

PATENT SPECIFICATION

(11) 1 522 524

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- (21) Application No. 37402/75 (22) Filed 11 Sept. 1975
 (61) Patent of Addition to No. 1 438 645 dated 5 July 1973
 (31) Convention Application No. 7 412 155
 (32) Filed 13 Sept. 1974 in
 (33) Netherlands (NL)
 (44) Complete Specification published 23 Aug. 1978
 (51) INT CL² C10G 34/00, 23/16
 (52) Index at acceptance C5E 21H4
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(54) IMPROVED PROCESS FOR THE CONVERSION OF HYDROCARBONS

(71) We, SHELL INTERNATIONAL-
 ALE RESEARCH MAATSCHAPPIJ B.V.,
 a company organised under the laws of The
 Netherlands, of 30 Carel van Bylandtlaan,
 The Hague, The Netherlands, do hereby
 declare the invention, for which we pray that
 a patent may be granted to us, and the
 method by which it is to be performed, to be
 particularly described in and by the following
 statement:—

The Patent Application No. 31966/72
 (cognated with 10528/73) (Serial No.
 1,438,645) to which the present application
 is an addition relates to a process for
 the catalytic conversion of a residual
 hydrocarbon oil, in which process the
 oil is first demetallized and subsequently
 catalytically converted. According to the
 said Patent Application No. 31966/72
 (cognated with 10528/73) (Serial No.
 1,438,645) the demetallization is carried out
 by contacting the oil at elevated temperature
 and pressure and in the presence of hydrogen
 with a catalyst comprising one or more metals
 having hydrogenation activity on a carrier,
 which catalyst meets a number of requirements
 with regard to particle diameter and porosity.
 In the said Patent Application No. 31966/72
 (cognated with 10528/73) (Serial No.
 1,438,645) it is stated that for the prepara-
 tion of the catalysts the well-known granula-
 tion (also called nodulizing) technique can be
 used. According to this technique catalyst
 particles or catalyst carrier particles, for
 example, having a diameter of at most 0.1 mm
 are agglomerated with the aid of a granula-
 tion liquid to larger particles, for example,
 having a diameter of at least 1.0 mm.

Continued investigation of the demetalliza-
 tion or residual hydrocarbon oils using cata-
 lysts that meet the requirements of the said
 Patent Application No. 31966/72 (cognated
 with 10528/73) (Serial No. 1,438,645) with

regard to particle diameter and porosity
 showed that the activity of such catalysts pre-
 pared according to the nodulizing technique
 greatly depends on their pore volume that con-
 sists of pores with a diameter larger than
 50 nm. It has been found that these catalysts
 have an optimum activity when the said pore
 volume is at least 0.2 ml/g.

The present invention therefore relates to
 an improved process for the catalytic conver-
 sion of a residual hydrocarbon oil according to
 Patent Application No. 31966/72 (cognated
 with 10528/73) (Serial No. 1,438,645) in
 which process the oil is first demetallized and
 subsequently catalytically converted and in
 which demetallization is carried out by con-
 tacting the oil at elevated temperature and
 pressure and in the presence of hydrogen with
 a catalyst comprising one or more metals
 having hydrogenation activity on a carrier,
 which catalyst meets the following require-
 ments:

- (1) $p/d > 3.5 - 0.02 v$, in which p is the
 specific average pore diameter in nm,
 d is the specific average particle diameter
 in mm and v is the percentage of the
 total pore volume that consists of pores
 with a diameter larger than 100 nm,
- (2) the total pore volume is larger than
 0.40 ml/g,
- (3) v is smaller than 50, and
- (4) the specific surface area is larger than
 100 m²/g; for the case that the catalyst
 has such a p and d that the quotient p/d
 is larger than $3.5 - 0.02 v$, but at most
 $10 - 0.15 v$, the catalyst has to meet the
 following additional requirements:
 - (a) the nitrogen pore volume is larger
 than 0.60 ml/g
 - (b) the specific surface area is larger
 than 150 m²/g, and
 - (c) p is larger than 5 nm.

The improvement consists in the fact that the demetallization is carried out in the presence of a catalyst, which catalyst or the carrier component thereof is prepared according to the nodulizing technique and whose pore volume consisting of pores with a diameter larger than 50 nm is at least 0.2 ml/g.

In the process according to the invention preference is given to a catalyst whose pore volume consisting of pores with a diameter larger than 50 nm is at least 0.3 ml/g.

In carrying out the nodulizing technique catalyst particles or catalyst-carrier particles, for example, having a diameter of at most 0.1 mm are agglomerated with the aid of a granulation liquid to larger particles, for example, having a diameter of at least 1.0 mm. In actual practice the nodulizing technique is usually effected as follows. Catalyst-carrier material having a diameter of at most 0.1 mm is placed on a rotating disc provided with a raised edge and a scraping device. The disc is disposed at a specific angle to the horizontal plane. A granulation liquid is sprayed onto the carrier material that is in continuous motion on the disc. In practice, when alumina is used as a carrier, a dilute aqueous solution of acetic acid or citric acid is usually employed as the granulation liquid. During the residence of the small particles on the disc larger particles are formed from the small ones by agglomeration. The nodulizing technique can be carried out both batchwise and continuously. When the continuous process is used finely dispersed material is continuously supplied to the rotating disc and agglomerated material continuously leaves the disc via the top of the raised edge when this is in its lowest position. After the agglomerated particles have left the disc a sieve fraction with the desired diameter is separated from it. Particles with a diameter smaller than that of the desired sieve fraction may be recycled to the disc. If the agglomerated material contains particles with a diameter larger than that of the desired sieve fraction, these particles, after reduction of the particle size, for instance by grinding, may also be recycled to the disc. The conversion of the agglomerated material with the desired particle size into a suitable carrier material takes place by drying and calcination. The emplacement of one or more metals with hydrogenation activity on the carrier material thus prepared, is usually effected by impregnation with an aqueous solution of compounds of the respective metals, followed by drying and calcination of the impregnated material.

In the process according to the invention use is preferably made of catalysts comprising 0.1—15 pbw of one or more metals having hydrogenation activity per 100 pbw carrier. The metals having hydrogenation activity are preferably selected from nickel, cobalt, molybdenum and vanadium. It is further preferred

that the catalysts should comprise at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum and vanadium and further that the atomic ratio between nickel and/or cobalt on the one hand and molybdenum and/or vanadium on the other hand is between 0.05 and 3.0. Suitable metal combinations are nickel-vanadium, cobalt-molybdenum and nickel-molybdenum.

The quantity of metals having hydrogenation activity present in the catalysts preferably amounts to 0.5—10 pbw and in particular 2.0—7.5 pbw per 100 pbw carrier. Especially preferred demetallization catalysts according to the invention are catalysts comprising about 0.5 pbw nickel and about 2 pbw vanadium per 100 pbw carrier, as well as catalysts comprising about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier. The metals may be present on the carrier in the metallic form or in the form of their oxides or sulphides. Preference is given to catalysts in which the metals are present on the carrier in the form of their sulphides. Sulphidation of the present catalysts may be carried out by any technique for the sulphidation of catalysts known in the art.

Suitable carriers for the present catalysts are oxides of the elements of Group II, III or IV of the Periodic Table of elements or mixtures of the said oxides, such as silica, alumina, magnesia, zirconia, silica-alumina and silica-magnesia. If for the preparation of the present catalysts use is made of any of the above-mentioned oxidic carriers, preference is given to the application of alumina or silica for this purpose. Another type of material that is very suitable to serve as a carrier for the present catalysts is soot, in particular a soot obtained as by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam. In addition to the suitability of soot as a carrier for the present demetallization catalysts, the use of soot for this purpose carries with it an additional advantage that is not achieved if any of the oxidic carriers mentioned hereinbefore is applied. This can be elucidated as follows. Although the catalysts according to the invention show a long life in the demetallization of residual hydrocarbon oils, even these catalysts will in the long run be deactivated as result of the deposition of large amounts of metals, in particular vanadium and nickel, and therefore, after a certain time of operation, they have to be replaced. If it is intended to recover the deposited metals from the deactivated catalyst, the use of a catalyst on soot as the carrier offers the considerable advantage over catalysts on other carrier materials that the carrier can simply be removed from the deactivated catalyst by combustion, after which a mixture of the metals concerned is left behind in the form of their

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oxides for further working up.

During the investigation of the preparation of demetallization catalysts according to the nodulizing technique five modifications of the usual procedure were found by the Applicants, which modifications will each produce a favourable effect. These modifications will be described in more detail hereinafter.

1. In the preparation of catalysts on the basis of alumina as a carrier an aqueous solution of acetic acid or citric acid is usually applied as the granulation liquid. It has been found that when dilute nitric acid is applied as the granulation liquid, alumina-based catalysts can be obtained with a crushing strength and density that are considerably higher than when an aqueous solution of citric acid or acetic acid is applied.

2. When in the preparation of the catalysts the starting material is mixed with a certain amount of glass powder and, in addition, the particles formed by the nodulizing technique are subjected to a calcination at a temperature above the softening temperature of glass, catalysts can be obtained with a considerably increased crushing strength. The amount of glass powder applied is preferably 0.5—15%w based on the amount of starting material with which it is mixed.

3. When phosphorus is incorporated into the catalysts their activity in the demetallization of residual hydrocarbon oils is considerably increased. The incorporation of phosphorus into the catalysts can take place during any stage in the catalyst preparation. The incorporation of phosphorus can, for instance, very suitably take place by addition of a phosphorus compound to the granulation liquid and/or to the impregnation liquid that is applied for the emplacement of the metals with hydrogenation activity on the particles formed. The amount of phosphorus compound is preferably chosen in such a way that a catalyst is obtained comprising 0.5—5%w phosphorus per 100 pbw carrier.

4. In the catalyst preparation according to the nodulizing technique larger particles, which are more or less spherical, are formed from the starting material. The size of the particles formed is determined, among other factors, by the residence time of the material on the rotating disc. After the particles have attained approximately the desired size they are removed from the disc and are dried and calcined. It has been found that catalysts with a considerably higher density can be prepared, when the particles formed, after they have left the rotating disc but before drying and calcination, are rotated for some time, for instance in a rotating drum. Such

rotation of the particles formed preferably takes place during a period of time at least equal to the residence time of the material on the rotating disc.

5. In the catalyst preparation according to the nodulizing technique the usual procedure is for the carrier particles, after they have been formed on the disc, to be dried and calcined, followed by emplacement of the desired metals with hydrogenation activity on the calcined material, for instance by impregnation with an aqueous solution containing salts of the relevant metals. Finally, the impregnated material is dried and calcined. It has been found that this catalyst preparation can be considerably simplified by incorporating the metal salts into the granulation liquid. When the emplacement of the metals in the catalyst is carried out in this way the separate impregnation step as well as the second drying and calcination steps can be omitted, which in the large-scale preparation of the present catalysts obviously affords a considerable saving.

Examples of suitable water-soluble metal compounds which may be applied in the preparation of the present catalysts are nitrates, chlorides, formates and acetates of nickel and cobalt, ammonium molybdate, vanadyl oxalate, vanadyl sulphate and vanadyl acetyl acetate and ammonium vanadate.

For the catalytic hydrodemetallization of residual hydrocarbon oils according to the invention use is preferably made of catalyst particles having a d of 1.0—4.0 mm and in particular of 1.5—3.5 mm.

If in the preparation according to the invention a catalyst is applied with such a p and d that the quotient p/d is larger than 10—0.15 v, it is preferred to choose a catalyst having a total pore volume of at least 0.50 ml/g and a specific surface area above 150 m²/g.

The invention will now be further described with the aid of the following example, which refers to the demetallization step of the process.

Example.

A residual hydrocarbon oil having a total vanadium and nickel content of 62 ppmw, a C₆-asphaltenes content of 6.4%w and a sulphur content of 3.9%w, which oil had been obtained as a residue in the atmospheric distillation of a Middle East crude oil (oil B according to Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) was catalytically hydrometallized at different space velocities and using 5 different catalysts. To this end the oil together with hydrogen was passed downwards through a cylindrical vertically disposed fixed catalyst bed at a temperature of 420°C, a total pres-

sure of 150 bar and an exit gas rate of 250 Nl H_2 /kg of fresh feed. The catalysts were applied in the form of their sulphides.

The preparation of the 5 catalysts which were applied in the demetallization experiments as well as the preparation of 3 other catalysts according to the invention, which had been prepared via the nodulizing technique are mentioned hereinafter. The results of the demetallization experiments together with the space velocities applied and the properties of the catalysts have been collected in the table.

Catalyst preparation

Catalyst A

As starting material use was made of an alumina obtained by spray-drying with a d smaller than 0.09 mm, this alumina having a pore volume of 1.2 ml/g consisting of pores with a diameter larger than 50 nm. Of this alumina 100 g was put on a rotating disc and 100 ml of an aqueous solution containing 3.5 g citric acid was gradually sprayed onto it. The rotating disc, which was provided with a raised edge of 10 cm high, had a diameter of 40 cm. The disc made 40 revolutions per minute and was disposed at an angle of 45° to the horizontal plane. After 15 minutes' residence time the nodules formed were removed from the disc. After drying at 120°C a sieve fraction with a d of 2.0 mm was isolated from the dried material. After 1 hour's calcination at 600°C the particles were impregnated with an aqueous solution comprising nickel nitrate and ammonium molybdate. Finally, the impregnated material was dried at 120°C and calcined for 1 hour at 500°C. The catalyst thus prepared comprised 1 pbw nickel and 4 pbw molybdenum per 100 pbw alumina.

Catalyst B

This catalyst was prepared in substantially the same way as catalyst A, the difference being however, that in the present case 100 ml of an aqueous solution comprising 3.5 g nitric acid was used as the granulation liquid.

Catalyst C

This catalyst was prepared in substantially the same way as catalyst A, the difference being, however, that in the present case 2 g glass powder with a d smaller than 0.09 mm was added to the alumina starting material and that after calcination at 600°C another calcination was carried out for 1 hour at 800°C.

Catalyst D

This catalyst was prepared in substantially the same way as catalyst C, the difference being, however, that in the present case so much $NH_4H_2PO_4$ was added to the impregnation liquid comprising nickel and molybdenum

that a catalyst was obtained comprising in addition to 1 pbw nickel and 4 pbw molybdenum, 1 pbw phosphorus per 100 pbw alumina.

Catalyst E

This catalyst was prepared in substantially the same way as catalyst C, the difference being, however, that in the present case the nodules, after having left the disc, were rotated for another hour in a rotating drum.

Catalyst F

This catalyst was prepared in substantially the same way as catalyst A, the difference being, however, that in the present case the starting material was an alumina obtained by spray-drying having a pore volume of 0.36 ml/g consisting of pores with a diameter larger than 50 nm.

Catalyst G

The starting material was a soot with a d smaller than 0.1 mm, which soot had a pore volume of 0.58 ml/g consisting of pores with a diameter larger than 50 nm. The soot had been obtained as a by-product of the partial oxidation of hydrocarbons with air. The soot being available in the form of a slurry in water, was isolated from it by filtering, drying of the filter cake and grinding of the dried material to the particle size mentioned. The nodules were prepared from the soot in substantially the same way as the nodules from alumina as described for catalyst A, the difference being, however, that in the present case an aqueous solution of ligno sulphonate was used as the granulation liquid. After 15 minutes' residence time the nodules were removed from the disc. After drying at 120°C a sieve fraction with a d of 1.8 mm was isolated from the dried material. After 1 hour's calcination in a nitrogen stream at 700°C these particles were impregnated with an aqueous solution comprising nickel nitrate and vanadyl oxalate. Finally, the impregnated material was dried at 120°C and calcined for 1 hour at 500°C in a nitrogen stream. The catalyst thus prepared comprised 0.5 pbw nickel and 2 pbw vanadium per 100 pbw soot.

Catalyst H

This catalyst was prepared in substantially the same way as catalyst G, the difference being, however, that in the present case the starting material was a soot obtained as a by-product of the partial oxidation of hydrocarbons with air and having a pore volume of 0.26 ml/g consisting of pores with a diameter larger than 50 nm and that the nodules formed, after having left the disc, were rotated for another hour in a rotating drum.

TABLE

Catalyst No.	A	B	C	D	E	F	G	H
Specific surface area, m ² /g	312	270	248	264	239	230	450	495
Total pore volume, ml/g	1.28	1.18	1.41	1.39	1.10	0.85	1.50	1.24
Nitrogen pore volume, ml/g	0.73	0.69	0.69	0.74	0.65	0.70	0.80	0.88
Pore volume consisting of pores with a diameter larger than 50 nm, ml/g	0.59	0.63	0.75	0.80	0.55	0.10	0.36	0.14
v, %	36	41	44	47	38	7	8	6
d, mm	2.0	2.3	2.4	2.9	2.5	1.5	1.8	1.2 ^s
p, mm	38	62	67	90	60	7.8	38	27
Crushing strength, kg/cm ²	8.0	9.5	9.4	9.1	9.3	7.8	6.5	7.2
Density, g/cm ³	0.29	0.36	0.31	0.30	0.39	0.35	0.31	0.35
Experiment No.			1	2		3	4	5
Space velocity, 1.1 ⁻¹ h ⁻¹			4.6	4.6		3.0	3.1	3.1
V+Ni removal (%w) after processing 5 tons feed/kg catalyst			50	55		41	51	42

All catalysts mentioned in the table are catalysts that can be applied according to Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645). Catalysts A—E, G and H with $p/d > 10.0 - 0.15 v$ also meet the other requirements of the said Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) with respect to $v (< 50\%)$, total pore volume (> 0.40 ml/g) and specific surface area (> 100 m²/g). Catalyst F with $10.0 - 0.15 v > p/d > 3.5 - 0.02 v$ also meets the other requirements of the said Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) with respect to $v (< 50\%)$, $p (> 5\text{nm})$, nitrogen pore volume (> 0.60 ml/g) and specific surface area (> 150 m²/g).

Of the catalysts mentioned in the table, catalysts A—E and G, which have been prepared according to the nodulizing technique and the pore volume of which consisting of pores with a diameter larger than 50 nm is at least 0.2 ml/g, are catalysts that can be applied according to the present patent application. Catalysts F and H, although prepared according to the nodulizing technique, but whose pore volume consisting of pores with a diameter larger than 50 nm is less than 0.2 ml/g, fall outside the scope of the present patent application. They have been included in the table for comparison.

Comparison of the crushing strengths and the densities of catalysts A and B shows the favourable effect of the use of dilute nitric acid as the granulation liquid instead of an aqueous citric acid solution.

The favourable effect of the incorporation of glass powder in the starting material in combination with calcination at a temperature above the softening temperature of glass is found when comparing the crushing strengths of catalysts A and C.

Comparison of the densities of catalysts C and E shows the favourable effect of post-rotation of the nodules after these have attained the desired size on the rotating disc.

According to Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) a catalyst, under the conditions applied in the present demetallization experiments, preferably meets the criterion that the catalyst is still capable of removing more than 40%w of the total amount of vanadium and nickel present in oil B after 5 tons of this oil have been processed over the catalyst at a space velocity of at least $2.9 \text{ l.l}^{-1} \cdot \text{h}^{-1}$.

All the experiments shown in the table (in which the catalysts met the above requirements concerning %w Ni+V removal) are demetallization experiments within the scope of Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645). Of the experiments shown in the table, experiments 1, 2 and 4 (in which catalysts C,

D and G were applied, respectively) are demetallization experiments according to the present invention. Experiments 3 and 5 (in which catalysts F and H were applied, respectively) fall outside the scope of the present invention. They have been included for comparison.

The influence of the catalysts' pore volume consisting of pores with a diameter larger than 50 nm on their demetallization activity is found when comparing the results of experiments 1 and 2 with those of experiment 3 and comparing the results of experiment 4 with those of experiment 5. It has been found that catalysts C and D (in which the said pore volume is more than 0.20 ml/g) are still capable of removing 50 and 55%w V+Ni, respectively, after processing 5 tons feed/kg catalyst at a space velocity of $4.6 \text{ l.l}^{-1} \cdot \text{h}^{-1}$, whereas catalyst F (in which the said pore volume is less than 0.20 ml/g) is only capable of removing 41%w V+Ni after processing of the same amounts of feed/kg catalyst, while, moreover, the space velocity is only $3.0 \text{ l.l}^{-1} \cdot \text{h}^{-1}$. A comparable situation is found with catalysts G and H. Catalyst G (in which the said pore volume is more than 0.20 ml/g) is still capable of removing 51%w V+Ni after processing 5 tons feed/kg catalyst at a space velocity of $3.1 \text{ l.l}^{-1} \cdot \text{h}^{-1}$, whereas catalyst H (in which the said pore volume is less than 0.20 ml/g), is only capable of removing 42%w V+Ni after processing of the same amount of feed/kg catalyst at the same space velocity.

Comparison of the demetallization activities of catalysts C and D shows the favourable influence of the incorporation of phosphorus in the catalysts.

WHAT WE CLAIM IS:—

1. An improved process for the catalytic conversion of a residual hydrocarbon oil according to Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) in which process the oil is first demetallized and subsequently catalytically converted and in which demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst meets the following requirements:

- (1) $p/d > 3.5 - 0.02 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm,
- (2) the total pore volume is larger than 0.40 ml/g,
- (3) v is smaller than 50, and
- (4) the specific surface area is larger than

All catalysts mentioned in the table are catalysts that can be applied according to Patent Application No. 31966/72 (cognated with 10528/73 (Serial No. 1,438,645). Catalysts A—E, G and H with $p/d > 10.0-0.15 v$ also meet the other requirements of the said Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) with respect to $v(<50\%)$, total pore volume (>0.40 ml/g) and specific surface area (>100 m²/g). Catalyst F with $10.0-0.15 v > p/d > 3.5-0.02 v$ also meets the other requirements of the said Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) with respect to $v(<50\%)$, $p(>5\text{nm})$, nitrogen pore volume (>0.60 ml/g) and specific surface area (>150 m²/g).

Of the catalysts mentioned in the table, catalysts A—E and G, which have been prepared according to the nodulizing technique and the pore volume of which consisting of pores with a diameter larger than 50 nm is at least 0.2 ml/g, are catalysts that can be applied according to the present patent application. Catalysts F and H, although prepared according to the nodulizing technique, but whose pore volume consisting of pores with a diameter larger than 50 nm is less than 0.2 ml/g, fall outside the scope of the present patent application. They have been included in the table for comparison.

Comparison of the crushing strengths and the densities of catalysts A and B shows the favourable effect of the use of dilute nitric acid as the granulation liquid instead of an aqueous citric acid solution.

The favourable effect of the incorporation of glass powder in the starting material in combination with calcination at a temperature above the softening temperature of glass is found when comparing the crushing strengths of catalysts A and C.

Comparison of the densities of catalysts C and E shows the favourable effect of post-rotation of the nodules after these have attained the desired size on the rotating disc.

According to Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) a catalyst, under the conditions applied in the present demetallization experiments, preferably meets the criterion that the catalyst is still capable of removing more than 40%w of the total amount of vanadium and nickel present in oil B after 5 tons of this oil have been processed over the catalyst at a space velocity of at least $2.9 \text{ l.l}^{-1} \cdot \text{h}^{-1}$.

All the experiments shown in the table (in which the catalysts met the above requirements concerning %w Ni+V removal) are demetallization experiments within the scope of Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645). Of the experiments shown in the table, experiments 1, 2 and 4 (in which catalysts C,

D and G were applied, respectively) are demetallization experiments according to the present invention. Experiments 3 and 5 (in which catalysts F and H were applied, respectively) fall outside the scope of the present invention. They have been included for comparison.

The influence of the catalysts' pore volume consisting of pores with a diameter larger than 50 nm on their demetallization activity is found when comparing the results of experiments 1 and 2 with those of experiment 3 and comparing the results of experiment 4 with those of experiment 5. It has been found that catalysts C and D (in which the said pore volume is more than 0.20 ml/g) are still capable of removing 50 and 55%w V+Ni, respectively, after processing 5 tons feed/kg catalyst at a space velocity of $4.6 \text{ l.l}^{-1} \cdot \text{h}^{-1}$, whereas catalyst F (in which the said pore volume is less than 0.20 ml/g) is only capable of removing 41%w V+Ni after processing of the same amounts of feed/kg catalyst, while, moreover, the space velocity is only $3.0 \text{ l.l}^{-1} \cdot \text{h}^{-1}$. A comparable situation is found with catalysts G and H. Catalyst G (in which the said pore volume is more than 0.20 ml/g) is still capable of removing 51%w V+Ni after processing 5 tons feed/kg catalyst at a space velocity of $3.1 \text{ l.l}^{-1} \cdot \text{h}^{-1}$, whereas catalyst H (in which the said pore volume is less than 0.20 ml/g), is only capable of removing 42%w V+Ni after processing of the same amount of feed/kg catalyst at the same space velocity.

Comparison of the demetallization activities of catalysts C and D shows the favourable influence of the incorporation of phosphorus in the catalysts.

WHAT WE CLAIM IS:—

1. An improved process for the catalytic conversion of a residual hydrocarbon oil according to Patent Application No. 31966/72 (cognated with 10528/73) (Serial No. 1,438,645) in which process the oil is first demetallized and subsequently catalytically converted and in which demetallization is carried out by contacting the oil at elevated temperature and pressure and in the presence of hydrogen with a catalyst comprising one or more metals having hydrogenation activity on a carrier, which catalyst meets the following requirements:

- (1) $p/d > 3.5-0.02 v$, in which p is the specific average pore diameter in nm, d is the specific average particle diameter in mm and v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm,
- (2) the total pore volume is larger than 0.40 ml/g,
- (3) v is smaller than 50, and
- (4) the specific surface area is larger than



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100 m²/g; for the case that the catalyst has such a p and d that the quotient p/d is larger than 3.5—0.02 v, but at most 10—0.15 v, the catalyst has to meet the following additional requirements:

- (a) the nitrogen pore volume is larger than 0.60 ml/g
- (b) the specific surface area is larger than 150 m²/g, and
- (c) p is larger than 5 nm,

wherein the demetallization is carried out in the presence of a catalyst, which catalyst or the carrier component thereof is prepared according to the nodulizing technique and whose pore volume consisting of pores with a diameter larger than 50 nm is at least 0.2 ml/g.

2. A process according to claim 1, in which process the demetallization is carried out in the presence of a catalyst whose pore volume consisting of pores with a diameter larger than 50 nm, is at least 0.3 ml/g.

3. A process according to claim 1 or 2, in which process the demetallization is carried out in the presence of a catalyst comprising 0.1—15 pbw of one or more metals having hydrogenation activity per 100 pbw carrier material.

4. A process according to claim 3, in which process the demetallization is carried out in the presence of a catalyst comprising 0.5—10 pbw and preferably 2.0—7.5 pbw of one or more metals having hydrogenation activity per 100 pbw carrier material.

5. A process according to any one of claims 1—4, in which process the demetallization is carried out in the presence of a catalyst comprising as metals with hydrogenation activity one or more metals selected from nickel, cobalt, molybdenum and vanadium.

6. A process according to claim 5, in which process the demetallization is carried out in the presence of a catalyst comprising at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum and vanadium.

7. A process according to claim 6, in which process the demetallization is carried out in the presence of a catalyst in which the atomic ratio between nickel and/or cobalt on the one hand and molybdenum and/or vanadium on the other hand is between 0.05 and 3.0.

8. A process according to claim 7, in which process the demetallization is carried out in the presence of a catalyst comprising either about 0.5 pbw nickel and about 2 pbw vanadium, or about 1 pbw nickel or cobalt and about 4 pbw molybdenum per 100 pbw carrier material.

9. A process according to any one of claims 1—8, in which process the demetallization is carried out in the presence of a catalyst containing silica, alumina or soot as a carrier.

10. A process according to claim 9, in

which process the demetallization is carried out in the presence of a catalyst containing soot as the carrier, which soot has been obtained as a by-product of the partial oxidation of hydrocarbons with air, oxygen or mixtures of air and oxygen, either in the presence or in the absence of steam.

11. A process according to any one of claims 1—10, in which process the demetallization is carried out in the presence of a catalyst comprising the metals with hydrogenation activity in the form of their sulphides.

12. A process according to any one of claims 9—11, in which process the demetallization is carried out in the presence of a catalyst comprising alumina as a carrier and in the preparation of which dilute nitric acid is applied as the granulation liquid.

13. A process according to any one of claims 1—12, in which process the demetallization is carried out in the presence of a catalyst in the preparation of which the starting material, from which larger particles are formed by the nodulizing technique, is mixed with a certain amount of glass powder and in which the particles formed by the nodulizing technique are subjected to a calcination at a temperature above the softening temperature of glass.

14. A process according to claim 13, in which process the amount of glass powder applied is 0.5—15%w based on the amount of starting material with which it is mixed.

15. A process according to any one of claims 1—14, in which process the demetallization is carried out in the presence of a catalyst comprising phosphorus, preferably in amounts of 0.5—5%w per pbw carrier material.

16. A process according to any one of claims 1—15, in which process the demetallization is carried out in the presence of a catalyst in the preparation of which the particles formed by nodulizing with the aid of a rotating disc provided with a raised edge and a scraping device are post-rotated, after they have left the rotating disc but before drying and calcination, during a period of time at least equal to the residence time of the material on the rotating disc.

17. A process according to any one of claims 1—16, in which process the demetallization is carried out in the presence of a catalyst in the preparation of which a granulation liquid was applied in which one or more compounds of metals with hydrogenation activity are incorporated.

18. A process according to any one of claims 1—17, in which process the demetallization is carried out in the presence of a catalyst with a d of 1.0—4.0 mm and preferably of 1.5—3.5 mm.

19. A process according to any one of claims 1—18, in which process the demetallization is carried out in the presence of a

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catalyst with such a p and d that the quotient p/d is larger than $10-0.15v$, which catalyst has a total pore volume of at least 0.50 ml/g and a specific surface area above 150 m²/g.

- 5 20. A process for the catalytic conversion of a residual hydrocarbon oil, in which process the oil is first demetallized and subsequently catalytically converted and in which the demetallization is carried out substantially as

described hereinbefore with particular reference to any of experiments 1, 2 and 4.

21. Hydrocarbon oils obtained by a process as claimed in claim 20.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.