

[54] **HYDROCRACKING PROCESS AND CATALYST FOR PRODUCING MULTIGRADE OIL OF IMPROVED QUALITY**

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[58] **Field of Search** **208/124, 18, 112, 95, 96, 208/139, 59, 60, 58; 260/683.7, 683.74, 683.73, 683.68**

[56]

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[57]

ABSTRACT

Lube oils which may be used as direct multigrade lube oils are obtained from paraffins, particularly from hydrocracking paraffins, by hydrogenation in the presence of both a group VIII noble metal carried on halogenated alumina and ammonia, followed with dewaxing.

11 Claims, No Drawings

HYDROCRACKING PROCESS AND CATALYST FOR PRODUCING MULTIGRADE OIL OF IMPROVED QUALITY

This invention provides a process for manufacturing lubricating oils of high viscosity index and particularly direct multigrade motor oils by hydroisomerizing paraffin wax, preferably paraffin wax obtained by hydrocracking.

A multigrade oil may be defined as an oil which satisfies several SAE standards; it is an oil whose viscosity varies with temperature to a lesser extent as the conventional non-multigrade oils.

The following table summarizes the viscosity standards of the main multigrade oils such as defined by I.GROFF graph as modified according to ASTM D-56-7-53 standard (SAE Handbook 1966).

TABLE I

Multigrades	VI (ASTM D-567)	Viscosity cst at 37°8 C	Viscosity cst at 98°9 C
10 W 20	100 to 145	30 to 50	5.8 to 9.6
10 W 30	130 to 150	50 to 77	9.6 to 13
10 W 40	> 140	> 70	13 to 17
20 W 20	20 to 130	42 to 85	5.8 to 9.6
20 W 30	90 to 138	70 to 120	9.6 to 13
20 W 40	110 to 143	85 to 150	13 to 17

A multigrade oil is conventionally prepared by admixing a very fluid base oil with variable amounts of a polymer, for example of the polymethacrylate type, which both improves the viscosity characteristics versus temperature and thickens the oil. The conventional viscosity additives are usually less stable than the oil when subjected to mechanical actions (shearing effect) and to the temperature effect.

It would be quite advantageous to dispose of multigrade oils free of viscosity additives and therefore more stable. The process of the invention provides such oils.

When such oils are directly obtained by a refining process, they are called "direct multigrade oils."

The direct multigrade oils obtained according to the process of the invention may obviously be used with conventional viscosity additives so as to provide other types of multigrade oils.

The paraffins treated according to the process of the invention are preferably hydrocracking paraffins obtained by dewaxing a lubricating oil base resulting from the hydrocracking or hydrotreating of vacuum distillates or deasphalted vacuum residues, such as described, for example, in French Patent No. 1,582,758 (U.S. Pat. No. 3,365,390). These paraffins are normally solid at room temperature (20°C). Reference is also made to U.S. Pat. No. 3,560,370 and to the French patent application 7,112,416 and U.S. Pat. application 241,690 filed Apr. 6, 1972, now U.S. Pat. No. 3,793,191.

The state of the art may be illustrated by U.S. Pat. No. 3,365,390 according to which a lubricating oil, which is not a direct multigrade oil, is produced by hydroisomerizing a normally solid paraffin in the presence of a reforming catalyst such as platinum-on-alumina, the hydroisomerizing step being followed with a dewaxing step.

We have now found that the yield of direct multigrade oil can be increased provided that (1) the catalyst contains a critical halogen amount and (1) the op-

eration is carried out under a critical ammonia pressure.

The invention is thus concerned with a process for manufacturing multigrade oils, according to which a mixture of hydrogen and paraffin is contacted with a catalyst comprising an alumina carrier, at least one noble metal of group VIII of the periodic classification and from 0.1 to 5% by weight of halogen, at a temperature of from 300° to 450°C, the global product is fractionated and the oil obtained after said fractionation is dewaxed for removing at least a fraction of the unconverted paraffins, the process being remarkable in that said contacting step is carried out under an ammonia partial pressure of from 1 to 500 g/cm².

Normally solid hydrocracking paraffins may be obtained, for example, by contacting hydrogen and oil vacuum or deasphalted vacuum residues, normally boiling, at least partly, above 450°C, with a hydrocracking catalyst, under hydrocracking conditions, fractionating the resulting product so as to isolate therefrom a fraction normally boiling above 380°C and preferably above 430°C and dewaxing said fraction according to a known technique, for example as described hereinafter with respect to the isomerized paraffin.

Hydrocracking catalysts are known to contain, as a rule, one or more metals or compounds of metals from groups VI and/or VIII, for example molybdenum, tungsten, nickel, cobalt and/or platinum incorporated to or carried on an acidic carrier, for example alumina-silica or halogen-containing alumina. The process is carried out, for example, as follows:

temperature of from 300° to 480°C
pressure of from 30 to 200 kg/cm²
hydrocarbon hourly feed rate of from 0.3 to 5 volumes per volume of catalyst.
hydrogen feed rate of from 500 to 5000 liters per liter of feed charge.

The so-obtained hydrocracking paraffins, or at least a major portion thereof, have a molecular weight higher than 500, the average molecular weight of the paraffin feedstock being higher than about 400. Their viscosity is conventionally 8 to 20 centistokes at 98°9 C, their viscosity index about 130, their sulfur content lower than 30 ppm (parts per million of parts) by weight and their nitrogen content lower than 5 ppm by weight.

The hydroisomerization reaction is carried out at a temperature of from 250° to 450°C, preferably from 300° to 390°C. The pressure may range, for example, from 10 to 150 kg/cm² and preferably from 30 to 100 kg/cm². The hourly feed rate by volume (VVH) is usefully of from 0.2 to 5 liters, preferably from 0.5 to 2 liters of liquid hydrocarbons per liter of catalyst. The gaseous hydrogen feed rate is, for example, 300 to 3000, preferably 500 to 1500 liters per liter of liquid hydrocarbons under the normal temperature and pressure conditions. In these conditions, the hydrocarbon feed charge is practically 100% liquid. The feed charge may be supplied to the top of the reactor, which results in a trickling phase operation in hydrogen atmosphere, although an ascending flow of the reactants may also be used.

We have found that the quality of the final oil could be further improved by recycling a portion of the oil obtained after appropriate treatment of the reactor effluent, for example after distillation or dewaxing.

The specific catalysts employed and the purity of the charge permit the reaction to take place under moderate conditions (a pressure of from 50 to 80 kg/cm² and a temperature of from 300° to 390°C), so that the resulting oil has a negligible content of aromatics. When using platinum on fluorinated alumina as catalyst, we obtain at 350°C, 45% by weight of oil of a 135 VI, whose aromatic content is substantially negligible, whereas at 420°C the obtained oil contains 15% of aromatic hydrocarbons.

As a result of this negligible aromatic hydrocarbon content it is unnecessary to subject the liquid product obtained by the process of the invention to a hydrofinishing treatment, this being a great advantage from an economic point of view.

The hydroisomerization treatment according to the invention is carried out in the presence of catalysts consisting of one or more noble metals of group VIII and/or their alloys incorporated to- or carried on- an acid support of the halogen-containing alumina type. The use of noble metals is possible owing to the great purity of the feed charge, in particular its very low sulfur content. Mixtures of metals may be used, for example platinum + iridium, platinum + cobalt, platinum + rhenium, platinum + germanium or platinum + gold.

We have found that the best catalysts for the process of the invention are those of the platinum-alumina-halogen type, the preferred halogen being fluorine. The halogen content of the catalyst may be advantageously selected within the range of from 0.1 to 5% by weight and preferably 0.3 to 0.8% for fluorine and 0.3 to 3% for chlorine.

The halogen and noble metal of the catalyst may be supplied according to well-known methods, for example those used when manufacturing reforming catalysts.

The results obtained by using both ammonia and a halogen-containing catalyst are unobvious since ammonia has a detrimental effect (yield decrease) when employed with a halogen-free platinum-on-alumina catalyst.

The hydroisomerization product may be fractionated, for example, as follows:

a cut boiling above 380°C which is dewaxed to yield a base oil whose viscosity index is from 130 to 150 with a viscosity higher than 7 centistokes at 98.9°C and a melting point of, for example, -20°C; this base oil conforms to the 10 W 20 multigrade oil standard;

a gas oil cut (250°-380°C) whose diesel number is at least 90; its cetane number is higher than 70 (the motor gas oil specification requires a cetane number of at least 50);

a jet fuel cut (150°-250°C) whose smoke point is better than 45 mm (the kerosene specification mentions a smoke point of at least 21 mm);

a 80°-150°C cut of high isoparaffin content, substantially free of naphthenes and aromatics, which may constitute a reforming feed charge or a good constituent of the gasoline pool;

a light fraction (<80°C) of high isoparaffin content (iso C₆, iso C₅ and iso C₄).

The high quality of the by-products, their very low content of impurities (nitrogen and sulfur) give an additional value to the conversion: the jet cut is of particular interest since it constitutes about 50% of the 80°-380°C cut, i.e. it represents a yield of from 10 to 20% with respect to the initial paraffin.

The dewaxing treatment applied to the oil obtained by hydroisomerization may be carried out according to any known method, for example by treatment with a solvent such as methyl-isobutyl-ketone or a pair of solvents such as a mixture of methyl-ethyl-ketone with toluene, at a temperature from 0°C to 70°C. The invention is not limited to a particular mode of dewaxing. The paraffin obtained may also be deoiled according to known methods.

The paraffins obtained after dewaxing of the fraction boiling above 380°C may be recycled, if so desired, before or after a second deoiling step depending on the fact that the oil is recycled or not; in many cases, a second deoiling step increases the oil yield.

The oils according to the invention have the further advantage of remarkably homogeneous distributions of both the viscosity and the viscosity index. These distributions may be determined from the rheological characteristics of the various fractions obtained by thermal diffusion of the base oil.

In the following examples, the hydroisomerization charge has been prepared as follows:

A deasphalted vacuum residuum ($d_4^{20} = 0.928$; S = 2.58 % by weight; N = 800 ppm by weight; viscosity at 98.9°C = 35.7 cst) has been hydrorefined in the presence of a catalyst whose characteristics are as follows:

Composition:	Al ₂ O ₃	56 % by weight
	SiO ₂	20 % by weight
	MoO ₃	16 % by weight
	NiO	8 % by weight
	Specific surface : 250 m ² /g	

The catalyst was previously sulfurized with H₂S diluted with H₂ in the following conditions:

T = 320°C (6 hours)

H₂S/H₂ = 4/100 (molar)

The operating conditions were the following:

Pressure : 120 kg/cm²

VVH : 0.5 liter of feed charge per liter of catalyst per hour

T : 400°C

H₂/hydrocarbon charge : 1000 liters per liter.

The resulting oil was distilled and the distillation residue, boiling above 380°C was collected and dewaxed at -22°C by means of methyl-isobutyl-ketone.

We have obtained, on the one hand, an oil of a 125 V.I. (yield : 42 % by weight) and, on the other hand, solid paraffins (yield : 8 % by weight) which constitute the hydroisomerization charge of the following examples and whose essential characteristics are given in example 1.

EXAMPLE 1 (comparison)

Manufacture of a direct 10 W 20 multigrade oil by hydroisomerization of hydrotreated paraffins with a halogen-free catalyst, without ammonia.

Characteristics of the feed charge

d_4^{20} : 0.850

S < 20 ppm by weight

N < 2 ppm by weight

Viscosity at 98.9°C : 10 cst

Average molecular weight : 620

CH₃/CH₂ ratio : 0.065

Catalyst of platinum on alumina

Composition : Al_2O_3 : 99.2%

Pt : 0.8 %

Specific surface : 232 m^2/g

Operating conditions

Pressure : 60 kg/cm^2

T : 410°C

VVH : 1

Hydrogen gas/liquid hydrocarbons : 1000 liters per liter (NTP)

Ammonia partial pressure : 0

After hydroisomerization by distillation of the reactor effluent, we obtained the following fractions:

B.P. < 80°C : light gasoline

80°–150°C : naphtha

150°–250°C : jet fuel

250°–380°C : motor gas oil

380°C : lubricating oil fraction

The lubricating oil fraction was dewaxed at –20°C by means of a mixture of methyl-ethyl-ketone and toluene in a ratio of 1/1 by volume.

In these conditions, the oil yield was 40 % by weight and the uncovered paraffin yield 25 % by weight.

The resulting oil complies with the 10 W 20 specification (Table 1) and has the following characteristics:

Viscosity at 37°C : 40.9 cst

Viscosity at 98°C : 7 cst

VI : 134

Pour point : –18°C

Initial boiling point : 380°C

Cleveland flash point : 228°C

 CH_3/CH_2 : 0.08

S ppm by weight 10

N ppm by weight 2

Conradson carbon : 0.02

EXAMPLE 2 (comparison)

The feed charge of example No. 1 is treated in the presence of the same catalyst to which 0.5 % by weight of fluorine has been added by impregnation with HBF_4 .

The operating conditions are as follows:

Pressure : 60 kg/cm^2

T : 350°C

VVH : 1

 H_2 /hydrocarbons : 1000 liters per liter (NTP) NH_3 partial pressure : 0

The outflow is fractionated as described in example 1. In these conditions 41 % by weight of oil and 25 % by weight of unconverted paraffins have been obtained.

The oil does not conform to the 10 W 20 specification since it has the following characteristics:

Viscosity at 37°C : 32 cst

Viscosity at 98°C : 5.5 cst

VI :

pour point : –18°C

Initial boiling point : 380°C

Cleveland flash point : 228°C

 CH_3/CH_2 : 0.10

S ppm by weight < 10

N ppm by weight < 2

Conradson carbon < 0.02

EXAMPLE 3

The feed charge of example No. 1 is treated with the catalyst of example No. 2 with an ammonia partial pressure of 30 g/cm^2 in the reactor.

The operating conditions are:

Pressure : 60 kg/cm^2 pp NH_3 : 0.03 kg/cm^2

T : 350°C

VVH : 1

 H_2 /hydrocarbons : 1000 liters per liter (NTP)

The operation is carried out as in example 1 and we obtain 45 % by weight of 10 W 20 oil and 28 % by weight of unconverted paraffins.

The oil has the following properties:

Viscosity at 37°C :	41 cst
Viscosity at 98°C :	7 cst
VI :	135
Pour point :	–18°C
Initial boiling point :	380°C
Cleveland flash point :	232°C
CH_3/CH_2 :	0.16
S ppm by weight	< 10
N ppm by weight	< 2
Conradson carbon	< 0.02

The desired isomerizing effect is illustrated by the change of the ratio from 0.065 to 0.16.

The oil has the following hydrocarbon composition:

	% by volume
Isoparaffins	83.7
Naphthenes	16.3
Aromatics	about 0

The yields of other products are

	% weight/charge
$\text{C}_1 + \text{C}_2 + \text{C}_3$	0.97
C_4	2.73 (i/n = 1.5)
C_5	1.98 (i/n = 3.2)
$\text{C}_5 - 80^\circ\text{C}$	1.32
80 – 150°C	2.40
150 – 250°C	8.80
250 – 380°C	8.80

EXAMPLE 4

This example is given for comparative purpose (the catalyst has an excessive fluorine content).

The feedstock of example 1 is treated with the catalyst of example 1 to which 6 % by weight of fluorine have been added by impregnation with HBF_4 .

The operating conditions are:

Pressure : 60 kg/cm^2 Partial pressure of NH_3 : 0.03 kg/cm^2

T : 350°C

VVH : 1

 H_2 /hydrocarbons : 1000 liters per liter (NTP)

We obtain 34 % by weight of oil and 22 % by weight of unconverted paraffins. The oil has the following characteristics:

Viscosity at 37°8:	18 cst
Viscosity at 98°9:	4 cst
VI:	130
Pour point:	-18°C
Initial boiling point:	380°C
Cleveland flash point:	220°C
CH ₃ /CH ₂ :	0.15
S ppm by weight	< 10
N ppm by weight	< 2
Conradson carbon	< 0.02

This oil does not satisfy the requirements of 10 W/20 multigrade oil standard.

EXAMPLE 5

Example 3 is repeated, except that the first dewaxing step is followed with a second deoiling step.

In that case, the overall yields of oil and paraffins are:

Paraffins : 25 % by weight

oil : 48 % by weight

In that case, a second deoiling step resulted in a 3 points increase of the yield of 10 W/20 oil; the rheological properties of this oil are the following:

Viscosity at 37°8 C : 44 cst

Viscosity at 98°9 C : 7.2 cst

viscosity index : 135

This yield increase is accompanied with a slight viscosity improvement which is a further advantage. The deoiling step following the first dewaxing step of the hydroisomerization product has resulted in the recovery of highly paraffinic heavy compounds.

EXAMPLE 6

Example 3 is repeated with the catalyst of example 1 to which 0.5 % by weight of fluorine have been added by impregnation, with hydrofluoric acid.

The resulting 10 W 20 oil has practically the same characteristics as the oil obtained in example 3. The oil yield is 44 %; 29 % by weight of unconverted paraffins have been recovered.

We claim:

1. A process for manufacturing a multigrade oil, in which a mixture of hydrogen with a paraffin wax containing less than 5 p.p.m. by weight of nitrogen is contacted with a catalyst comprising an alumina carrier, at least one noble metal of group VIII and 0.1 to 5% by weight of halogen at a temperature of from 250° to 450°C, the oil obtained is dewaxed so as to remove therefrom at least one fraction of unconverted paraffin wax, said process comprising carrying said contact under an ammonia partial pressure of from 1 to 500 g/cm².
2. A process according to claim 1, wherein said paraffin wax is wax recovered from hydrocrackate
3. A process according to claim 2, wherein the ammonia partial pressure is from 10 to 100 g/cm².
4. A process according to claim 2, wherein the catalyst contains from 0.3 to 0.8 % by weight of fluorine.
5. A process according to claim 2, wherein the catalyst contains from 0.3 to 3 % by weight of chlorine.
6. A process according to claim 1, wherein the contacting pressure is from 10 to 150 kg/cm².
7. A process according to claim 2, wherein the temperature is 300°-390°C and the pressure is from 50 to 80 kg/cm².
8. A process according to claim 2, wherein the group VIII metal is platinum.
9. A process according to claim 2, wherein the average molecular weight of the paraffin wax is higher than 400.
10. A process according to claim 1, wherein the said paraffin wax is obtained by dewaxing an oil fraction boiling in the range of the lubricating oils.
11. A process according to claim 1, wherein the unconverted paraffin wax is contacted again with the catalyst and hydrogen.

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