

1

3,684,695

HYDROCRACKING PROCESS FOR HIGH VISCOSITY INDEX LUBRICATING OILS

Emmanuel E. A. Neel, Michel Gaucher, and Claude J. Clement, all % Centre de Recherche Shell Berre, Grand Couronne, France
No Drawing. Filed Feb. 9, 1971, Ser. No. 113,925
Claims priority, application France, Mar. 9, 1970,
7008323

Int. Cl. C10g 13/02, 37/10

U.S. Cl. 208—110

10 Claims

ABSTRACT OF THE DISCLOSURE

A process for the manufacture of high viscosity index base oils by hydrocracking a high boiling hydrocarbon feedstock, e.g., deasphalted residual oil, over a catalyst containing nickel and molybdenum hydrogenating components and phosphorous oxide on a refractory oxide support, e.g., alumina or silica-magnesia, and recovering from the liquid product at least one lubricating oil fraction boiling in the range from about 350° to 550° C.

THE INVENTION

The present invention relates to a hydrocracking process for the preparation of lubricating oil with a high viscosity index.

Lubricating oil with a high viscosity index can be prepared from high boiling mineral oil fractions by converting the latter by means of hydrogen in the presence of a phosphorus-containing catalyst.

The invention therefore relates to a process for the preparation of lubricating oil with a high viscosity index, in which a high boiling mineral oil fraction is contacted at elevated temperature and pressure, in the presence of hydrogen, with a catalyst consisting of nickel and/or cobalt, molybdenum and/or tungsten in metallic, oxidic and/or sulfidic form, and of phosphorus oxide supported on a carrier consisting of refractory oxide.

Suitable starting materials for the process according to the invention are high boiling hydrocarbon mixtures, e.g., heavy petroleum fractions and heavy fractions obtained by pyrolysis of coal, bituminous shale or tar sand. Petroleum fractions boiling at least in part above the boiling range of lubricating oil may be used to advantage. As feed for the present process use is preferably made of a distillate fraction recovered by vacuum distillation from a residual oil fraction obtained by atmospheric distillation. The boiling range of such a vacuum distillate is usually between 350° C. and 550° C. However, deasphalted residual petroleum fractions are particularly preferred.

The process according to the invention is carried out at elevated temperature and pressure and in the presence of hydrogen or a hydrogen containing gas. Pure hydrogen may be used, but this is not advisable. A gas with a hydrogen content of 70% or more by volume is perfectly suitable. In practice it will be preferable to use a hydrogen containing gas originating from a catalytic reforming plant. Such a gas not only has a high hydrogen content but also contains low-boiling hydrocarbons, for example, methane, and a small quantity of propane.

The temperature and pressure used in the present process may vary between very wide limits, depending on the desired degree of conversion. In general, the temperature selected will not be below 350° C. and not above 550° C. At temperatures below 350° C. the rate of conversion is reduced, whereas at temperatures above 550°

2

cracking occurs to such an extent that only a limited quantity of the desired product is obtained. A temperature between 400° C. and 550° C. is preferred. Pressures lower than 725 p.s.i. are less desirable since they reduce the life of the catalyst while involving the risk of two high aromatics content in the product, as a result of which the viscosity index is adversely affected. A pressure above 3600 p.s.i. would require a very costly installation. For this reason it is preferable to use a pressure between 10 1450 and 2900 p.s.i.

The liquid hourly space velocity and the hydrogen/oil ratio may likewise be selected between very wide limits. It is preferred, however, to select a liquid hourly space velocity between 0.1 and 10 kg. of oil per hour per liter of catalyst. A liquid hourly space velocity of less than 0.1 kg./hour per liter of catalyst would require an uneconomically large reactor for a given degree of conversion, whereas a liquid hourly space velocity of more than 10 kg. per hour per liter of catalyst would give only 15 a low degree of conversion into the desired product. The hydrogen/oil ratio is preferably between 100 and 5000 standard liters (liters at 14.5 p.s.i. and at 0° C.) per kg. of oil. A very low H₂/oil ratio would adversely affect the life of the catalyst, whereas a very high H₂/oil ratio 20 would cause a considerable loss of pressure over the catalyst beds, so that much energy for compression would be required for circulating the hydrogen-rich gas.

The catalyst used in the process according to the invention contains at least two hydrogenative metal components, a carrier and phosphorus.

One of the metal components consists of nickel and/or its compounds. Moreover, the catalyst should contain molybdenum and/or its compounds. Important factors in this respect are the quantity of hydrogenative metal 35 component expressed as a percentage of the total catalyst, as well as the ratio between nickel on the one hand and molybdenum on the other.

The metal component should preferably not be used 40 in too small quantities since this would have an adverse effect on the desired hydrogenating action. A very high load of metal component would cause the pores of the porous catalyst support to become clogged in such a manner that part of the surface of the catalyst would be rendered inaccessible to the material to be converted. It 45 has now been found that a catalyst containing between 3% and 16% by weight of nickel and between 6% and 24% by weight of molybdenum is pre-eminently suitable for the process according to the invention. For this reason it is preferred to apply the above-mentioned percentages by weight of hydrogenative metal components to the catalyst before using the latter for the present process.

The amount of phosphorus applied to the catalyst may 55 likewise vary between wide limits. It has been found, however, that the activity of the catalyst depends on the percentage by weight of phosphorus present in the catalyst. Good activity of the catalyst is ensured by a phosphorus content of between 1% and 12% by weight, 60 based on P₂O₅. For this reason it is preferred to use a catalyst having such a phosphorus content. More preferably, the phosphorus content is selected between 2% and 9% by weight calculated as P₂O₅ on the total catalyst and it has been found that the maximum activity of the 65 catalyst is obtained at a phosphorus content between 3% and 7% by weight, likewise calculated as P₂O₅ on the total catalyst.

"Activity" in this specification means the temperature required for obtaining under given operating conditions 70 (pressure, liquid hourly space velocity, H₂/oil ratio) and starting from a given feed, a product with a pre-

determined viscosity index. The higher the activity of the catalyst used the lower will be the temperature required.

In principle any refractory oxide material may be employed as carrier for the catalyst to be used. Suitable materials are, for example, alumina (aluminum oxide), silica (silicium oxide), magnesia (magnesium oxide), titanium oxide and mixtures and compounds of these metal oxides.

It has now been found that the use of alumina or a mixture of silica and magnesia as carrier material permits the preparation of catalysts with a particularly good activity, selectivity and stability. For this reason use is preferably made of these carrier materials.

Commercial alumina usually contains small quantities of impurities, for example, silica and sodium. It has been found that alumina containing between 0.5% and 3% by weight of silica and up to 0.005% by weight of sodium is an excellent carrier material for the catalyst. This alumina is therefore preferred.

If the alumina contains more than 0.005% by weight of sodium, the sodium content may be reduced to the required level by ion exchange with a solution of an ammonium salt.

Of the supports composed of silica and magnesia, a mixture of between 50% and 90% by weight of silica and between 10% and 50% by weight of magnesia is preferred.

In this specification the selectivity of the catalyst is understood to mean the product volume of lubricating oil with a specified viscosity index under given conditions (temperature, pressure, liquid hourly space velocity and H₂/oil ratio). This stability of the catalyst is the extent to which the catalyst retains its activity during prolonged use in the process according to the invention.

To further increase the activity and selectivity of the catalyst fluorine is added thereto. It has been found that a considerable improvement is even obtained by adding only 1% by weight of fluorine. If more than 6% by weight is added there is a risk, however, that the selectivity of the catalyst may be adversely affected. For this reason it is preferred to add between 1% and 6% by weight of fluorine to the catalyst.

The catalyst may be prepared in any manner desired, for example, by impregnating the carrier with one or more aqueous solutions of compounds of the other components, followed by drying and calcination.

As indicated above, a preferred catalyst contains a carrier, nickel, molybdenum and phosphorus. Such a catalyst can be prepared very conveniently by impregnating a catalyst carrier with an aqueous phosphoric acid solution, drying the impregnated carrier and subsequently impregnating it with an aqueous solution of a molybdate and a nickel salt, whereupon the catalyst is obtained by drying and calcination.

It has been found, however, that catalysts of even better activity, stability and selectivity can be prepared by impregnation with an aqueous solution of a phosphomolybdate and a nickel salt rather than in a separate step with phosphoric acid and with a molybdate and nickel salt containing solution.

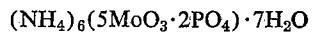
Accordingly, the catalysts which are used to advantage in the process according to the invention, are prepared as follows:

A catalyst carrier is impregnated with an aqueous solution of an acid or non-acid phosphomolybdate and a nickel salt, whereupon the impregnated carrier is dried and calcined.

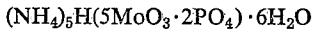
As a nickel salt, use is preferably made of nickel hexamine dichloride ([Ni(NH₃)₆]Cl₂), or nickel formate, although any water-soluble nickel salt, such as nickel nitrate and nickel chloride may be employed.

As phosphomolybdate and acid phosphomolybdate, use is preferably made of ammonium 2-phospho-5-molybdate and acid ammonium 2-phospho-5-molybdate, re-

spectively. These substances have respectively the following chemical formulae:



and



Although it is preferred in the above-described methods for the preparation of catalysts to apply the nickel salt to the catalyst by impregnation together with the molybdate, the phosphomolybdate and/or the acid phosphomolybdate, good results may also be obtained by treating the catalyst with two separate solutions, one containing the nickel salt and the other containing the molybdate, phosphomolybdate and/or acid phosphomolybdate.

In order to ensure that the nickel salt, the molybdate, the phosphomolybdate and/or the acid phosphomolybdate are thoroughly dispersed on the catalyst during impregnation, it is preferred to add ammonium hydroxide to the solutions of these components, the quantity to be added being such that the pH of these solutions is between 7 and 12.

As noted previously, the catalyst preferably contains fluorine. This element may be applied to the catalyst by any suitable method. For this purpose it is preferred to impregnate the catalyst with a solution of hydrogen fluoride, ammonium fluoride and/or ammonium bifluoride. These components have the advantage that they do not leave behind less desirable cations such as Na, K and Ca ions on the catalyst after calcination.

The catalyst is completed by calcination. This treatment is preferably carried out at a temperature between 450° C. and 850° C., for between 0.5 and 5 hours.

After calcination, the phosphorus and the metals, viz., nickel and/or cobalt and molybdenum and/or tungsten, are probably present in the catalyst in the form of oxides, although the possibility cannot be excluded that they have combined, at least in part, with the catalyst carrier.

It has been found that, in the catalytic conversion of heavy hydrocarbon mixtures to lubricating oil by means of hydrogen, better results can be obtained if the catalyst is previously sulfided, by which process the metal oxides are converted, at least in part, to the corresponding metal sulfides.

For this reason it is preferred to use a sulfided catalyst.

A very good and hence preferred sulfiding method consists in contacting the catalyst at a temperature of between 259° C. and 450° C., a pressure of between 435 and 1015 p.s.i., a hourly space velocity of between 1 and 10 kg. of oil per hour per liter of catalyst and a hydrogen/oil ratio of between 50 and 500 standard liters of H₂ per kg. of oil with an oil which contains sulfur compounds, preferably with a gas oil which contains sulfur compounds. This treatment is preferably given in the same reaction vessel in which the hydrogenative conversion to lubricating oil is carried out.

Once the catalyst has been sulfided, the starting material for the production of lubricating oil with a high viscosity index is introduced into the reactor at a suitable temperature, pressure, hourly space velocity and H₂/oil ratio and passed over the catalyst which is preferably present in one or more beds of particles with a size between 1 and 3 mm.

After passing through the reactor the reaction product is cooled and separated into a hydrogen-rich gas and a liquid product.

The hydrogen-rich gas is preferably recycled, at least in part to the reactor. The liquid product contains hydrocarbons boiling below the boiling range of lubricating oil and hydrocarbons boiling within the boiling range of lubricating oil, i.e., from about 350° to 550° C.

The hydrocarbons boiling below the boiling range of lubricating oil are preferably separated from the higher boiling residue by fractional distillation. The cut point of this distillation is preferably so chosen that the higher

boiling residue has an initial boiling point from 350° C. to 400° C.

In addition to excellent lubricating components, this residue normally contains paraffins which solidify at a slightly reduced temperature and thus have an adverse effect on the pour point of the desired lubricating oil. In order to prepare a useful lubricating oil or lubricating oil component from the residue, it is therefore preferred to dewax this residue. This treatment can be carried out in any manner desired. The dewaxing is preferably carried out by means of a mixture of methylethylketone and toluene at a temperature between -10° C. and -30° C. and a volume ratio of solvent to oil between 1:1 and 10:1.

The dewaxed residue has a high viscosity index, for example, a viscosity index between 100 and 140, depending on the conditions under which the hydrogenative conversion of the starting material took place. For this reason it is eminently suitable for use as multigrade lubricating oil or multigrade lubricating oil component. Moreover this dewaxed residue permits the preparation by means of vacuum distillation of one or more lubricating oils or lubricating oil components with high viscosity indices and mutually different viscosities, which oils or components in their turn may be worked up into excellent multigrade lubricating oils by blending them together or with other components.

The invention will now be illustrated with reference to the following examples.

Example I

A catalyst A for the hydrogenative conversion of heavy hydrocarbon oils to lubricating oil with a high viscosity index was prepared as follows:

250 g. of particles obtained by extrusion, with a diameter of 1.3 mm. and consisting of alumina, were impregnated for 20 hours at a temperature of 22° C. with a solution of 15.5 ml. of 85% phosphoric acid (H_3PO_4) in 241.5 ml. of water.

The impregnated carrier was subsequently dried for 2 hours.

After this period, a solution of 93 g. of ammonium paramolybdate in 270 ml. of water was mixed with a solution of 118 g. of nickel hexamine dichloride in a mixture of 160 ml. of water and 11 ml. of 27% ammonium hydroxide.

The dried catalyst carrier was impregnated three times for 10 minutes at a temperature of 22° C. with the solution of ammonium paramolybdate, nickel hexamine dichloride and ammonium hydroxide described above, the carrier being dried between the impregnating steps, each time for 2 hours at 200° C. After the final impregnating step, the impregnated carrier was dried for 16 hours at 120° C. and calcined for 2 hours at a temperature of 650° C.

The catalyst thus prepared had the following composition:

	Percent by weight
Alumina (Al_2O_3)	66
Phosphorus pentoxide (P_2O_5)	4
Molybdenum oxide (MoO_3)	20
Nickel oxide (NiO)	10

Example II

A catalyst B for the hydrogenative conversion of heavy hydrocarbon oils to lubricating oil with a high viscosity index was prepared in the following manner:

116 g. of ammonium 2-phospho-5-molybdate were dissolved in 395 ml. of water to which 100 ml. of 27% ammonium hydroxide had been added.

117 g. of nickel hexamine dichloride were dissolved in 800 ml. of water to which 20 ml. of 27% ammonium hydroxide had been added. The phosphomolybdate solution and the nickel hexamine dichloride solution were subsequently mixed together.

250 g. of alumina extrudates, which were identical to

the alumina extrudates used in Example I, were subsequently impregnated for 10 minutes with the aqueous mixture containing phosphomolybdate, nickel hexamine dichloride and ammonium hydroxide. This impregnation was repeated six times, the impregnated carrier being dried between the steps, each time at 200° C. for 2 hours.

After the final impregnation, the carrier was dried for 2 hours at 120° C. and subsequently calcined for 2 hours at 650° C.

The catalyst thus produced had the following composition:

	Percent by weight
Alumina (Al_2O_3)	66
Phosphorus pentoxide (P_2O_5)	4
Molybdenum oxide (MoO_3)	20
Nickel oxide (NiO)	10

Example III

A catalyst C was prepared by impregnating a quantity of 150 g. of catalyst B for 1 hour at 20° C. with a mixture of 11 ml. of 40% hydrogen fluoride and 90 ml. of water. The fluorinated catalyst was subsequently dried for 12 hours at 120° C. and calcined for 2 hours at 650° C.

Catalyst C had the following composition:

	Percent by weight
Alumina (Al_2O_3)	64.0
Phosphorus pentoxide (P_2O_5)	3.9
Molybdenum oxide (MoO_3)	19.4
Nickel oxide (NiO)	9.7
Fluorine (F)	3.0

Example IV

A residual oil fraction obtained from a North African crude oil and deasphalted by means of a liquid propane was used to test the activity, the selectivity and the stability of catalysts A, B and C.

This oil fraction had the following properties:

40	Specific gravity 20/4: 0.907
	Viscosity at 99° C.: 32.8 cs.
	Viscosity index (VI_E) ASTM D-2270 after dewaxing at -19° C.: 77
45	Yield of dewaxed oil after dewaxing at -19° C.: 89.2% by weight.

Quantities of this oil fraction were passed over three identical beds of the catalysts A, B and C under the following reaction conditions:

50	Pressure: 2030 p.s.i. absolute
	Hourly space velocity: 1 kg. of oil per hour per liter of catalyst
55	Hydrogen/oil ratio: 1000 standard liters of H_2 per kg. of oil.

During the catalytic conversions over the three catalyst beds the temperatures were controlled in such a manner that the products of the three treatments, after distillative removal of components boiling below 375° C. and after dewaxing, had a viscosity index (VI_E) of 130.

The dewaxing was effected by means of a mixture of methylethylketone and toluene (50/50) in the ratio of three parts by volume of mixture to one part by volume of oil at a temperature of -19° C.

The following temperatures were required to obtain the abovementioned results:

	° C.
For catalyst A	457
For catalyst B	452
For catalyst C	441

At these temperatures the following yields of dewaxed oil with a VI_E of 130 and an initial boiling point of 350° C. calculated on the original North African dewaxed

residual oil fraction used as starting material were obtained:

Percent by weight

For catalyst A	25
For catalyst B	29
For catalyst C	32

From the foregoing it is evident that phosphorus-containing catalysts display a very good activity and selectivity for the production of lubricating oil with a very high viscosity index and that these properties can be further improved by preparing the catalysts with the aid of phosphomolybdate and adding fluorine thereto.

The three catalysts A, B and C also have an excellent stability. This was borne out by the fact that during the first 700 hours the temperature had to be increased by approximately 2° C. per 100 hours to ensure maintenance of the desired viscosity index $VI_E=130$, whereas after 700 hours and up to the end of the experiments described above, i.e., after 1100 hours, the temperature could be kept constant to achieve the desired result ($VI_E=130$) at all times.

What is claimed is:

1. A hydrocracking process for preparing high viscosity index lubricating oils which comprises contacting a high boiling hydrocarbon feedstock under hydrocracking conditions with a catalyst comprising at least two hydrogenative components in the form of metals, oxides or sulfides, said components consisting of 3-16% w. nickel and 6-24% w. molybdenum, and 2-9% w. phosphorus oxide on a refractory oxide support selected from the group consisting of alumina and silica-magnesia to form a reaction effluent; cooling and separating the effluent into a hydrogen-rich gas and a liquid product; then further separating the liquid product into a light fraction boiling below the lubricating oil range and a higher boiling residue having an initial boiling point from 350° C. to 400° C.; and recovering from the residue at least one lubricating oil fraction boiling in the range from about 350° to 550° C.

2. The process of claim 1 wherein the high boiling hydrocarbon feedstock is a vacuum distillate boiling between 350° C. and 550° C. or a deasphalted residual oil.

3. The process of claim 1 wherein the hydrocracking conditions are a temperature between 400° C. and 500° C., a pressure between 1450 and 2900 p.s.i., a liquid hourly space velocity between 0.1 and 10 kg. of oil per hour per liter of catalyst, and a hydrogen/oil ratio be-

tween 100 and 5000 standard liters of hydrogen per kg. of oil.

4. The process of claim 1 wherein the refractory oxide support is alumina and contains between 0.5% and 3% w. silica and not more than 0.005% w. sodium.

5. The process of claim 1 wherein the refractory oxide support consists of between 50-90% w. silica and between 10-50% w. magnesia.

6. The process of claim 1 wherein the catalyst contains between 1 and 6% w. fluorine.

7. The process of claim 1 wherein the catalyst is sulfided by contact with a sulfur compound before it is brought into contact with the feedstock.

8. The process of claim 1 wherein the lubricating oil fraction recovered from the residue is dewaxed by means of a mixture of methylethylketone and toluene at a temperature between -10° C. and -30° C. and a volume ratio of solvent to oil between 1:1 and 10:1.

9. The process of claim 1 wherein a lubricating oil fraction having a viscosity index of about 130 is produced by contacting a deasphalted residual oil with a catalyst comprising 3-16% w. nickel, 6-24% w. molybdenum, 2-9% w. phosphorus oxide, and 1-6% w. fluorine on an alumina support under hydrocracking conditions, and then dewaxing the lubricating oil fraction recovered from the residue.

10. The process of claim 9 wherein the catalyst is prepared by impregnating the alumina with an aqueous solution of phosphomolybdate and a nickel salt to achieve the desired metals and phosphorus content, and then drying and calcining the composite.

References Cited

UNITED STATES PATENTS

3,142,635	7/1964	Coonradt et al.	208—111
3,308,055	3/1967	Kozlowski	208—111
3,493,493	2/1970	Henke et al.	208—264
3,494,854	2/1970	Gallagher et al.	208—59
3,506,565	4/1970	White et al.	208—59
3,530,061	9/1970	Orkin et al.	208—60
3,579,435	5/1971	Olenzak et al.	208—59

DELBERT E. GANTZ, Primary Examiner

45 G. E. SCHMITKONS, Assistant Examiner

U.S. Cl. X.R.

208—18; 252—435, 437