COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

Huls Aktiengesellschaft, incorporated in the Federal Republic of Germany, of Paul-Baumann-Strasse 1, 4370 Marl, FEDERAL REPUBLIC OF GERMANY, hereby apply for the grant of a standard patent for an invention entitled:

Oligomerization of Olefins

which is described in the accompanying complete specification.

Details of basic application(s):-

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<th>Basic Applic. No:</th>
<th>Country:</th>
<th>Application Date:</th>
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<td>P 39 14 817.3</td>
<td>DE</td>
<td>5 May 1989</td>
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DATED this TWENTY SIXTH day of APRIL 1990

Huls Aktiengesellschaft

By: [Signature]

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 121300
S&F CODE: 52640

SPRUSON & FERGUSON

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SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

"Verfahren zur Oligomerisierung von Olefinen"

We, Wolfgang Sticherling and Karl Stocks, both care of Huls Aktiengesellschaft, Kreis Recklinghausen, Paul-Baumann-Str. 1, D-4370 Marl 1, Federal Republic of Germany do solemnly and sincerely declare as follows:-

1. We are authorised by Huls Aktiengesellschaft, the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in Federal Republic of Germany on 5 May, 1989 by

FRANZ NIERLICH, JOACHIM NEUMEISTER, THOMAS WILDT, WILHELM DROSTE and FRITZ OBENAUS, of Vikariestrasse 16, D-4370 Marl; Bitterfelder Strasse 4, D-4370 Marl; Bruktererstrasse 9, D-4358 Haltern; Pommernstrasse 4 a, D-4370 Marl and Jupiterweg 60, D-4370 Marl, all in the Federal Republic of Germany respectively, are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

HULS AKTIENGESELLSCHAFT is entitled by Contract of Employment between the inventors as employees and HULS AKTIENGESELLSCHAFT as employer, as a person who would be entitled to have the patent assigned to it if a patent were granted upon an application made by the inventors.

3. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at 4370 Marl, this 07. day of February 1990

HÜLS AKTIENGESELLSCHAFT

[Signature]

Sticherling

[Signature]

Stocks

Signature of Declarant

TO: THE COMMISSIONER OF PATENTS

AUSTRALIA

SBR/JS/0029F
In support of the Convention Application made for a patent for an invention entitled:

Oligomerization of olefins

Dr. Wolfgang Sticherling and
We, Dr. Karl Stocks, both care of Huls Aktiengesellschaft, Kreis Recklinghausen, Paul-Baumann-Str. 1, D-4370 Marl 1, Federal Republic of Germany do solemnly and sincerely declare as follows:-

1. We are authorised by Huls Aktiengesellschaft, the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in Federal Republic of Germany on 05.05.1989 by Huls Aktiengesellschaft.

   1) FRANZ NIERLICH of Vikariestrasse 16, 4370 Marl, Germany
   2) JOACHIM NEUMEISTER of Bitterfelder Strasse 4, 4370 Marl, Germany
   3) THOMAS WILD of Bruktererstrasse 9, 4358 Haltern, Germany
   4) WILHELM DROSTE of Pommernstrasse 4 a, 4370 Marl, Germany
   5) FRITZ OBENAUS of Jupiterweg 60, 4370 Marl, Germany

All in the Federal Republic of Germany [respectively], are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

HULS AKTIENGESELLSCHAFT is entitled by Contract of Employment between the inventors as employees and HULS AKTIENGESELLSCHAFT as employer, as a person who would be entitled to have the patent assigned to it if a patent were granted upon an application made by the inventors.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at 4370 Marl this 21st day of June 1990

Dr. Wolfgang Sticherling
Dr. Karl Stocks

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

SBR/JS/0029F
OLIGOMERIZATION OF OLEFINs

1. A process for oligomerizing olefins of from 2 to 8 carbon atoms or mixtures thereof present in a hydrocarbon mixture over a nickel-containing catalyst at temperatures of from 0 to 200°C and pressures of from 1 to 70 bar absolute, characterized in that the hydrocarbon feedstock mixture is passed over a molecular sieve having a pore diameter of from greater than 4 angstrom to 15 angstrom prior to the oligomerization.
Complete Specification for the invention entitled:

Oligomerization of Olefins

The following statement is a full description of this invention, including the best method of performing it known to me/us
Abstract:

1. Oligomerization of olefins

2.1 In existing processes for oligomerizing olefins of from 2 to 8 carbon atoms, the nickel-containing catalyst only has a short life, so that the catalytic oligomerization processes have hitherto been uneconomical on a large scale. The novel process is to be notable for a long catalyst lifetime.

2.2 The hydrocarbon feedstock mixture is passed over a molecular sieve having a pore diameter of from greater than 4 angström to 15 angström prior to the oligomerization.

2.3 Preparation of olefin oligomers of from 4 to 16 carbon atoms.
Oligomerization of olefins

The present invention relates to a process for oligomerizing olefins of from 2 to 8 carbon atoms or mixtures thereof present in a hydrocarbon mixture over a nickel-containing catalyst at temperatures of from 0 to 200°C and pressures of from 1 to 70 bar absolute.

Olefins of from 2 to 8 carbon atoms or mixtures thereof, in particular olefins of from 2 to 5 carbon atoms, are available in large quantities from refinery crackers, and therefore are important raw materials for the entire petrochemical industry. For instance, polymers of ethylene, propylene and 1-butylene or mixtures thereof have found numerous applications.

Equally, however, the branched oligomers of olefins of from 2 to 8 carbon atoms prepared by acid catalysis have become important in industry. For instance, polymer gasoline has been produced from C$_3$/C$_4$-olefin mixtures for decades, and various fractions isolated from polymer gasoline are used as starting materials, for example for PVC plasticizers or detergents.

The importance of petrochemical products produced from polymer gasoline fractions is exceeded by that of products produced from more linear olefin oligomers because for example such detergents or detergent bases are more biodegradable or because such PVC plasticizers have inter alia lower viscosities and improved low temperature properties yet a similar vapour pressure. Less branched oligomers of from 10 to 16 carbon atoms produced from C$_5$/C$_6$-olefin cuts are highly suitable for use as diesel motor fuel component. This aspect is of great importance in those countries where the motor fuel supply is chiefly based on coal.
The more linear oligomers of lower olefins are obtainable by reacting the latter at temperatures of about 0-200°C and pressures of about 1-70 bar not only over homogeneous but also over heterogeneous catalysts when the active component is predominantly nickel. However, there are other possible catalytically active metals, for example ruthenium (G. Braca, G. Slzana; La Chimica e l'Industria, 56 (1974), 110-116), palladium according to US Patent 4,436,946, and copper, cobalt, iron, chromium and titanium according to GB Patent 824,002. However, only the nickel-containing catalysts have become industrially important.

DE Patent 2,855,423 discloses a homogeneous catalyst system consisting of the nickel(II) salt of octanoic acid, ethylaluminium dichloride and a free fatty acid. A catalyst system of this kind is also used in the only homogeneously catalyzed olefin oligomerization process of industrial importance (DIMERSOL®) (Y. Chauvin et al., Chemistry and Industry, 1974, 375-378).

Homogeneously catalyzed processes for oligomerizing olefins are very cost-intensive owing to the technically complicated removal of the catalyst system and, what is more, necessitate a complicated disposal of the inevitable waste product formed in the course of the destruction of the catalyst.

Besides homogeneous catalysts the prior art also reveals numerous heterogeneous catalysts based on nickel and silicon which frequently contain aluminium in addition and are prepared in various ways. DD Patent 160,037 for example discloses the preparation of an Ni/Al precipitation catalyst on SiO₂ as carrier material. Other catalysts are obtained by exchanging the positively charged particles, such as protons or sodium ions, present on the carrier surface for nickel ions. A wide variety of different carrier materials are used in the catalysts, for example amorphous aluminium silicate according to R.

It is known that nickel-containing catalysts are sensitive to a wide range of catalyst poisons. Such catalyst poisons are inter alia polyunsaturated hydrocarbons, for example propyne or butadiene, halogen compounds, oxygen compounds, e.g. water or alcohols, sulphur compounds, e.g. hydrogen sulphide, carbon oxysulphide, thioalcohols and thioethers, and also nitrogen compounds, for example amines present in the FCC C₄-hydrocarbon cut (FCC is the abbreviation for fluid catalytic cracker), or traces of butadiene-extracting agents, e.g. acetonitrile or N-methylpyrroloidine in SC raffinate I (SC being the abbreviation for steam cracker).

The mechanism of these catalyst poisons, however, is not well known, but it is suspected that their effect is due to their being more strongly adsorbed on the catalytically active centres than the olefins to be oligomerized. The presence of such catalyst poisons in the olefins to be oligomerized gradually reduces the activity of the catalyst.

Consequently, there are processes in the prior art for removing the various compounds from a hydrocarbon mixture. According to DE Patent 2,057,269, prior to the oligomerization, polyenes are preferably catalytically hydrogenated to the corresponding monoolefins to an extent of up to 75%. US Patent 4,153,638 teaches that after catalytic hydrogenation the diolefin content should be below 1% by weight.

Since the nickel-containing oligomerization catalysts in
general also show hydrogenation activity, it is possible, according to EP Patent 0,091,232, to convert the diolefins into the corresponding olefins by passing the hydrogen-saturated hydrocarbon feedstock mixture over the oligomerization catalyst.

According to US Patent 4,153,638, any dissolved water present in the hydrocarbon feedstock mixture can be removed down to levels of less than 10 ppm by weight by means of customary drying agents, for example a molecular sieve having a pore diameter of 3 angström or activated bauxite. Other high-boiling oxygen compounds are removed according to DE Patent 2,057,269 as the bottom product in a distillation of the hydrocarbon mixture.

Sulphur compounds can be removed by an alkali wash and nitrogen compounds by a water wash, the preference of US Patent 4,153,638 being hydrocarbon oligomerization mixtures containing less than 1 ppm by weight of sulphur and 0.3 ppm by weight of nitrogen.

However, the prior art processes are only suitable for the coarse removal of such compounds.

For instance, a refinery-produced propene/propane mixture (about 75 % by weight of propene and about 25 % by weight of propane) still contains even after prior art desulphurization high-boiling sulphur compounds, for example dimethyl sulphide (boiling point: 38°C) or dimethyl disulphide (boiling point: 109°C), in concentrations of less than 0.5 ppm by weight. However, these levels of sulphur compounds are sufficient to shorten the lifetime of the oligomerization catalyst to the point of it becoming uneconomical.

A further example are C₄-hydrocarbon cuts which despite prior distillation may still contain trace amounts of high-boiling oxygen compounds, for example methyl tert-butyl ether, tert-butyl alcohol or acetone. The same is
true of C₅-hydrocarbon cuts, for example pyrolysis gasoline.

Since, however, catalyst poisons are effective even in trace amounts, the abovementioned prior art coarse purification processes are not sufficient to ensure their removal from the hydrocarbon feedstock mixture for the oligomerization of olefins. For this reason and the consequent too short catalyst lifetime, the catalytic processes for oligomerizing olefins, in particular the heterogeneously catalyzed processes, have failed to become established in practice.

It is an object of the present invention to provide a more economical process for oligomerizing olefins wherein any catalyst poisons are removed to such an extent from the hydrocarbon feedstock mixture prior to oligomerization that the nickel-containing catalyst has a long lifetime.

Surprisingly, passing the hydrocarbon feedstock mixture over a molecular sieve having a pore diameter of from greater than 4 angstrom to 15 angstrom prolongs the lifetime of the nickel-containing catalyst to such an extent that even the industrial use of the catalytic process for oligomerizing olefins is now an economic proposition.

The present invention accordingly provides a process for oligomerizing olefins of from 2 to 8 carbon atoms or mixtures there present in a hydrocarbon mixture over a nickel-containing catalyst at temperatures of from 0 to 200°C and pressures of from 1 to 70 bar absolute, which is characterized in that the hydrocarbon feedstock mixture is passed over a molecular sieve having a pore diameter of from greater than 4 angstrom to 15 angstrom prior to oligomerization.

The olefins in the hydrocarbon feedstock mixture can be
oligomerized not only over a homogeneous but also over a heterogeneous nickel-containing catalyst. Preferably they are oligomerized over a heterogeneous nickel-containing catalyst, particularly preferably over a nickel-containing fixed-bed catalyst and very particularly preferably over a nickel-, silicon- and aluminium-containing fixed-bed catalyst.

Furthermore, the olefins in the hydrocarbon feedstock mixture can be oligomerized in the liquid phase, in the gas-liquid mixed phase or in the gas phase. Preferably they are oligomerized in the liquid phase.

The molecular sieves used according to the invention can be not only crystalline, natural aluminium silicates, for example phyllo silicates, but also synthetic ones. The process according to the present invention can also be carried out using commercial molecular sieves, for example products from Bayer AG, Dow, Union Carbide, Laporte or Mobil. These molecular sieves can be for example zeolites of the A-, X- and Y-type.

It is also possible to use synthetic molecular sieves which besides silicon and aluminium as main constituents contain other atoms as secondary constituents. These can be incorporated for example into the zeolite by ion exchange with the exchangeable cations. Examples are the exchange with rare earths, for example gallium, indium or lanthanum, or with nickel, cobalt, copper, zinc or silver.

In addition, it is also possible to use in the process according to the present invention synthetic zeolites in which other atoms, for example boron or phosphorus, have been incorporated into the lattice by coprecipitation.

Although in principle of no significance, the concentration of the catalyst poisons to be removed does have economic significance, since their concentration
determines the volume of molecular sieve to be used according to the invention per unit time. Normally, it will be favourable to use prior art agents to reduce the level of catalyst poisons down to about 1000 ppm by weight and then to pass the reduced catalyst poison content hydrocarbon feedstock mixture thus obtained over the molecular sieve used according to the present invention. For this reason, it is preferable to remove essentially water, alcohols, nitrogen compounds, sulphur compounds and halogen compounds from the hydrocarbon feedstock mixture before it is passed over the molecular sieve having a pore diameter of from greater than 4 angström to 15 angström.

In this embodiment, the coarse removal of water and/or methanol from the hydrocarbon feedstock mixture can preferably be effected with the aid of a molecular sieve having a pore diameter of up to 4 angström. An alternative is to remove water and/or methanol and/or ethanol from the hydrocarbon feedstock mixture by azeotropic distillation. The latter option is particularly suitable for hydrocarbon feedstock mixtures from a methyl tertiary-butyl ether plant or a tertiary-amyl methyl ether plant, since dimethyl ether, a by-product of the synthesis of the aforementioned ethers, can be separated off at the same time in the course of the azeotropic distillation.

If polyunsaturated hydrocarbons are present in the hydrocarbon feedstock mixture, they must be removed therefrom prior to the oligomerization.

They are preferably removed from the hydrocarbon feedstock mixture by selective hydrogenation, for example as described in EP Patent 81,041 and DE Patent 1,568,542, particularly preferably by a selective hydrogenation down to a residual level of less than 5 ppm by weight.

The polyunsaturated hydrocarbons can be removed from the
hydrocarbon feedstock mixture not only before said mixture is passed over the molecular sieve to be used according to the present invention but also afterwards.

Quantitative predictions about the efficiency of removal of catalyst poisons from the hydrocarbon feedstock mixture over the molecular sieve used according to the present invention are very difficult because frequently the nature of the catalyst poisons is not known.

Preferably the hydrocarbon feedstock mixture is passed prior to the oligomerization over a molecular sieve having a pore diameter of from 7 to 13 angström.

In some instances it can also be advantageous for economic reasons to connect two or more of the molecular sieves to be used according to the present invention in series. It is thus also possible to pass the hydrocarbon feedstock mixture prior to the oligomerization over two or more successive molecular sieves having a pore diameter of from greater than 4 angström to 15 angström.

The passing of the hydrocarbon feedstock mixture over the molecular sieve to be used according to the invention can be carried out both in the gas phase and in the liquid phase and also in the gas-liquid mixed phase. The weight hourly space velocity (WHSV) is preferably from 0.05 to 100 l/h, particularly preferably from 1 to 40 l/h.

The hydrocarbon feedstock mixture is preferably passed prior to the oligomerization over the molecular sieve used according to the present invention at pressures of from 1 to 200 bar absolute, particularly preferably at pressures of from 1 to 50 bar absolute, and preferably at temperatures of from 0 to 200°C, particularly preferably at temperatures of from 20 to 160°C.

The direction of flow of the hydrocarbon feedstock mixture over the molecular sieve used according to the
present invention is freely choosable, but is preferably upward.

In general, the protective effect afforded by the molecular sieve used according to the present invention for the downstream oligomerization catalyst is long-lasting. If, however, a breakthrough of the catalyst poisons through the molecular sieve used according to the present invention is observed after a certain period, a sure sign of such a breakthrough being a certain drop-off in the olefin conversion, it is possible to switch to a reserve molecular sieve and regenerate the exhausted sieve in the meantime.

The frequency of regeneration of the molecular sieve used according to the present invention depends inter alia on the size of the molecular sieve beds, the operating temperatures and the concentration of catalyst poison.

The molecular sieves used according to the present invention can be regenerated in a conventional manner, for example with an inert regeneration gas, e.g. nitrogen or hydrogen, or a gaseous hydrocarbon, e.g. methane or n-butane, at temperatures of from about 160-250°C.

The invention is illustrated in more detail by the following Examples:

Example 1

A 15% strength by weight solution of ethylene in n-butane is prepared. This solution is passed at room temperature over an adsorption bed comprising a molecular sieve having a pore diameter of 3 Ångström at an LHSV of 5 l of solution per l of adsorbent per hour, and thereafter the acetylene still present in traces is selectively hydrogenated over a catalyst based on 0.5% by weight of Pd on Al₂O₃ at a WHSV of 20 h⁻¹.
The solution thus pretreated is then passed at a temperature of 25°C and a pressure of 50 bar absolute over a molecular sieve of type 13 X from Bayer AG (pore diameter 9 angström) at a WHSV of 4 h⁻¹. Any catalyst poisons were below the limit of detection both upstream and downstream of the molecular sieve of type 13 X from Bayer AG. The solution thus prepared is then oligomerized at a temperature of 70°C, a pressure of 50 bar and a WHSV of 4 h⁻¹ over a nickel-exchanged montmorillonite (montmorillonite from Fluka AG, preparation: J.R. Sohn, H.B. Park, J. kor. chem. Soc. 26(5), pp. 282, 1982). The ethylene conversion remains unchanged over a week at 99%.

Comparative Example 1

The ethylene oligomerization is carried out as described in Example 1, except that the molecular sieve of type 13 X from Bayer is left out. The ethylene conversion decreases by about 0.5 % per day and is only 95.5 % after a week.

Example 2

Refinery propene containing about 75 % by weight of propene and 0.45 ppm by weight of sulphur is pretreated and then oligomerized as described in Example 1, except that prior to oligomerization the refinery propene is passed over a copper-exchanged X-zeolite containing 4.5 % by weight of Cu (pore diameter 8 angström prior to the exchange with copper) at a temperature of 120°C, a pressure of 50 bar absolute and a WHSV of 0.75 h⁻¹. After passing through this Cu-zeolite, the sulphur content of the refinery propene is only 7 ppb by weight. The oligomerization was carried out over a nickel-aluminium-silica catalyst comprising 15.3 % by weight of NiO, 9.3 % by weight of Al₂O₃ and 75.4 % by weight of SiO₂, prepared as described in DE Patent 2,051,402 by coprecipitation of Ni(NO₃)₂ with sodium silicate in the
presence of colloidal aluminium oxide. A WHSV of 5 h⁻¹, a pressure of 50 bar absolute and a temperature of 60°C gives a propene conversion of 53.5% which is virtually still unchanged four weeks later at 53.0%.

Comparative Example 2

Refinery propene is pretreated and oligomerized as in Example 2, except that the copper-exchanged X-zeolite is left out. At the end of a one-week run the propene conversion had dropped to 21.5%.

Example 3

A C₄-hydrocarbon cut from an MTB-plant, having an n-butene content of 75% by weight, is stripped of isobutane by distillation. At the same time the distillation removes any residual moisture content and the entire methanol and dimethyl ether content overhead. The n-butene concentrate obtained as bottom product, comprising 79% by weight of n-butene, 0.05% by weight of isobutene, 0.7 ppm by weight of tert-butyl alcohol and 1.1 ppm by weight of methyl tert-butyl ether, is selectively hydrogenated as described in Example 1, passed over a molecular sieve of type 13 X from Union Carbide (pore diameter 10 angstrom) at a temperature of 20°C, a pressure of 50 bar absolute and a WHSV of 6 h⁻¹, and then oligomerized at a temperature of 140°C, a pressure of 20 bar absolute and a WHSV of 6.1 h⁻¹. Downstream of the molecular sieve of type 13 X from Union Carbide, the level of tert-butyl alcohol is 40 ppb by weight and that of methyl tert-butyl ether is 90 ppb by weight.

The catalyst used for the oligomerization is prepared as follows:

500 g of a molecular sieve of type 13 X from Bayer AG are covered with 1 l of 1 M nickel nitrate solution and left at a temperature of 80°C for 6 hours with occasional
shaking. The solution is then decanted off, and the catalyst is dried at a temperature of 120°C for 5 hours and is then calcined at a temperature of 350°C under nitrogen for 48 hours. The ready-produced oligomerization catalyst contains 9.7% by weight of nickel.

The butene conversion is 32%, following a running-in period of 3 days, and remains unchanged over the next 14 days.

Comparative Example 3

The oligomerization is carried out as described in Example 3, except that the molecular sieve of type 13 X from Union Carbide is replaced by a molecular sieve of type 4 A from Bayer AG (pore diameter 4 angstrom). Initially the butene conversion is the same, but after 14 days it has dropped to 20%.

Example 4

A butadiene-free C₄-hydrocarbon mixture containing 83.9% by weight of n-butenes is admixed with 0.8 ppm by weight of dimethylamine. This hydrocarbon feedstock mixture is passed over a molecular sieve of type 5 A from Bayer AG (pore diameter 5 angstrom) at a temperature of 23°C, a pressure of 25 bar absolute and a WHSV of 2 h⁻¹ and thereafter contains only 60 ppb by weight of the added amine. This is followed by the oligomerization of the butene at a WHSV of 1 h⁻¹ at a temperature of 100°C and a pressure of 25 bar absolute over the catalyst prepared as follows:

250 g of a Y-zeolite from Ventron, Karlsruhe, are covered with 500 ml of 1 M nickel nitrate solution and maintained at a temperature of 70°C for 6 hours. The solution is then decanted off and discarded. The Y-zeolite thus treated is then extracted with hot water for 24 hours and calcined at a temperature of 350°C under nitrogen for 24
hours. The ready-produced oligomerization catalyst contains 4.9 % by weight of nickel.

The butene conversion is 29.4 %, following a running-in period of three days, and is virtually unchanged after three weeks, at 29.0 %.

**Comparative Example 4**

The oligomerization as per Example 4 is repeated, except that the dimethylamine is not separated off beforehand over the molecular sieve of type 5 A from Bayer AG. The butene conversion decreases continuously. After three days it is 27 % and after a week only 12 %.

**Example 5**

A C₅-hydrocarbon fraction containing 99.5 % by weight of octenes additionally contains 400 ppm by weight of polyunsaturated olefins and 1 ppm by weight of sulphur. It is selectively hydrogenated and then passed over a zinc-exchanged molecular sieve containing 2 % by weight of zinc at a temperature of 20°C, a pressure of 50 bar absolute and a WHSV of 1 h⁻¹. The zinc-exchanged molecular sieve is obtained by ion exchange of the phyllosilicate of type K10 from Südchemie (pore diameter 13 angström). The C₅-hydrocarbon fraction thus pretreated, which had no detectable polyunsaturated olefin content but still had a sulphur content of 43 ppm by weight, is oligomerized at a temperature of 100°C, a pressure of 5 bar absolute and a WHSV of 1 h⁻¹. The oligomerization catalyst used herein is prepared as described in Example 3, except that the catalyst is extracted with hot water for 24 hours prior to drying. The nickel content of the ready-produced oligomerization catalyst is 5.5 % by weight.

Following a running-in period of 3 days, the octene conversion is 24 % and is still unchanged three weeks later.
Comparative Example 5

The oligomerization as per Example 5 is repeated, except that the C₆-hydrocarbon fraction is not passed beforehand over the zinc-exchanged molecular sieve. The butene conversion after three days is down to 17 %, and after three weeks it has dropped to zero.
The claims defining the invention are as follows:

1. A process for oligomerizing olefins of from 2 to 8 carbon atoms or mixtures thereof present in a hydrocarbon mixture over a nickel-containing catalyst at temperatures of from 0 to 200°C and pressures of from 1 to 70 bar absolute, characterized in that the hydrocarbon feedstock mixture is passed over a molecular sieve having a pore diameter of from greater than 4 ångström to 15 ångström prior to the oligomerization.

2. A process according to Claim 1, characterized in that essentially water, alcohols, nitrogen compounds, sulphur compounds and halogen compounds are removed from the hydrocarbon feedstock mixture before it is passed over the molecular sieve having a pore diameter of from greater than 4 ångström to 15 ångström.

3. A process according to Claims 1 and 2, characterized in that the olefins in the hydrocarbon feedstock mixture are oligomerized over a heterogeneous nickel-containing catalyst.

4. A process according to Claim 3, characterized in that the olefins in the hydrocarbon feedstock mixture are oligomerized over a nickel-, silicon- and aluminium-containing fixed-bed catalyst.

5. A process according to Claims 1 to 4, characterized in that the olefins in the hydrocarbon feedstock mixture are oligomerized in the liquid phase.

6. A process according to Claims 1 to 5,
characterized in that
the hydrocarbon feedstock mixture is passed prior to the
oligomerization over the molecular sieve at pressures of
from 1 to 200 bar absolute.

7. A process according to Claims 1 to 6,
characterized in that
the hydrocarbon feedstock mixture is passed prior to the
oligomerization over the molecular sieve at temperatures
of from 0 to 200°C.

8. A process according to Claims 1 to 7,
characterized in that
the polyunsaturated hydrocarbons are removed from the
hydrocarbon feedstock mixture prior to the
oligomerization.

9. A process according to Claim 8,
characterized in that
the polyunsaturated hydrocarbons are removed from the
hydrocarbon feedstock mixture by selective hydrogenation.

10. A process according to Claim 9,
characterized in that
the polyunsaturated hydrocarbons are removed from the
hydrocarbon feedstock mixture by selective hydrogenation
down to a residual level of less than 5 ppm by weight.

11. A process for oligomerizing olefins of from 2 to 8 carbon atoms
or mixtures thereof present in a hydrocarbon mixture over a
nickel-containing catalyst at temperatures of from 0 to 200°C and pressures
of from 1 to 70 bar absolute substantially as hereinbefore described with
reference to any one of the Examples.

12. The product of the process of any one of claims 1 to 11.

DATED this TWENTY-FIRST day of FEBRUARY 1990
Huls Aktiengesellschaft
Patent Attorneys for the Applicant
SPRUSON & FERGUSON