the organic materials except the bottoms were withdrawn overhead as a distillate fraction. The distillate fraction was passed downward over a reduced 12 percent cobalt-on-pumice catalyst at 375° F., 3000 pounds per square inch, and a liquid space velocity of 0.5/hour, in parallel flow with a stream of hydrogen in 1000 percent excess over the quantity theoretically required for complete hydrogenation of the aldehydes contained in the distillate fraction. Under these conditions, 98 percent of the aldehydes were converted into the corresponding alcohols. From the hydrogenation product was recovered a total hydrocarbon fraction having a bromine number of 126.5. Thus, only 3 percent of the noncarbonylated C₇ olefins contained in the distillate fraction were hydrogenated.

While the above examples illustrate preferred forms of our invention, it is to be distinctly understood that we do not wish to be limited to the specific charging stocks and operating conditions described therein, since our invention is broadly applicable, as defined elsewhere in the specification. In general, it may be said that any modifications or equivalents that would ordinarily occur to those skilled in the art are to be considered as lying within the scope of our invention.

The products of our invention are alcohols of a wide range of chemical and physical properties. They are useful as solvents and as ingredients of hydraulic fluids, and are capable of being converted into a wide variety of chemical de-

rivatives. For example, they may be oxidized to aldehydes and carboxylic acids; they may be reacted with ammonia to form amines, and with other amines to form secondary and tertiary mixed amines; they may be dehydrated to form olefins and ethers; they may be used to alkylate aromatics; and they may be converted by conventional methods into esters. Especially useful esters may be prepared from the mixed octyl alcohols obtainable from propylene-butylene copolymers and from the mixed nonyl alcohols obtainable from n-butylene-isobutylene codimer according to our invention. Among such esters may be cited the phthalates, phosphates, sebacates, adipates, stearates, citrates, and the like, which are useful as plasticizers for numerous plastics, elastomers, and resins, including vinyl polymers, butadiene-styrene rubbers, and cellulose plastics; the sulfates, which are useful as wetting agents; and the acrylates and methacrylates, which, after being polymerized, are excellent viscosity index improvers for lubricating oils.

This application is a continuation-in-part of our application Serial No. 788,847, filed November 29, 1947, now abandoned.

In accordance with the foregoing specification, we claim as our invention:

1. In a process for selectively hydrogenating aldehydes in a mixture containing aldehydes and olefins obtained by subjecting a secondary olefin-tertiary olefin copolymer to reaction with carbon monoxide and hydrogen, the step which comprises contacting said mixture with hydrogen at a temperature between about 150 and 700° F., an elevated pressure above about 500 pounds per square inch, and a liquid space velocity between about 0.1 and 5.0 volumes of charging stock per volume of reaction zone per hour in the presence of a cobalt catalyst.

2. The process of claim 1 wherein said catalyst consists essentially of metallic cobalt and an inert carrier.

3. The process of claim 1 wherein said copolymer is a copolymer of an olefin selected from the group consisting of propylene, 1-butene, 2-butene, and the secondary amylenes, and an olefin selected from the group consisting of isobutylene, 2-methyl-1-butene, and 2-methyl-2-butene.

4. In a process for selectively hydrogenating aldehydes in a mixture containing aldehydes and olefins obtained by subjecting a secondary olefin-tertiary olefin copolymer to reaction with carbon monoxide and hydrogen, the step which comprises contacting said mixture with hydrogen at a temperature between about 150 and 700° F., an elevated pressure between about 500 and 4000 pounds per square inch, and a liquid space velocity between about 0.1 and 5.0 volumes of charging stock per volume of reaction zone per hour in the presence of a cobalt catalyst.

5. The process of claim 4 wherein said copolymer is a propylene-butylene copolymer.

6. The process of claim 4 wherein said copolymer is a n-butylene-isobutylene codimer.

7. In a process for selectively hydrogenating aldehydes in a mixture containing aldehydes and olefins obtained by subjecting a secondary olefin-tertiary olefin copolymer to reaction with carbon monoxide and hydrogen, the step which comprises passing said mixture downward over a supported cobalt catalyst in an atmosphere of hydrogen at a temperature between about 350 and 600° F., a pressure between about 500 and 4000 pounds per square inch, and a liquid space velocity between about 0.2 and 2.0 volumes of

13

charging stock per volume of catalyst zone per hour.

8. In a process for the preparation of alcohols from a secondary olefin-tertiary olefin copolymer, the steps which comprise subjecting said copolymer to reaction with carbon monoxide and hydrogen in a carbonylation zone, contacting the resulting product with hydrogen at an elevated pressure between about 500 and 4000 pounds per square inch, at a temperature between about 150 and 700° F., and a liquid space velocity between about 0.1 and 5.0 volumes of charging stock per volume of reaction zone per hour in the presence of a cobalt catalyst, separating alcohols and unreacted olefins from the resulting product, and recycling part of said unreacted olefins to said carbonylation zone.

9. In a process for selectively hydrogenating aldehydes in a mixture containing nonyl aldehydes and isooctenes obtained by subjecting a n-butylene-isobutylene codimer to reaction with carbon monoxide and hydrogen, the step which comprises contacting said mixture with hydrogen at a pressure between about 500 and 4000 pounds per square inch, a temperature between about 350 and 600° F., and a space velocity between about

14

0.2 and 2.0 volumes of liquid per volume of reaction zone per hour in the presence of a cobalt catalyst.

10. In a process for selectively hydrogenating aldehydes in a mixture containing octyl aldehydes and isoheptenes obtained by subjecting a propylene-isobutylene copolymer to reaction with carbon monoxide and hydrogen, the step which comprises contacting said mixture with hydrogen at a pressure between about 500 and 4000 pounds per square inch, a temperature between about 350 and 600° F., and a space velocity between about 0.2 and 2.0 volumes of liquid per volume of reaction zone per hour in the presence of a cobalt catalyst.

DONALD E. BURNEY.
WILLIAM J. CERVENY.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,327,066	Roelen	Aug. 17, 1943
2,414,276	Sensel et al.	Jan. 14, 1947
2,437,000	Gresham et al.	Mar. 9, 1948
2,464,916	Adams et al.	Mar. 22, 1949