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**REMOVAL OF PHOSPHORUS-CONTAINING COMPOUNDS
FROM AN OLEFIN FEEDSTOCK**

Field of the Invention

The present invention pertains to a process of removing contaminants from olefin feedstocks using a sorbent comprising a metal. The contaminants removed preferably are phosphorus-containing compounds, most preferably organophosphines and/or organophosphine oxides. Preferred olefin feedstocks are made by oligomerizing ethylene to linear olefins having from 6 to 36 carbon atoms, preferably from 11 to 20 carbon atoms, and most preferably from 14 to 18 carbon atoms.

Background of the Invention

Depending upon the method of their production, olefin feedstocks may comprise a variety of impurities. Impurities found in olefins that are produced by oligomerization of ethylene units include phosphorus-containing impurities, including, but not necessarily limited to, organophosphines and organophosphine oxides. These phosphorus-containing compounds are largely removed from many olefin streams during the process of distillation to separate various "cuts" of olefins. Unfortunately, the organophosphines and organophosphine oxides found in C₁₄-C₁₈ streams tend to co-distill with the C₁₄-C₁₈ in the product, making it difficult, if not impossible, to remove these phosphine impurities by simple distillation.

C₆-C₃₆ olefins have utility in the fields of paper and pulp processing, drilling fluids, and machine or metal working oils. Alcohols of such olefins have commercial importance in a variety of applications, including detergents, soaps, surfactants, and freeze point depressants in lubricating oils. These alcohols are produced by a number of commercial processes, such as by oxo or hydroformylation of long chain olefins. In many of these applications, the olefin feedstocks are treated using acid catalysts.

Unfortunately, any phosphorus-containing compounds in these olefin feedstocks will negatively affect acid catalysts. The phosphorus-containing moieties are basic in nature and will neutralize the active acid sites of the catalyst, which lowers catalyst activity and performance. The organophosphine moieties may even cause the olefins to oligomerize into undesirable forms.

Methods are needed to reduce the phosphorus-content of olefin feedstocks.

Summary of the Invention

The present invention provides a process for purifying an olefin feed comprising a content of phosphorus-containing impurities, said process comprising contacting said olefin feed with a sorbent comprising a metal under conditions and for a time effective to reduce said content of phosphorus-containing impurities and to produce a purified olefin feed.

The present invention also provides a process of making a branched primary alcohol composition, comprising:

contacting an olefin feed comprising a content of phosphorus-containing impurities with a sorbent comprising a metal under conditions and for a time effective to permit said metal to reduce said content of phosphorus-containing impurities and to produce a purified olefin feed;

contacting said purified olefin feed with a skeletal isomerization catalyst under conditions effective to yield skeletally isomerized olefins; and

converting said skeletally isomerized olefins into said primary alcohol composition.

Said converting preferably comprises hydroformylating said skeletally isomerized olefins.

The present invention further provides a process for purifying an olefin feed comprising a content of phosphorus-containing compounds, said process comprising contacting said olefin feed with a sorbent comprising an effective amount of a metal selected from the group consisting of copper and silver under conditions and for a time effective to reduce said content of phosphorus-containing compounds and to produce a purified olefin feed, said olefin feed comprising primarily olefins having at least 6 carbon atoms.

Detailed Description of the Invention

The present invention provides a process and sorbents which efficiently and effectively reduce the content of phosphorus-containing compounds in olefin streams. In a preferred embodiment, the content is reduced to 1 ppm or less, preferably 0.5 ppm or less, most preferably to 0.1 ppm or less. Given sufficient run

time, the sorbents reduce the content of phosphorus-containing compounds in the olefin stream to parts per billion (ppb) levels.

5 The present invention may be used to treat substantially any olefin stream. Preferred olefin streams are linear olefin streams made by oligomerizing ethylene. Some of the known processes for oligomerizing ethylene use organophosphorus compounds that result in phosphorus as a contaminant in the resulting olefin
10 stream. A preferred commercially available olefin feed for the treatment of the present invention is the product marketed in the United States by Shell Chemical Company under the trademark NEODENE. In a preferred embodiment, the olefin feedstock is treated before exposure to an
15 acid catalyst, or before exposure to other conditions which would be adversely affected by the basic nature of phosphorus-containing contaminants.

In a most preferred embodiment, the olefin stream is the feedstock for the skeletal isomerization catalyst
20 used in the method described in US-A-5849960. The olefins used in the feed to this skeletal isomerization catalyst are mono-olefins having at least 6 carbon atoms, preferably having from 11 to 20 carbon atoms, and most preferably having from 14 to 18 carbon atoms.

25 In general, the olefins in the feed to the skeletal isomerization catalyst are predominately linear. While the olefin feed can contain some branched olefins, the olefin feed processed for skeletal isomerization preferably contains greater than 50 percent, more
30 preferably greater than 70 percent, and most preferably

greater than 80 mole percent of linear olefin molecules.

The olefin feed to the skeletal isomerization catalyst does not consist of 100% olefins, and usually contains a distribution of mono-olefins having different carbon lengths, with at least 50 wt. % of the olefins being within the stated carbon chain range or digit, however specified. Preferably, the olefin feed will contain greater than 70 wt. %, more preferably 80 wt. % or more of mono-olefins in a specified carbon number range, the remainder of the product being olefins of other carbon number or carbon structure, diolefins, paraffins, aromatics, and other impurities resulting from the synthesis process. The location of the double bond is not limited. The olefin feed composition may comprise alpha olefins, internal olefins, or a mixture thereof.

The sorbent of the present invention comprises a suitable metal, preferably comprising metal oxide, on a suitable support. Preferred metals are transition metals, including, but not necessarily limited to, those selected from Groups 3-12 of the Periodic Table of the Elements. When the Periodic Table of the Elements is referred to herein, the source of the Periodic Table is: F. Cotton et al. *Advanced Inorganic Chemistry* (5th Ed. 1988). Suitable metals include, but are not necessarily limited to, Sc, V, Cr, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mn, Ag and combinations thereof. Preferred metals are Fe, Co, Ni, Mn, Ag and Cu. In a preferred embodiment, the metal is silver or copper, preferably in the form of oxides. The sorbent suitably comprises from 0.1 wt. % to 50 wt. % of the metal oxide of the foregoing metals, preferably

copper. Preferably, the sorbent comprises from 1 wt. % to 20 wt. %, more preferably from 5 wt. % to 15 wt. %, and most preferably from 8 wt. % to 10 wt. % of the metal oxide.

5 The metal oxide resides on a suitable support material. Although the surface area of the support is not a critical feature, the surface area preferably is at least 10 m²/g in order to provide sufficient contact between the sorbent and the olefin stream. In a
10 preferred embodiment, the support has a surface area of from 100 m²/g to 900 m²/g. Acidic supports are more advantageous than basic supports. Suitable support materials are acidic or neutral, most preferably acidic. Suitable support materials include, but are not
15 necessarily limited to, alumina, silica, molecular sieves, such as zeolites, activated carbon, aluminosilicate clays and amorphous silicoaluminas. Where the support material surface is porous, the pores preferably are sufficiently large to permit entry of
20 bulky phosphorus-containing compounds in the feed. A most preferred support material for copper is an acidic or neutral alumina. A most preferred support material for silver is X-zeolite. A commercially available sorbent that is suitable for use in the present invention
25 is SELEXSORB AS (trade mark), which is commercially available from Alcoa Industrial Chemicals.

It is preferred for the particles of supported sorbent to be as small as possible; however, if the size of the particles is too small, the pressure drop through
30 the bed becomes too large. Very small particles also are

difficult to retain in the sorbent bed. SELEXSORB AS is purchased in the form of 3.2 mm (1/8 inch) spheres, and may be used in the process as purchased. However, spheres are not the most efficient particle shape for purposes of maximizing particle surface to volume ratio. Because of this, if SELEXSORB AS is used as the sorbent, it is preferred to grind or otherwise reduce the 3.2 mm (1/8 inch) spheres into the smallest particles possible without inducing an undue pressure drop or loss of sorbent from the sorbent bed. The particles may have substantially any form, including, but not necessarily limited to, spherical form, tablet form, cylindrical form, multi-lobed cylindrical forms, and their corresponding hollow counterparts. In a preferred embodiment, the particles have a diameter of from 50 mesh to 6 mm, preferably 0.8 mm (1/32 inch) to 1.6 mm (1/16 inch), most preferably 0.8 mm. The length of the particles is not critical, with suitable lengths including, but not necessarily limited to, less than 10 mm, preferably from 3 mm to 5 mm.

In a preferred embodiment, the support material is an alumina extrudate which is extruded as a paste using an acidic or neutral alumina powder. The "paste" is extruded or otherwise moulded into a multilobed cylindrical form. The resulting material preferably is dried at temperatures of at least 100 °C and calcined at 500 °C or more in the presence of flowing air in a muffle furnace or purged high temperature air drier or rotary calciner. The copper oxide may be deposited on to the support using any suitable technique, including, but not

necessarily limited to, ion exchange, co-mulling, or impregnation. A preferred technique is pore volume impregnation using a solution of a copper salt, such as copper nitrate, copper carbonate, or other suitable salts. Although the following illustration uses a copper nitrate solution, the use of other Cu salt solutions may produce a more uniform Cu loading. Copper nitrate is very soluble in water, and tends to wick out of the pores during drying. The result may be more CuO on the outside of the pellets, although smaller pellets are less prone to this effect.

Persons of ordinary skill in the art have the knowledge required to calculate how to incorporate a given wt% of CuO or other material on to a sorbent using the foregoing techniques. For example, where 100g of an alumina has a water pore volume of 83 mL, the following is a formula by which a sorbent containing 9 wt. % CuO is formed:

$$\begin{aligned} & \left[(9 \text{ g. CuO}/100 \text{ g. final sorbent}) \times (1 \text{ mole CuO}/79.54 \text{ g.}) \right. \\ & \times [1 \text{ mole Cu(NO}_3)_2 \cdot 2.5 \text{ H}_2\text{O}/\text{mole CuO}] \times (232.59 \text{ g.} \\ & \left. \text{Cu(NO}_3)_2 \cdot 2.5 \text{ H}_2\text{O}/\text{mole Cu(NO}_3)_2 \cdot 2.5 \text{ H}_2\text{O}) \right] \end{aligned}$$

In other words, it requires 0.26 g. $\text{Cu(NO}_3)_2 \cdot 2.5 \text{ H}_2\text{O}$ per g., of final sorbent to form a 9 wt. % CuO on alumina sorbent where the water pore volume is 83 mL of water per 100 g. of copper oxide on alumina.

In order to prepare the 9 wt. % CuO on alumina, the pores of 91 g. of the alumina are filled with a solution containing 26 g. (0.26 g. of $\text{Cu(NO}_3)_2 \cdot 2.5 \text{ H}_2\text{O}$ /g. sorbent x 100 g.) copper nitrate salt dissolved in 75.5 mL. of

water to incipient wetness. Slightly more or less liquid solution may be added until the catalyst is uniformly filled with solution. In the case of Cu salts, the colour of the filled pellets is light blue and the unfilled pellets remain white. The sorbent is dried in an oven at a temperature sufficient to boil water from the pores without fracturing the sorbent-about 121 °C (250 °F)-for from 4 to 8 hours. Then, the temperature is ramped to about 482 °C (900 °F) to decompose the nitrate salt to CuO on the support. Prior to use, the sorbent is stripped with nitrogen in order to avoid contaminating the olefin feed with oxygen.

Preferably, the olefin feedstock is contacted in the liquid phase in a reaction zone with the sorbent of the present invention at effective process conditions to reduce the content of phosphorus-containing compounds in the feedstock, i.e. an effective temperature, pressure, and LHSV (Liquid Hourly Space Velocity). A preferred embodiment of a reactor system for the process is an upflow or downflow fixed bed reactor. An upflow reactor is preferred for better wetting of the sorbent bed. The temperature employed may vary. Although not limited to a particular temperature, best results will be obtained if the process is conducted at temperatures of from 0 °C to 100 °C, preferably from 10 °C to 50 °C. The pressures may vary over a range including, but not limited to, autogeneous pressures and pressures in the range of from 0.01 MPa to 50 MPa. A preferred pressure is in the range of from 0.1 MPa to 10 MPa. Pressures outside the stated ranges may be used and are not excluded from the scope of

the present invention.

The feedstock may flow at a wide range of liquid hourly space velocities (LHSV), defined as liquid feed per hour per volume of sorbent. The LHSV is calculated as follows:

$$\frac{\text{Volume of olefin containing feed}}{\text{Volume of sorbent}} \times \frac{1}{\text{hr}}$$

The lower the LHSV, the greater will be the reduction in content of phosphorus-containing compounds in the feedstock. The LHSV generally is from 0.01 hr⁻¹ to 10 hr⁻¹, preferably from 0.1 hr⁻¹ to 1 hr⁻¹.

The process is continued for a period of time sufficient to achieve a desired reduction in the content of phosphorus-containing compounds in the olefin stream. The content of phosphorus-containing compounds preferably is reduced to 1 ppm or less, most preferably to 0.1 ppm or less. The reaction cycle time may vary from tenths of seconds to a number of hours. The reaction cycle time is largely determined by the reaction temperature, the pressure, the sorbent selected, the liquid hourly space velocity, and the desired reduction in content of phosphorus-containing compounds.

At some point, the sorbent becomes saturated, and must be regenerated. SELEXSORB AS has an absorptive capacity of about 0.6 grams of phosphorus per gram of sorbent. The sorbent may be regenerated by exposing the sorbent to regeneration conditions comprising an oxygen-containing atmosphere at an effective temperature, preferably from 200 °C to 550 °C, more preferably from

450 °C to 600 °C. Suitable oxygen containing atmospheres include, but are not necessarily limited to, air, oxygen gas, and a combination of oxygen gas with nitrogen gas. A preferred gas is a commercially available combination comprising about 1% oxygen, with the remainder being nitrogen. After exposure to these increased temperatures for a period of time of from 0.5 hour to 100 hours, the bed is cooled to at least 100 °C, and preferably to 25 °C, or ambient temperature, in order to avoid overheating upon reuse. The cooled bed is purged with nitrogen or air before reuse in the process. Ten regeneration cycles under these conditions have been shown to produce no loss in sorbent capacity. Some slight loss in sorbent capacity was seen beginning after about 10 regeneration cycles.

Typical olefin feedstocks comprise from 100 ppm to 2000 ppm dienes that tend to lower the efficiency of skeletal isomerization catalysts. In a preferred embodiment, the support of the present invention preferably is a sorbent which sorbs dienes present in initial olefin streams. In a preferred embodiment, the alumina support for copper oxide performs this function. The dienes are sorbed on to the alumina prior to skeletal isomerization. The dienes also may be removed by sorption from the skeletally isomerized product.

C₆ to C₃₃ olefins have a variety of uses, including, but not necessarily limited to, uses in paper processing, drilling fluids, and machine or metal working. In a preferred embodiment, the olefin feedstock is converted to branched primary alcohols in the process described in

US-A-5849960. Most preferably, the olefin feedstock is treated before the olefins are fed to a skeletal isomerization catalyst, as described in US-A-5849960. A preferred skeletal isomerization catalyst for use in conjunction with the present invention is a hydrogen ferrierite catalyst, as described in US-A-5510306.

In a preferred embodiment, the skeletally isomerized olefins are converted to any of a broad range of surfactants, including nonionic, anionic, cationic, and amphoteric surfactants, with a degree of branching of at least 1.0. The skeletally isomerized olefins serve as a surfactant intermediate. Specifically, the skeletally isomerized olefins serve as the hydrophobic moiety of the surfactant molecule, while the moiety added to the olefin during the conversion process serves as the hydrophile.

The present invention will be better understood with reference to the following examples, which are illustrative only and not intended to limit the present invention to any particular embodiment.

EXAMPLE I

NEODENE 16 containing 20 ppm phosphorus was placed in a jar with SELEXSORB AS sorbent crushed to 20 x 40 mesh and shaken intermittently by a flat bed shaker over a period of 15 hours at 23 °C to achieve equilibration. The NEODENE to SELEXSORB AS weight ratios used ranged from 100 to 1000. After equilibration, the NEODENE was separated from the sorbent and analyzed for phosphorus using inductively coupled plasma (ICPO). The results are given in the following Table:

NEODENE to Sorbent weight ratio	Equilibrium P (ppm)	P loading (g/100 g)
100	0.5	0.16
200	2.2	0.36
150	2.5	0.26
250	2.6	0.43
350	4.9	0.52
450	7.8	0.54
550	9.7	0.56
1000	13.1	0.67

With an excess of sorbent, phosphorus was reduced to very low levels in the olefin. The capacity of the sorbent also was determined to be about 0.6 grams of phosphorus/100 grams of sorbent.

EXAMPLE II

Phosphorus uptake from NEODENE 16 containing about 20 ppm phosphorus (for 20x40 mesh particles) and 23 ppm phosphorus (for 3.2 mm (1/8 inch) spheres) was compared using SELEXSORB AS particles having different sizes. The olefin to sorbent weight ratio was 200. The olefin was contacted with the sorbent under the conditions given in Example I for the specified period of time, and then the olefin was separated and analyzed for phosphorus. The results, which are given in the following Table, clearly show that the smaller particles removed phosphorus much more quickly than the larger spheres.

Contact time (hr)	P in hydrocarbon (ppm) 20x40 mesh particles	P in hydrocarbon (ppm) 1/8" spheres
0	20	23
0.17	14.4	23

0.5	10.1	23
1	7.5	
2	4.3	
3	3.2	22
5	2.4	
7	2.2	21
112		10.3

EXAMPLE III

One gram of SELEXSORB AS (crushed to 20 x 40 mesh) was equilibrated with 550 grams of NEODENE containing about 20 ppm phosphorus as described in Example I. The sorbent and the olefin were then separated and the olefin was analyzed to determine the uptake of phosphorus by the sorbent. Following this, the sorbent was regenerated by the following procedure:

- a. The sorbent was rinsed with from about 75 to about 100 mL cyclohexane per gram of sorbent to displace the olefin;
- b. The rinsed sorbent was heated under air flow at 125 °C for 6 minutes;
- c. The temperature was increased at 3 °C/min to 200 °C and held for 2 hours
- d. The temperature was increased at 2 °C/min to 500 °C and held for 2 hours; and
- e. The regenerated sorbent was cooled in air to ambient temperature.

The regenerated sorbent was contacted with a fresh batch of NEODENE at the same weight ratio of 550 gm NEODENE to 1 gm sorbent. This procedure was repeated for a total of 14 sorption cycles and 13 regeneration cycles.

The capacity of the sorbent for phosphorus after each cycle was calculated and compared to the capacity data for the virgin sorbent. The results are given in the following Table:

Equilibrium P (ppm)	Virgin Sorbent	Regen 1X	Regen 2X	Regen 3X	Regen 6X	Regen 9X	Regen 12X	Regen 13X
0	0							
0.5	0.16							
2.2	0.36							
2.5	0.26							
2.6	0.43							
4.9	0.52							
7.5		0.55						
7.7				0.51				
7.8	0.54							
8.4	0.47							
8.5			0.46					
9.7	0.56							
10.4					0.51			
12.6								0.36
13.6						0.6		
14.2							0.3	

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After 9 regenerations (10 sorption cycles) the capacity of the sorbent was still comparable to that of the virgin material. However, a decline in capacity was observed after the tenth regeneration.

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EXAMPLE IV

A variety of materials were studied as sorbent beds for removing phosphorus impurities. A C16 olefin feed

having a density of 0.78 g/cc. and comprising 20.2 ppm phosphorus was fed to a reactor tube having a diameter of 1.73 cm at a target flow rate of 54 g/hr. The reactor tube was partially filled, to about 50 cm³, with the test sorbent. In this experiment, the test sorbent was SELEXSORB AS (3.2 mm (1/8 inch) spheres). Samples were taken at various times and the parameters given in the following Table were recorded:

Elapsed time (hr.)	Product Collected (g.)	Fluid flow (g./hr.)	ppm P in fluid coming out of bed
0	0		1.6
2	136.4	68.20	1.8
18.5	812.5	40.98	3.4
25.5	1184.7	53.17	3.9
42.5	2204.5	59.99	7.3
49.5	2602.7	56.89	11.1
66.5	3397.1	46.73	11.6
73.5	3718.4	45.90	12.1
90.5	3831.8	6.67	12.5
96.5	4109.8	46.33	16.1
116	5194.8	55.64	17.1
125	5534.8	37.78	17

The sorbent removed 50% of the phosphorus from the feedstock for about 60 bed volumes. At the flow conditions of the test, the relatively large spheres of sorbent were not able to lower phosphorus to <0.5 ppm.

EXAMPLE V

5 A C16 olefin feed having a density of 0.78 g/cc and comprising 20.2 ppm of phosphorus was fed to a reactor tube having a diameter of 1.73 cm at a target flow rate of 54 g/hr. The reactor tube was partially filled with the test sorbent. In this experiment, the test sorbent was "AX-200," a trilobe alumina having a particle size of about 0.8 mm (1/32 inch). Samples were taken at various times and the following results recorded:

Elapsed time (hr)	gm Product Collected	Fluid Flow (gm/hr)	ppm P in fluid coming out of bed
0	0		0.1
2	117.2	58.6	0.5
18.5	1089.6	58.93	1.7
25.5	1506.2	59.51	7.8
42.5	2482.	57.42	17.6
49.5	2833.4	50.16	22.2
66.5	3730.6	52.78	29.5
73.5	4018.9	41.19	28.8
90.5	4115.3	5.67	23.8
96.5	4421.3	51.00	23.4
116	5675.3	64.31	21.9
125	6115.3	48.89	20.6

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The small, multilobed particles of sorbent successfully removed substantially all of the phosphorus from the feedstock for about 3 bed volumes, and removed 50% of the phosphorus in the feed for about 40 bed volumes.

EXAMPLE VI

5 A C16 olefin feed having a density of 0.78 g/cc and comprising 22.6 ppm phosphorus was fed to a reactor tube having a diameter of 1.73 cm at a target flow rate of 30 g/hr. The reactor tube was partially filled, to about 50 cm³, with the test sorbent. The test sorbent was crushed and sieved SELEXSORB AS having a particle size of about 14-24 mesh. Samples were taken at various times and the following results recorded:

Elapsed time (hr.)	Product Collected (g.)	Fluid Flow (g./hr.)	ppm P in fluid coming out of bed
0			
17.25	719.7	41.72	0.1
65.25	2098.7	28.73	<0.1
137.75	3967.7	25.78	<0.1
185.75	5069.7	22.96	1.3
210.25	5639.7	23.27	3.3
234.25	6189.7	22.92	6.6
267	7003.7	24.85	10.6
305.25	7993.7	25.88	11.9
330.25	8630.7	25.48	14.6

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The small particles of sorbent successfully removed substantially all of the phosphorus from the feedstock for about 125 bed volumes.

EXAMPLE VII

15 Example VI was repeated using 9% CuO/AX-300 (1.3 mm (1/20 inch) trilobe extrudate). Samples were taken at various times and the following results were recorded:

Elapsed time (hr)	gm Product Collected	Fluid Flow (gm/hr)	ppm P in fluid coming out of bed
0			
17.25	625.3	36.25	0.1
65.25	2064.3	29.98	0.
137.75	3752.3	23.28	0.4
185.75	4810.3	22.04	<0.1
210.25	5375.3	23.06	3.2
234.25	5951.3	24.00	6.8
267	6839.3	27.11	11.6
305.25	7915.3	28.13	16.9
330.25	8581.3	26.64	18.9

The intermediate sized, multilobed particles of sorbent successfully removed substantially all of the phosphorus from the feedstock for about 130 bed volumes.

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EXAMPLE VIII

Example VII was repeated using 18% CuO/AX-300 (1.3 mm (1/20 inch) trilobe extrudate). Samples were taken at various times and the following results were recorded:

Elapsed time (hr.)	Product Collected (g.)	Fluid Flow (g./hr)	ppm P in fluid coming out of bed
0			
17.25	798.7	46.30	0.1
65.25	2540.7	36.29	0.1
137.75	4275.7	23.93	0.4
185.75	5500.7	25.52	3.1
210.25	6100.7	24.49	5.5

234.25	6682.7	24.25	8.3
267	7600.7	28.03	13.1
305.25	8680.7	28.24	17.7
330.25	9410.7	29.20	19.9

The sorbent, which had a size and shape similar to that in Example VII, successfully removed substantially all of the phosphorus from the feedstock for about 130 bed
 5 volumes. No additional capacity was observed with the higher metal loading (9 wt. % in Example VII vs. 18 wt. % in Example VIII).

EXAMPLE IX

A C16 olefin feed having a density of 0.78 gm/cc and
 10 comprising 10.5 ppm phosphorus was fed to a reactor tube having a diameter of 1.73 cm at a target flow rate of 30 gm/hr. The reactor tube was partially filled with the test sorbent. The test sorbent was 9% CuO/AX200, which has a particle size of about 0.8 mm (1/32 inch) trilobe
 15 extrudate. Samples were taken at various times and the following results were recorded:

Elapsed time (hr)	gm Product Collected	Fluid Flow (gm/hr)	ppm P in fluid coming out of bed
0			
18.5	558.8	30.21	1
43	1163.8	24.69	<0.1
139.5	2960.8	18.62	0.1
163	3706.8	31.74	<0.1
186.75	4435.8	30.69	0.1
210.75	5119.8	28.50	<0.1
241.25	5953.8	27.34	0.1
307.5	7747.8	27.08	<0.1

331	8469.8	30.72	<0.1
379.5	9924.6	30.00	0.1
427	11073.6	24.19	0.3
474.75	12184.6	23.27	0.6
523.2	13440.6	25.90	1.3

The small, multilobed sorbent successfully removed substantially all of the phosphorus from the feedstock for about 275 bed volumes.

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EXAMPLE X

The procedures of Example IX were repeated using 9% CuO on AX-300 (1/20"). The results are given in the following Table:

Elapsed time (hr)	gm Product Collected	Fluid Flow (gm/hr)	ppm P in fluid coming out of bed
0			0.1
18.5	545.3	29.48	0
43	1220.3	27.55	0
139.5	2415.3	12.38	0.1
163	3036.3	26.43	0
186.75	3676.3	26.95	0.1
210.75	4340.3	27.67	0.1
241.25	5185.3	27.70	0.2
307.5	6989.3	27.23	1
331	7743.3	32.09	1.1
379.5	9127.6	28.54	1.8
427	10400.6	26.80	2.6
474.75	11660.6	26.39	2.8
523.25	12947.6	26.54	

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The intermediate sized, multilobed particles of sorbent

successfully removed substantially all of the phosphorus from the feedstock for about 170 bed volumes. The larger size particles produced a lower capacity at the same target flow rate as Example IX using the same phosphorus containing feedstock.

EXAMPLE XI

A series of experiments was performed to demonstrate higher temperature performance (80 °C and 120 °C) using 0.8 mm (1/32 inch) trilobe sorbent particles. A C16 olefin feed having a density of 0.78 gm/cc and comprising 20 ppm phosphorus was fed to a reactor tube having a diameter of 1.73 cm² at a target flow rate of 23 gm/hr. The reactor tube was partially filled with the test sorbent. The test sorbent was 9% CuO/AX300, which has a particle diameter of about 0.8 mm (1/32 inch) as a trilobe extrudate. The temperature in the reactor tube was maintained at 80 °C. Samples were taken at various times and the following results were recorded:

Elapsed time (hr)	gm Product Collected	Fluid Flow (gm/hr)	ppm P in fluid coming out of bed
0			
3.25	76.2	23.45	0.2
5.75	119.6	17.36	0.2
22.5	438.3	19.03	0
29.5	552.1	16.26	0.1
45.5	665.5	7.09	-
53.5	869.5	25.50	0.1
71.5	1393.8	29.13	0.1
80.25	1638.3	27.94	0

95.75	1747.7	7.06	-
103.75	1954.3	25.83	0
119.75	2555.8	37.59	0
141.75	3322.7	34.86	0.1
149.75	3565.7	30.37	0
165.75	4064.2	31.16	0
174.5	4302.9	27.28	0
189.75	4747.7	29.17	0
197.75	4969.4	27.71	0.1
213.75	5432.6	28.95	0.2
237.75	6126.3	28.90	0.7
244.75	6322.5	28.03	1.2
264.25	6887.7	28.98	3
271.5	7031.1	19.78	
288.5	7032.1	0.06	10.8
295.5	7342.8	44.39	5.2
309.75	7837.5	34.72	7.3
316.5	8059.4	32.87	10.2
334	8667.1	34.73	
341	8908.2	34.44	

Even at the higher temperature, the sorbent successfully removed substantially all of the phosphorus from the feedstock for about 150 bed volumes.

5

EXAMPLE XII

The procedures of Example XI were repeated at a temperature of 120 °C. The results appear in the following Table:

Elapsed time (hr)	gm Product Collected	Fluid Flow (gm/hr)	ppm P in fluid coming out of bed
0			
3.25	103.2	0.00	0.1
5.75	160	22.72	0.1
22.5	566.7	24.28	0.1
29.5	686.5	17.11	0.1
45.5	788.6	6.38	-
53.5	827.1	4.81	0.1
71.5	1364.7	29.87	0.4
80.25	1614.7	28.57	0.4
95.75	1986.5	23.99	0.3
103.75	2178.4	23.99	0.3
119.75	2570.1	24.48	0.3
141.75	3107.9	24.45	0.3
149.75	3298.4	23.81	0.2
165.75	3689.4	24.44	0.3
174.5	3892.1	23.17	0.2
189.75	4270.7	24.83	0.3
197.75	4459.8	23.64	0.2
213.75	4854.5	24.67	0.3
237.75	5443.7	24.55	0.6
244.75	5611.2	23.93	0.9
264.25	6091.1	24.61	3.8
271.5	6260	23.30	
288.5	6683.8	24.93	10.8
295.5	6848.6	23.54	13.1

309.75	7193	24.17	7.3
316.5	7348.4	23.02	22.2
334	7772.8	24.25	
341	7941.6	24.11	

Again, the higher temperature did not interfere with successful removal of substantially all of the phosphorus from the feedstock for about 140 bed volumes.

5 **EXAMPLE XIII**

The procedures of Example I were repeated using different sorbents using a feed containing 18 ppm P and a NEODENE 16 to solvent weight ratio of 100 with the following results:

Sorbent	Equilibrium P (ppm)	P loading (g/100 g sorbent)
BARNABEY SE carbon	7	0.11
BARNABEY CE carbon	3	0.15

10

EXAMPLE XIV

The following examples illustrate the nature of the present invention and its impact on skeletal isomerization of detergent range olefins.

15 A glass column with an inner diameter of 50mm was packed with 3.2mm Selexsorb AS spheres obtained from Alcoa Company of America to produce a bed 400 mm in length. 20 litres of NEODENE 16 olefin, a C₁₆ linear, alpha olefin commercially available from Shell Chemical
20 Company, was passed through the packed bed of Selexsorb AS spheres at a weight hourly space velocity of 0.01 per hour and the liquid effluent was collected in a container

purged with nitrogen. The phosphorus content of the NEODENE 16 olefin was reduced from 20 ppm to 0.2 ppm in the process.

EXAMPLE XV

5 A catalyst was prepared in accordance with Example C of US-A-5510306, which is reproduced in part herein for convenience. An ammonium-ferrierite having a molar silica to alumina ratio of 62:1, a surface area of 369 square metres per gram ($P/P_o = 0.03$), a soda content of 480 ppm
10 and n-hexane sorption capacity of 7.3 g per 100 g of zeolite was used as the starting zeolite. The catalyst components were milled using a Lancaster mix miller. The milled catalyst material was extruded using a 5.7 cm (2.25 inch) Bonnot pin barrel extruder.

15 The catalyst was prepared using 1 weight percent acetic acid and 1 weight percent citric acid. The Lancaster mix miller was loaded with 645 grams of ammonium-ferrierite (5.4% LOI) and 91 grams of CATAPAL D alumina (LOI of 25.7%). The alumina was blended with the
20 ferrierite for 5 minutes during which time 152 millilitres of de-ionized water was added. A mixture of 6.8 grams glacial acetic acid, 7.0 grams of citric acid and 152 millilitres of de-ionized water was added slowly to the miller in order to peptize the alumina. The
25 mixture was milled for 10 minutes. 0.20 grams of tetraammine palladium nitrate in 153 grams of de-ionized water were then added slowly as the mixture was milled for a period of 5 additional minutes. Ten grams of
30 METHOCEL F4M[®] hydroxypropyl methylcellulose was added and the zeolite/alumina mixture was milled for 15

additional minutes. The extrusion mix had an LOI of 43.5%. The 90:10 zeolite/alumina mixture was transferred to the 5.7 cm (2.25 inch) Bonnot extruder and extruded using a die plate with 1.6 mm (1/16 inch) holes.

5 The moist extrudates were tray dried in an oven heated to 150°C for 2 hours, and then increased to 175°C for 4 hours. After drying, the extrudates were broken manually. The extrudates were calcined in flowing air at 500°C for two hours.

10 EXAMPLE XVI

Skeletal isomerization of the NEODENE 16 olefin was conducted using an olefin isomerization reactor. A stainless steel tube, 25.4 mm OD, 15 mm ID and 685 mm long was used to contain the catalyst. One end of the tube was screwed into a stainless steel head equipped with a thermowell which extended up the centre of the tube. The tube was loaded with a small plug of glass wool, then filled to a depth of 150 mm with 20 mesh silicon carbide, and then a small plug of glass wool was added above the SiC. 6.00 grams of the catalyst described in Example XV was admixed with 45 grams of 60-80 mesh SiC and added in three parts to distribute it evenly inside the reactor tube. Another piece of glass wool was added and the remaining volume of the reactor tube was filled with 20 mesh SiC topped by a final piece of glass wool. The tube was screwed into another stainless steel head and a multipoint thermocouple was inserted into the thermowell to allow the temperature above, below and inside the catalyst bed to be monitored. The reactor tube was then installed inside an electric

furnace. Connections were made at the top of the reactor to allow nitrogen and the olefin to be passed through the reactor. The bottom of the reactor was connected to a condenser and a product collection system.

5 Nitrogen at a rate of 6 litres per hour was passed through the reactor while the catalyst bed was heated to 290 °C over a period of 2 hours. NEODENE 16 olefin prepared by the method of example Example A (with phosphorus content of 0.2 ppm) was pumped to the reactor at a rate of 60.0 grams per hour, allowed to mix with the incoming nitrogen and then passed through the catalyst bed. During the testing the inlet pressure was held at 11.0 kPa g (1.6 psig) while the outlet pressure of the reactor was maintained at 6.9 kPa g (1.0 psig). The liquid product was collected in a 19L (5 gallon) vessel while the uncondensed gas was passed through a gas meter. Sampling ports incorporated in the reactor allowed the liquid and gas products to be analyzed regularly. The products were analyzed by gas chromatography. The results of the testing are presented in the following Table.

TABLE The Effect of the Phosphorus Content in NEODENE 16 linear alpha olefin on the Degree of Branching During Skeletal Olefin Isomerization

Olefin Used	Treated NEODENE 16	Untreated NEODENE 16
Phosphorus Content	0.2 ppm	20 ppm
Time On Stream, Hr	% Branching In Liquid Product	
13.5	97	81
24.5	97	68

37.8	97	56
64.0	97	33
110	97	20
230	96	Stopped Test after 110 hours

In the presence of 20 ppm of phosphorus in the untreated NEODENE 16, the degree of branching declined rapidly with time on stream. In the case of the treated stream, where the phosphorus was reduced to 0.2 ppm, the degree of branching stayed much higher for a much longer time on stream.

EXAMPLE XVII

The procedures of Example I were repeated using a feed containing 20 ppm P, a NEODENE 16 to sorbent weight ratio of 100, and the following sorbents in place of the SELEXSORB AS. The results are shown in the following Table:

Sorbent	Equilibrium P (ppm)	P loading (g/100g sorbent)
Ag mordenite (15-20% Ag)	16	0.04
Ag X-zeolite (35% Ag)	<2	>0.18

The procedures of Example I were repeated except the feed contained 16 ppm P. The results are shown in the following Table:

Sorbent	NEODENE to sorbent weight ratio	Equilibrium P (ppm)	P loading (g/100g sorbent)
Ag mordenite (15-20% Ag)	100	11.2	0.05
Ag X-zeolite (35% Ag)	400	6.3	0.39

In the above Tables, the X-zeolite, which contains larger pores than the mordenite, allows for uptake of a greater amount of the bulky phosphorus-containing compounds. Also, the load of Ag on the zeolite was
5 higher, which increased the phosphorus uptake.

C L A I M S

1. A process for purifying an olefin feed comprising a content of phosphorus-containing impurities, said process comprising contacting said olefin feed with a sorbent comprising a metal under conditions and for a time
5 effective to reduce said content of phosphorus-containing impurities and to produce a purified olefin feed.
2. A process of making a branched primary alcohol composition, comprising:
 - 10 contacting an olefin feed comprising a content of phosphorus-containing impurities with a sorbent comprising a metal under conditions and for a time effective to permit said metal to reduce said content of phosphorus-containing impurities and to produce a purified olefin feed;
 - 15 contacting said purified olefin feed with a skeletal isomerization catalyst under conditions effective to yield skeletally isomerized olefins; and
 - 20 converting said skeletally isomerized olefins into said primary alcohol composition.
3. The process of claim 1 or 2 wherein said metal is selected from the group consisting of Groups 3-12 of the Periodic Table of the Elements.

4. The process of claim 1, 2 or 3 wherein said sorbent further comprises a support, and said support is selected from the group consisting of an acidic alumina and a neutral alumina.
5. A process for purifying an olefin feed comprising a content of phosphorus-containing compounds, said process comprising contacting said olefin feed with a sorbent comprising an effective amount of a metal selected from the group consisting of copper and silver under conditions and for a time effective to reduce said content of phosphorus-containing compounds and to produce a purified olefin feed, said olefin feed comprising primarily olefins having at least 6 carbon atoms.
6. The process of any one of the preceding claims wherein said olefin feed comprises primarily olefins having at least 6 carbon atoms.
7. The process of any one of the preceding claims further comprising regenerating said sorbent.
8. The process of claim 7 wherein said regenerating comprises exposing said sorbent to regeneration conditions comprising a quantity of oxygen and a temperature effective to regenerate said sorbent.
9. The process of any one of the preceding claims wherein said purified olefin feed comprising 0.5 ppm or less of said phosphorus-containing compounds.
10. The process of claim 2, or any one of claims 3, 4 and 7 to 9 when dependant from claim 2, wherein said converting comprises hydroformylating said skeletally isomerized olefins.