

PATENT SPECIFICATION

(11) 1 505 886

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- (21) Application No. 13668/75 (22) Filed 3 April 1975/
 (31) Convention Application No. 7 406 730
 (32) Filed 20 May 1974 in
 (33) Netherlands (NL)
 (44) Complete Specification published 30 March 1978
 (51) INT CL² C10G 23/02, 23/16
 (52) Index at acceptance C5E 21H4
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(54) A PROCESS FOR THE CATALYTIC HYDRODESULPHURISATION OF VANADIUM- AND NICKEL-CONTAINING RESIDUAL HYDROCARBON OILS

(71) We, SHELL INTERNATIONALE 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 present invention is concerned with a process for the catalytic hydrodesulphurization of vanadium- and nickel-containing residual-hydrocarbon oils without catalyst replenishment, which process is carried out in the presence of a quantity of water corresponding with a water vapour partial pressure during the process of 0.5—30 bar. A process of this type is described in our U.K. Patent Specification 1,468,160. According to Specification 1,468,160, catalysts are used for this purpose showing a life and average activity which exceed established minimum values if they are used for residue desulphurization in a standard catalyst test. They have a total pore volume of more than 0.30 ml/g, less than 10% of the total pore volume being present in pores having a diameter of more than 100 nm, and they have a specific average pore diameter (p) and a specific average particle diameter (d) such that the quotient $p/(d)^{0.9}$ satisfies the requirement:

$$4 \times 10^{-4} \times (P_H)_2^2 \leq p/(d)^{0.9} \leq 5 + 24 \times 10^{-4} \times (P_H)_2^2,$$

where P_H represents the hydrogen partial pressure used (p in nm, d in mm, P_H in bar). As is demonstrated in Specification 1,468,160, catalysts having a quotient $p/(d)^{0.9}$ of less than $4 \times 10^{-4} \times (P_H)_2^2$ or larger than $5 + 24 \times 10^{-4} \times (P_H)_2^2$ show a life in the standard catalyst test which is too short and/or an average activity which is too low to satisfy the minimum requirements in respect of life and average activity stated in the patent application.

Since the life of a catalyst for the hydrodesulphurization of vanadium- and nickel-containing residual hydrocarbon oils in the presence of water without catalyst replenishment, is shorter according as the catalyst displays a higher average desulphurization activity, the invention disclosed in Specification 1,468,160 is in fact based on a compromise between these two catalyst properties.

Continued research by the Applicants into this subject has shown that considerably better results can be obtained if the residual hydrocarbon oil is successively contacted with two or more different catalysts as compared with a process in which only one catalyst is used. The use of two or more different catalysts (such two or more different catalysts being referred to herein as a "combination", the latter not implying a mixture however) produces an improvement in activity and/or life of the combination in respect of each of the catalysts individually, i.e. under the same conditions a more thorough desulphurization is effected or by maintaining a certain desulphurization level (as is

customary in practice) the catalyst life is prolonged. However, these better results are only achieved if the catalysts used satisfy a number of requirements in respect of their porosity, particle size and volumetric ratio.

A combination of two or more catalysts is defined herein as consisting of a catalyst I and a catalyst II, the designation "catalyst II" referring to the second catalyst when the combination comprises only two catalysts, or to the last catalyst when the combination comprises more than two catalysts, and the designation "catalyst I" referring to the first catalyst when the combination comprises only two catalysts, or to all the catalysts with the exception of the last one when the combination comprises more than two catalysts ("first", "second" and "last" as seen in the direction of the liquid flow over the various catalysts of the combination).

When a combination of two catalysts is used, the requirements in respect of porosity, particle size and volumetric ratio of the catalysts are as follows:

(a) in respect of the total pore volume and the percentage thereof present in pores having a diameter in excess of 100 nm the same requirements apply to catalyst I and catalyst II as to the catalysts according to the U.K. patent specification mentioned above, i.e. they have a total pore volume of more than 0.30 ml/g, less than 10% of the total pore volume being present as pores having a diameter in excess of 100 nm;

(b) catalyst II has a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

$$10^{-4} \times (P_H)_2^2 \leq [p/(d)^{0.9}]_{\text{cat. II}} \leq 4 + 13 \times 10^{-4} \times (P_H)_2^2$$

(c) catalyst I has a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. I}}$ satisfies the requirement:

$$1.2 \times [p/(d)^{0.9}]_{\text{cat. II}} \leq [p/(d)^{0.9}]_{\text{cat. I}} \leq 5 + 30 \times 10^{-4} \times (P_H)_2^2$$

(d) the percentage of the total catalyst volume taken up by catalyst II (% vol. of catalyst II) lies between 10 and 90% and satisfies the following requirement:

$$40 \times \left(\frac{S_F - S_P}{S_P} \times 100 \right)^2 \times (P_H)_2^{-2} \leq \% \text{ vol. cat. II} \leq 300 \times \left(\frac{S_F - S_P}{S_P} \times 100 \right)^2 \times (P_H)_2^{-2},$$

where S_F represents the sulphur content of the feed and S_P the desired sulphur content of the desulphurized product, expressed in percentage by weight.

When a combination of more than two catalysts is used, the requirements in respect of porosity, particle size and volumetric ratio of the catalysts are essentially in agreement with those mentioned above under (a)—(d) for a combination of two catalysts, with the proviso that:

(e) the requirements mentioned under (a) in respect of the total pore volume and the percentage thereof in pores having a diameter in excess of 100 nm now apply to each of the individual catalysts comprised in catalyst I and catalyst II,

(f) the requirement mentioned under (c) in respect of $[p/(d)^{0.9}]_{\text{cat. I}}$ now applies to the average $p/(d)^{0.9}$ of catalyst I, determined as the weight average of the values $p/(d)^{0.9}$ of each of the individual catalysts of which catalyst I is composed, and

(g) each of the individual catalysts of which catalyst I is composed has a p and d such that the quotient $p/(d)^{0.9}$ of each of these catalysts exceeds $[p/(d)^{0.9}]_{\text{cat. II}}$.

The present invention is therefore concerned with a process for the catalytic hydrodesulphurization of vanadium- and nickel-containing residual hydrocarbon oils without catalyst replenishment, which process is carried out in the presence of a quantity of water corresponding with a water vapour partial pressure during the process of 0.5—30 bar, the hydrocarbon oil being consecutively contacted with a catalyst I and a catalyst II which satisfy the requirements indicated above under (a)—(g).

When the requirements which are now made of the quotient $p/(d)^{0.9}$ of catalyst I and catalyst II are compared with those which were made in the past of this quotient of the catalysts employed in the process described in Specification 1,468,160 mentioned above, it is found that a number of the catalysts which were rejected in the past are now eligible for application in the catalyst combination according to the present invention. Catalysts outside the scope of Specification 1,468,160 which are now eligible for application are:

- (a) As catalyst II, a catalyst having a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

$$10^{-4} \times (P_H)_2^2 \leq [p/(d)^{0.9}]_{\text{cat. II}} < 4 \times 10^{-4} \times (P_H)_2^2$$

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- (b) When using one catalyst as catalyst I, a catalyst I having a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. I}}$ satisfies the requirement:

$$1.2 \times 10^{-4} \times (P_H)_2^2 \leq [p/(d)^{0.9}]_{\text{cat. I}} < 4 \times 10^{-4} \times (P_H)_2^2$$

- (c) When using one catalyst as catalyst I, a catalyst I having a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. I}}$ satisfies the requirement:

$$5 + 24 \times 10^{-4} \times (P_H)_2^2 \leq [p/(d)^{0.9}]_{\text{cat. I}} \leq 5 + 30 \times 10^{-4} \times (P_H)_2^2$$

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In addition to an extension in respect of the catalysts referred to in Specification 1,468,160, the present invention also entails limitations. Catalysts usable according to Specification 1,468,160 which are not eligible for application in the process of the present invention are inter alia:

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- (a) as catalyst II, a catalyst having a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

$$5 + 24 \times 10^{-4} \times (P_H)_2^2 \geq [p/(d)^{0.9}]_{\text{cat. II}} > 4 + 13 \times 10^{-4} \times (P_H)_2^2$$

- (b) When using one catalyst as catalyst I, a catalyst I having a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. I}}$ satisfies the requirement:

$$4 \times 10^{-4} \times (P_H)_2^2 \leq [p/(d)^{0.9}]_{\text{cat. I}} < 1.2 \times [p/(d)^{0.9}]_{\text{cat. II}}$$

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This situation occurs if as catalyst II a catalyst is used having a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

$$[p/(d)^{0.9}]_{\text{cat. II}} > 3.3 \times 10^{-4} \times (P_H)_2^2$$

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For the way in which p and d are determined, reference is made to U.K. Patent Specifications 1,408,759 and 1,406,804, wherein the determination of these parameters has been described in detail.

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According to the present invention the hydrodesulphurization is carried out in the presence of a quantity of water corresponding with a water vapour partial pressure during the process of 0.5—30 bar. The quantity of water used preferably corresponds with a water vapour partial pressure during the process of 1—15 bar and in particular of 1—5 bar. The required quantity of water may be added to the gas and/or liquid stream which is passed over the catalysts. The water may be added as such or in the form of steam. Water as such may, for example, be added to the residual hydrocarbon oil to be desulphurized, or steam may be added to the hydrogen stream which is supplied to the process. If desired, instead of water a compound may be added from which water is formed under the prevailing reaction conditions, such as a lower alcohol.

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The catalysts which are used in the process according to the invention as catalyst II preferably have a total pore volume in excess of 0.45 ml/g and a surface in excess of 100 m²/g and in particular a surface in excess of 150 m²/g. In addition, they preferably have a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

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$$[p/(d)^{0.9}]_{\text{cat. II}} \geq 1.2 \times 10^{-4} \times (P_H)_2^2$$

In the hydrodesulphurization according to the invention there is particular preference for using a catalyst II which has a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

$$1.2 \times 10^{-4} \times (P_H)_2^2 \leq [p/(d)^{0.9}]_{\text{cat. II}} \leq 4 + 13 \times 10^{-4} \times (P_H)_2^2$$

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which catalyst also has a total pore volume in excess of 0.45 ml/g of which at least 0.4 ml/g is present in pores having a diameter of at least $0.7 \times p$ and at most $1.7 \times p$ and a sharp pore diameter distribution characterized in that

- (a) less than 20% of the total pore volume is present in pores having a diameter smaller than $0.7 \times p$ and
- (b) less than 20% of the total pore volume is present in pores having a diameter greater than $1.7 \times p$.

As has already been noted above, one catalyst or two or more catalysts can be used as catalyst I in the process according to the invention. The process is preferably carried out using one catalyst as catalyst I. If use is made of two or more catalysts as catalyst I, the catalysts of which catalyst I is composed may occur in the desulphurization reactor either mixed with each other and/or separated from each other (for example in separate beds or layers). When two or more catalysts are used as catalyst I, preference is given to a process in which the catalysts of which catalyst I is composed occur in the reactor separated from each other, preferably in such a sequence that the quotient $p/(d)^{0.9}$ of each of the catalysts of which catalyst I is composed is smaller than that of the preceding catalyst, i.e. that the quotient $p/(d)^{0.9}$ decreases in the direction of the liquid flow over the catalyst combination. When one catalyst is used as catalyst I and also when two or more catalysts are used as catalyst I, catalysts having a total pore volume in excess of 0.40 ml/g are preferred. It is also preferred that a catalyst I is used with a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. I}}$ satisfies the requirement:

$$[p/(d)^{0.9}]_{\text{cat. I}} \geq 1.4 \times [p/(d)^{0.9}]_{\text{cat. II}}$$

with the proviso that when two or more catalysts are used as catalyst I, this preference in respect of $[p/(d)^{0.9}]_{\text{cat. I}}$ applies to the average $p/(d)^{0.9}$ of catalyst I, which is determined as the weight average of the values $p/(d)^{0.9}$ of each of the individual catalysts of which catalyst I is composed.

Catalysts which are used according to the invention preferably contain 0.5—20 parts by weight and in particular 0.5—10 parts by weight of nickel and/or cobalt and 2.5—60 parts by weight and in particular 2.5—30 parts by weight of molybdenum and/or tungsten per 100 parts by weight of carrier. The atomic ratio between nickel and/or cobalt on the one hand, and molybdenum and/or tungsten on the other, may vary within wide limits, but is preferably between 0.1 and 5. Examples of very suitable metal combinations for the present catalysts are nickel/tungsten, nickel/molybdenum, cobalt/molybdenum and nickel/cobalt/molybdenum. The metals may be present on the carrier in metallic form or in the form of their oxides or sulphides. It is preferred to use catalysts according to the invention in which the metals are present on the carrier in the form of their sulphides. In addition to the catalytically active metals mentioned above, the catalysts may also contain other catalytically active metals and promoters such as phosphorus, boron and halogens, such as fluorine and chlorine. Very suitable carriers for the present catalysts are oxides of elements of the Groups II, III and IV of the periodic system, such as silica, alumina, magnesia and zirconia, or mixtures of the said oxides, such as silica-alumina, silica-magnesia, alumina-magnesia and silica-zirconia. Aluminas and silica-aluminas are preferred as carriers for the present catalysts.

The metal loads of most commercial catalysts which contain the cobalt/molybdenum metal combination supported on alumina or silica-alumina as carrier and which are recommended for the treatment of hydrocarbons with hydrogen as a rule amount to approximately 15 parts by weight of metal per 100 parts by weight of carrier. In the experimental work upon which Specification 1,468,160 is based, which application refers to the relationship between porosity and particle size of catalysts and the hydrogen partial pressures used on the one hand, and the suitability of these catalysts for hydrosulphurization of vanadium- and nickel-containing residual hydrocarbon oils in the presence of water without catalyst replenishment on the other, it was assumed that the above metal load produces the most attractive results. As can be seen from the examples of Specification 1,468,160, the metal load of the cobalt-molybdenum catalysts is only varied between 13.3 and 16.1 parts by weight per 100 parts by weight of carrier. It has now become apparent that the metal load of these catalysts can be greatly reduced without impairing their suitability for the desulphurization of residual hydrocarbon oils. Thus, for example, it was found that a catalyst which contained 2.0 parts by weight of cobalt and 5.5 parts by weight of molybdenum per 100 parts by weight of alumina possessed the same excellent suitability for the desulphurization

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of residual hydrocarbon oils in the presence of water as a catalyst which contained 4.3 parts by weight of cobalt and 10.9 parts by weight of molybdenum per 100 parts by weight of alumina, p, d and P_H remaining the same. The discovery of the fact

that a lower metal load can be used than had been assumed to be necessary is, of course, very important with a view to the cost of catalyst preparation.

A lower metal load saves metals and may result in a simplification in the catalyst preparation. If use is made in the process according to the invention of a catalyst which contains cobalt and molybdenum supported on alumina or silica-alumina as a carrier, it is preferred, in view of the above, to select a catalyst which contains 5—10 parts by weight of metal per 100 parts by weight of carrier. This preference for a low metal load, of course, also applies if in the process according to Specification 1,468,160 a catalyst is used which contains cobalt and molybdenum supported on alumina or silica-alumina.

The catalysts which are applicable according to the invention may be prepared by supporting the relevant metals on a carrier having such a specific average pore diameter that after the metals have been supported thereon, a catalyst is obtained which satisfies the requirements of the invention, either as such or after the specific average particle diameter has been increased or reduced. The preparation of the present catalysts is preferably carried out by single-stage or multistage co-impregnation of a carrier with an aqueous solution comprising one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds, followed by drying and calcination of the composition. When drying the compositions, which drying is usually carried out at temperatures between 100 and 150° C, physically bound water is removed from the compositions; during calcination of the compositions, which calcination usually takes place by heating the compositions to a final temperature between 450 and 550° C and maintaining the compositions for some time at this final temperature, decomposition of the metal salts occurs with formation of the corresponding metal oxides. The nickel and cobalt compounds used in the preparation of the present catalysts are often the nitrates. As molybdenum and tungsten compounds ammonium molybdate and ammonium tungstate are often used.

It has been found that considerable thermal effects may occur in the calcination of the present compositions, which effects may have a detrimental influence on the activity of the ultimate catalysts. For the preparation of catalysts with high activity it is therefore important to keep these thermal effects in the calcination as small as possible. One of the causes of strong thermal effects in the calcination is the simultaneous decomposition of nitrates and ammonium compounds. The thermal effects associated with this decomposition can be avoided by using nickel or cobalt formates instead of nitrates in the preparation of the catalysts. Another possibility to keep the thermal effects occurring in the calcination as small as possible is to carry out the calcination very cautiously, for example by using a low rate of heating-up, step-by-step heating, etc. Local overheating of the composition during calcination with all its detrimental effects on the activity of the ultimate catalyst can largely be avoided by ensuring effective heat removal during calcination, for example by passing a high-velocity gas stream over the material to be calcined and by calcining the material in a relatively thin layer.

For information on methods which can be used to influence the porosity of the carrier material of the catalyst and for further particulars of preferred method of preparation for the present catalysts, reference is made to Specifications 1,408,759 and 1,406,804, wherein these subjects are discussed in detail.

The catalytic hydrodesulphurization of residual hydrocarbon oils without catalyst replenishment is preferably carried out by passing the hydrocarbon oil at elevated temperature and pressure and in the presence of hydrogen in an upward, downward or radial direction through two or more vertically arranged fixed catalyst beds. The hydrocarbon oil to be desulphurized may be completely or partly saturated with hydrogen and a hydrogen-containing gaseous phase may be present in the reactor in addition to the hydrocarbon phase and the catalyst phase.

The hydrodesulphurization according to the invention may be carried out in one reactor or in two or more reactors. If the process according to the invention is carried out in one reactor, it should contain at least two catalyst beds, the first catalyst bed of which (viewed in the direction of the liquid flow) and possibly one or more immediately subsequent beds contain a catalyst or combination of catalysts designated hereinbefore as catalyst I and the final catalyst bed (viewed in the direction of the liquid flow) and possibly one or more immediately preceding beds contain a catalyst designated hereinbefore as catalyst II. If the process according to the invention is carried out in two or more reactors, the first reactor and possibly one or more immedi-

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ately subsequent reactors should contain catalyst I and the final reactor and possibly one or more immediately preceding reactors should contain catalyst II. The catalysts which are applied in the individual catalyst beds and/or individual reactors may differ from each other as regards their chemical composition.

5 An attractive manner to supply steam in the process according to the invention is to add water between two or more of the catalyst beds or reactors. In this manner the addition of water assists in reducing the temperature of the partly desulphurized product, which has risen as a result of the exothermic desulphurization reaction.

10 The specific average particle diameter of the catalysts which are used in the process according to the invention is as a rule 0.5—2.5 mm and preferably 0.6—2.0 mm. If the value d which is required according to the invention to achieve a good catalyst performance at a given p and P_H is so small that practical plant

15 difficulties would arise in the application of the particles as such, the desulphurization can be carried out in the presence of porous agglomerates prepared from the small particles of which d is optimum in relation to p and H_2 as described in Specifications 1,408,759 and 1,406,804, the agglomerates having more than 10% of their pore volume as pores having a diameter in excess of 100 nm. Accordingly, the references to catalysts in this specification should be read as including catalysts in the form either of particles meeting the stated requirements or of agglomerates formed from said particles, said agglomerates having more than 10% of their pore volume as pores having a diameter in excess of 100 nm.

20 The reaction conditions used in the hydrodesulphurization according to the invention may vary between wide limits. The hydrodesulphurization is preferably carried out at a temperature between 300° C and 475° C, a hydrogen partial pressure of 30—200 bar, a space velocity of 0.1—10 parts by weight of fresh feed per part by volume of catalyst per hour and a hydrogen/feed ratio of 150—2000 NI of H_2 /kg of feed. Special preference is given to a temperature of 350° C—445° C, a hydrogen partial pressure of 40—160 bar, a space velocity of 0.3—3 parts by weight of fresh feed per part by volume of catalyst per hour and a hydrogen/feed ratio of 250—1000 NI of H_2 /kg of feed.

25 The hydrodesulphurization according to the invention may very suitably be preceded by a demetallization treatment. As a result of the demetallization the deactivation of the desulphurization catalyst combination is suppressed and its life is consequently prolonged. The demetallization of residual hydrocarbon oils is preferably carried out in the presence of hydrogen and a catalyst. Demetallization may very suitably be effected by passing the hydrocarbon oil at elevated temperature and pressure and in the presence of hydrogen in an upward, downward or radial direction through one or more vertically arranged reactors which contain a fixed or moving catalyst bed. In a very attractive embodiment of the demetallization, the hydrocarbon oil is passed through a vertically arranged catalyst bed into which, during operation, fresh catalyst is intermittently introduced at the top of the bed and spent catalyst is withdrawn from the lower part thereof (demetallization according to the bunker flow principle). In another very attractive embodiment of the demetallization treatment several reactors containing a fixed catalyst bed are present, which reactors are alternately used for the demetallization treatment. While demetallization is carried out in one or more of these reactors, the catalyst is replenished in the remaining reactors (demetallization according to the fixed bed swing principle. If desired, demetallization can also be carried out by suspending the catalyst in the hydrocarbon oil to be demetallized (demetallization according to the slurry phase principle).

30 If the desulphurization according to the invention is preceded by a demetallization treatment, steam may very suitably be introduced by adding water to the demetallized product after the latter has left the demetallization reactor and before it enters the first desulphurization reactor. In this manner the addition of water assists in reducing the temperature of the demetallized product, which has risen as a result of the exothermic demetallization reaction. Suitable catalysts for demetallizing residual hydrocarbon oils are catalysts which contain one or more metals having hydrogenating activity supported on a carrier.

35 If the desulphurization according to the invention is preceded by a demetallization treatment, the demetallization is preferably carried out according to the bunker flow principle or according to the fixed bed swing principle and the desulphurization is effected over two or more conventional fixed catalyst beds.

40 As has been noted above, the demetallization of a vanadium- and nickel-containing residual hydrocarbon oil results in a prolonged life of the catalyst combination which is used for the hydrodesulphurization of the demetallized oil. For the catalytic hydro-

demetallization of a vanadium- and nickel-containing residual hydrocarbon oil followed by desulphurization of the demetallized oil according to the present invention, applicant has derived the following equation:

$$M_2 = (1.05 \pm 0.20) \times M_1 \times (L_1/L_2)^{0.5},$$

wherein M_1 and M_2 represent the metal contents of the non-demetallized and the demetallized oil respectively and L_1 and L_2 represent the lives of the desulphurization catalyst combination when used for the non-demetallized and the demetallized oil respectively. In drawing up this equation the following limitations have been taken into account:

- (1) the metal content of the hydrocarbon oil before demetallization (M_1) may vary between 25 and 1500 ppmw (parts by weight per million);
- (2) the life of the desulphurization catalyst combination used for the demetallized oil (L_2) may vary between 2000 and 16,000 hours;
- (3) the quotient of the metal contents of the hydrocarbon oil after and before demetallization (M_2 and M_1) may vary between 0.75 and 0.10, and
- (4) the product of the metal content of the hydrocarbon oil before demetallization (M_1) and the life of the desulphurization catalyst combination used for the demetallized oil (L_2) may vary between 2×10^5 and 3×10^6 .

The above-mentioned relationship between L_1 , L_2 , M_1 and M_2 offers the possibility, during the hydrodesulphurization of a residual hydrocarbon oil according to the present invention, using prior catalytic hydrodemetallization of the feed, to establish to what value the metal content of the feed has to be reduced in order to prolong the life of the desulphurization catalyst combination by a certain number of hours.

As observed hereinbefore, the deactivation of the desulphurization catalyst combination can be suppressed and consequently its life prolonged, by preceding the desulphurization by a catalytic demetallization. This observation implies that, if a feed that has previously been catalytically demetallized is processed over a certain quantity by volume of the catalyst combination, the life of the catalyst combination will be longer than when the non-demetallized feed is processed over the same quantity by volume of the catalyst combination. Therefore, upon application of a catalytic demetallization as referred to hereinbefore, the feed will be contacted with a larger quantity by volume of catalyst than when no demetallization is applied, since in the former case, besides a specific quantity by volume of the desulphurization catalyst combination, which is the same in both cases, a certain quantity by volume of demetallization catalyst is used in addition.

Upon continuation of the studies concerning the catalytic hydrodemetallization of vanadium and nickel-containing residual hydrocarbon oils followed by catalytic hydrodesulphurization of the demetallized oil using a combination of two desulphurization catalysts in accordance with the present invention, it was found that the life of the desulphurization catalyst combination in maintaining a certain desulphurization level can be considerably prolonged, while keeping the total quantity by volume of catalyst constant, when part of the desulphurization catalyst combination is replaced by a demetallization catalyst and when, in addition, the following requirements are met.

- 1) The desulphurization catalyst combination comprises only two desulphurization catalysts, namely catalyst I and catalyst II;
- 2) the residual hydrocarbon oil that is used as the feed has a total vanadium and nickel content above 120 ppmw;
- 3) the demetallization catalyst, indicated as catalyst O, meets the following requirements:
 - a) the catalyst comprises one or more metals having hydrogenation activity on a carrier;
 - b) $p/d > 3.5 - 0.02 v$, in which v is the percentage of the total pore volume that consists of pores with a diameter larger than 100 nm;
 - c) the total pore volume is larger than 0.40 ml/g;
 - d) the specific surface area is larger than 100 m²/g, but in cases where 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:
 - e) the nitrogen pore volume is larger than 0.60 ml/g;
 - f) the specific surface area is larger than 150 m²/g, and
 - g) p is larger than 5 nm;
- 4) catalyst O has a larger total pore volume than catalyst I;
- 5) catalyst O and catalyst I have such a p , d and v that the following relation is met:

$$[p/(d)^{0.9}]_{cat.0} > 1.2 \times \{ [p/(d)^{0.9}]_{cat.I} - 0.8(v_0 - v_1) \};$$

- 6) the percentage of the joint catalyst volume of catalysts O, I and II that is occupied by catalyst O amounts to at least 10%v.

The catalytic hydrodemetallization of residual hydrocarbon oils using a catalyst which meets the requirements given hereinbefore under a) to g) is described in published Netherlands Patent Applications Nos. 7,309,387, 7,316,396, 7,410,162, 7,412,155 and 7,412,337.

The present invention therefore also includes a process for the catalytic hydrodesulphurization without catalyst replenishment of vanadium and nickel-containing residual hydrocarbon oils, which process is carried out in the presence of a quantity of water corresponding with a water vapour partial pressure during the process of 0.5—30 bar (further called "improved embodiment of the invention"), in which process the hydrocarbon oil is successively contacted with a catalyst I which consists of one catalyst and a catalyst II which also consists of one catalyst, which catalysts meet the following requirements:

- (a) Both catalysts have a total pore volume larger than 0.30 ml/g of which the percentage (v) that consists of pores with a diameter larger than 100 nm is less than 10;
(b) catalyst II has such a specific average pore diameter (p) and a specific average particle diameter (d) that the quotient $p/(d)^{0.9}$ meets the requirement

$$10^{-4} \times (P_H)^2 \leq [p/(d)^{0.9}]_{cat.II} \leq 4 + 13 \times 10^{-4} \times (P_H)^2$$

- (c) the percentage of the joint catalyst volume of catalysts I and II that is occupied by catalyst II (%v cat. II) lies between 10 and 90% and meets the requirement:

$$40 \times \left(\frac{S_F - S_P}{S_F} \times 100 \right)^2 \times (P_H)^{-2} \leq \%vol.cat.II \leq 300 \times \left(\frac{S_F - S_P}{S_F} \times 100 \right)^2 \times (P_H)^{-2},$$

in which S_F is the sulphur content of the feed and S_P is the desired sulphur content of the desulphurized product (p in nm, d in nm, P_H in bar, S_F and S_P in %w),

wherein the desulphurization is preceded by a catalytic hydrodemetallization using a demetallization catalyst O, the requirements given hereinbefore under 2) to 6) being met.

As demetallization catalysts preference is given to the catalysts described in above-mentioned published Netherlands Patent Application Nos. 7,309,387, 7,316,396, 7,410,162, 7,412,155 and 7,412,337.

Examples of feeds to which the present invention can be applied are crude oils and residues obtained by distillation of crude oils at atmospheric or reduced pressure. Residues obtained during the distillation of products originating from thermal or catalytic cracking of heavy hydrocarbon oils may also be treated in accordance with the invention.

The invention will now be elucidated with reference to the following Examples.

EXAMPLE I.

Seven combinations each of two different catalysts as well as each of these catalysts separately (catalysts A—M) were used for the hydrodesulphurization of five vanadium- and nickel-containing residual hydrocarbon oils (oils A—E) without catalyst replenishment. Desulphurization of the oils was effected by passing these oils at elevated temperature and pressure and in the presence of hydrogen and steam in a downward direction through two cylindrical fixed catalyst beds.

The experiments were carried out in series of three. Per series of three experiments the same oil was desulphurized under the same conditions and with the same volume of catalyst to the same sulphur content in the product (S_P). In one of the three experiments the first catalyst bed contained the catalyst referred to below as catalyst I and the second bed the catalyst referred to below as catalyst II. In the two remaining experiments both catalyst beds contained either exclusively catalyst I or exclusively catalyst II.

The desulphurization experiments were carried out at an initial temperature of $360 \pm 5^\circ \text{C}$, a space velocity of $0.7 \text{ kg} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$, a gas velocity of 600 NI of $\text{H}_2/\text{kg}^{-1}$, a hydrogen partial pressure varying from 75 to 150 bar and a water vapour partial

pressure varying from 2 to 10 bar. To prepare a product having a constant sulphur content, the temperature had to be gradually increased during the experiments. The desulphurization experiments were terminated at the moment when a temperature in excess of 420° C had to be used in order to prepare a product with the desired sulphur content.

The composition and properties of the catalysts, which were used in the form of their sulphides, are stated in Table A. For information on the preparation of the nine catalysts used in the present experiments reference is made to the examples of Specification 1,408,759, wherein the preparation of these catalysts has been described in detail. The preparation of the catalysts B* and D* was effected in the same manner as described for the catalysts B and D, with the proviso that a lower metal load was used in the preparation of the catalysts B* and D*. The five residual oils involved in the investigation are described in greater detail below. The results of the desulphurization experiments are stated in Table B.

OIL A.

Oil having a total vanadium and nickel content of 75 ppmw and a sulphur content of 4.0% by weight, obtained as residue in the distillation at atmospheric pressure of a Middle East crude oil.

OIL B.

Oil having a total vanadium and nickel content of 64 ppmw and a sulphur content of 4.0% by weight, obtained as residue in the distillation at atmospheric pressure of a Middle East crude oil.

OIL C.

Oil having a total vanadium and nickel content of 77 ppmw and a sulphur content of 2.0% by weight, obtained as residue in the distillation at atmospheric pressure of a product prepared by the thermal cracking of an atmospheric distillation residue of a Middle East crude oil.

OIL D.

Oil having a total vanadium and nickel content of 225 ppmw and a sulphur content of 2.0% by weight, obtained as residue in the distillation at atmospheric pressure of a Caribbean crude.

OIL E.

Oil having a total vanadium and nickel content of 130 ppmw and a sulphur content of 1.9% by weight, obtained by demetallization of oil D. The demetallization of oil D was carried out by passing it at elevated temperature and pressure and in the presence of hydrogen in a downward direction through a vertically arranged fixed bed of a demetallization catalyst. The demetallization catalyst contained 0.5 parts by weight of nickel and 2.0 parts by weight of vanadium per 100 parts by weight of silica carrier.

TABLE A

Cat. No.	Metal load, pbw per 100 pbw carrier			Carrier	Pore volume, ml/g	Pore volume in pores with a diameter $\geq 0.7\mu$ ml/g	B.E.T. surface area, m^2/g	% of the pore volume in pores with a diameter $< 0.7\mu$	% of the pore volume in pores with a diameter $> 1.7\mu$	% of the pore volume in pores with a diameter $> 100\text{ nm}$	p, nm	d, mm
	Ni	Co	Mo									
A	—	4.7	11.4	Al_2O_3	0.54	0.42	202	16.7	5.6	1.3	14.1	1.5
B	—	4.7	11.4	Al_2O_3	0.57	0.48	154	14.0	1.8	1.0	16.8	1.5
B*	—	2.0	5.5	Al_2O_3	0.58	0.49	160	13.9	1.9	1.1	16.4	1.5
C	—	4.7	11.4	Al_2O_3	0.58	0.51	177	10.3	1.7	1.1	18.3	1.5
D	—	3.8	9.5	Al_2O_3	0.50	0.47	303	2.8	3.2	6.0	4.7	0.8
D*	—	1.8	5.2	Al_2O_3	0.51	0.47	300	2.7	3.3	5.8	4.7	0.8
H	4.3	—	10.9	Al_2O_3	0.62	0.53	226	8.1	6.5	2.1	12.6	1.5
M	4.3	—	10.9	Al_2O_3	0.83	0.63	157	15.7	8.4	2.4	22.8	1.7

TABLE B

Exp. No.	Oil No.	SF, %w	Sp, %w	PH ₂ , bar	PH ₂ O, bar	Cat. I, No.	Cat. II, No.	% v, Cat. II	Life of cat. or cat. combination, hours
I	A	4.0	0.5	150	5	B*	D*	30	3000
I'	A	4.0	0.5	150	5	B*	—	0	1400
I''	A	4.0	0.5	150	5	—	D*	100	2000
II	B	4.0	1.0	125	10	M	D	30	5800
II'	B	4.0	1.0	125	10	M	—	0	4200
II''	B	4.0	1.0	125	10	—	D	100	3800
III	B	4.0	0.5	125	3	M	D	50	3600
III'	B	4.0	0.5	125	3	M	—	0	300
III''	B	4.0	0.5	125	3	—	D	100	2000
IV	A	4.0	0.5	100	7	B	D	35	4500
IV'	A	4.0	0.5	100	7	B	—	0	2200
IV''	A	4.0	0.5	100	7	—	D	100	2800
V	A	4.0	1.0	75	2	C	D	50	4200
V'	A	4.0	1.0	75	2	C	—	0	200
V''	A	4.0	1.0	75	2	—	D	100	2400
VI	D	2.0	0.5	150	10	M	D	30	1300
VI'	D	2.0	0.5	150	10	M	—	0	700
VI''	D	2.0	0.5	150	10	—	D	100	800
VII	E	1.9	0.5	150	10	M	D	40	4200
VII'	E	1.9	0.5	150	10	M	—	0	1500
VII''	E	1.9	0.5	150	10	—	D	100	2700
VIII	A	4.0	1.0	75	10	C	H	70	3800
VIII'	A	4.0	1.0	75	10	C	—	0	400
VIII''	A	4.0	1.0	75	10	—	H	100	3000
IX	A	4.0	1.0	100	5	A	D	35	5500
IX'	A	4.0	1.0	100	5	A	—	0	3300
IX''	A	4.0	1.0	100	5	—	D	100	4300
X	A	4.0	0.5	100	10	A	D	60	3900
X'	A	4.0	0.5	100	10	A	—	0	700
X''	A	4.0	0.5	100	10	—	D	100	2800
XI	D	2.0	0.5	100	5	A	D	35	2000
XI'	D	2.0	0.5	100	5	A	—	0	1300
XI''	D	2.0	0.5	100	5	—	D	100	1550
XII	C	2.0	0.5	100	5	A	D	50	2000
XII'	C	2.0	0.5	100	5	A	—	0	400
XII''	C	2.0	0.5	100	5	—	D	100	1200
A	A	4.0	0.5	150	5	A	H	40	1500
A'	A	4.0	0.5	150	5	A	—	0	1000
A''	A	4.0	0.5	150	5	—	H	100	2200

Of the experiments stated in Table B, only experiments I—XII are desulphurization experiments according to the invention. The remaining experiments have been incorporated in the Table for the purpose of comparison.

In the experiments I—XII, catalyst combinations were used of which each catalyst satisfied the requirements made in respect of porosity and particle size; in these experiments the requirements made in respect of "%vol. of catalyst II" were also satisfied.

When the life of each of the catalyst combinations used in the experiments I—XII as stated in the final column of Table B is compared with the life of the individual catalysts used in the relevant experiments I'—XII' and I''—XII'', the improvement in catalyst life which is achieved by using each of the catalyst combinations of the invention is clearly demonstrated.

The experiments A, A' and A'' have also been incorporated in Table B for the purpose of comparison. Although a combination of two catalysts was used in the experiment A, it did not satisfy the requirements set. In the experiment A a catalyst was used as catalyst I of which the quotient $p/(d)^{0.9}$ was too small. When the life of the catalyst combination used in the experiment A as stated in the final column of Table B is compared with the life of the individual catalysts used in the relevant experiments A' and A'', it is found that although application of this catalyst combination produces an improvement in catalyst life in respect of individual application of one of the two catalysts of the combination, it produces a loss in catalyst life in respect of separate application of the other catalyst of the combination.

EXAMPLE II.

This example demonstrates the "improved embodiment of the invention" discussed hereinbefore.

Catalyst combinations each consisting of a demetallization catalyst (catalysts 1, 11 and 40), a first desulphurization catalyst (catalyst A) and a second desulphurization catalyst (catalyst D) were employed for hydrodemetallization followed by hydrodesulphurization without catalyst replenishment of two vanadium and nickel-containing residual hydrocarbon oils (oils D and F). Moreover, catalyst combinations consisting of the two desulphurization catalysts A and D, and, also, each of these two catalysts separately, were employed for the hydrodesulphurization without catalyst replenishment of the two oils. Demetallization/desulphurization or only desulphurization of the oils was carried out by passing the oils together with hydrogen and steam downwards through three cylindrical vertically disposed fixed catalyst beds at elevated temperature and pressure.

The experiments were carried out four by four. In each set of four experiments the same oil was desulphurized under the same conditions and with the same volume of catalyst, down to the same sulphur content in the product. (In all the experiments S_p was 0.5%w). In one of the four experiments the first catalyst bed contained the demetallization catalyst indicated hereinafter as catalyst O, the second catalyst bed the desulphurization catalyst indicated hereinafter as catalyst I and the third catalyst bed the desulphurization catalyst indicated hereinafter as catalyst II. In the three remaining experiments the three catalyst beds contained either a combination of catalyst I and catalyst II successively or catalyst I exclusively or catalyst II exclusively.

The desulphurization experiments were carried out at an initial temperature of $360 \pm 5^\circ \text{C}$, a space velocity of $0.7 \text{ kg} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$, a gas rate of $600 \text{ NI H}_2 \cdot \text{kg}^{-1}$, a hydrogen partial pressure of 100 or 150 bar and a water vapour partial pressure varying from 5 to 15 bar. For the preparation of a product having constant sulphur content the temperature had to be gradually increased during the experiments. The desulphurization experiments were ended when a temperature of 420°C had to be applied to prepare a product having the desired sulphur content.

The demetallization was carried out at a constant temperature of 420°C and a hydrogen partial pressure and gas rate corresponding with those applied in the desulphurization. In case of demetallization followed by desulphurization the space velocity throughout the catalyst system amounted to $0.7 \text{ kg} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$.

The catalysts were applied in the form of their sulphides. The desulphurization catalysts A and D have already been described in Example I. The composition and properties of the demetallization catalysts 1, 11 and 40 are given in Table C. For information concerning the preparation of catalysts 1 and 11 reference is made to the working examples of published Netherlands Patent Application No. 7,309,387 in which the preparation of these catalysts is described in detail. Catalyst 40 is a demetallization catalyst within the scope of Netherlands Patent Application No. 7,309,387, which catalyst was prepared by co-impregnation of an alumina carrier with an aqueous solution containing vanadyl oxalate and nickel nitrate, followed by drying and calcination of the composition.

Of the two residual oils used in the experiments oil D has already been described in Example I. Oil F is further described hereinafter. The results of the experiments are given in Table D.

OIL F.

An oil having a total vanadium and nickel content of 410 ppmw and a sulphur content of 2.0%w, which oil had been obtained as a residue in the atmospheric distillation of a Caribbean crude oil.

TABLE C

Cat. No.	Metal load, pbw per 100 pbw of carrier		Carrier	Pore vol., ml/g	Total pore volume, ml/g	Nitrogen pore volume, ml/g	v, %	P, nm	d, mm
	Ni	V							
1	—	2.0	Al ₂ O ₃	225	0.57	0.56	<0.5	10.2	0.7
11	0.5	2.0	SiO ₂	243	0.81	0.74	9	9.0	2.2
40	0.5	2.0	Al ₂ O ₃	220	0.60	0.57	1.5	14.9	1.5

TABLE D

Exp. No.	Oil No.	P _{H₂} , bar	P _{H₂O} , bar	Cat. O No.	% v Cat. O	% v Cat. I (Cat. No. A)	% v Cat. II (Cat. No. D)	Cat. life of cat. or cat. combination, h
XIII	D	150	10	1	40	45	15	1900
XIII'	D	150	10	—	—	75	25	1300
XIII''	D	150	10	—	—	100	—	600
XIII'''	D	150	10	—	—	—	100	800
XIV	D	100	5	1	40	42	18	4000
XIV'	D	100	5	—	—	70	30	2800
XIV''	D	100	5	—	—	100	—	1300
XIV'''	D	100	5	—	—	—	100	1550
XV	F	150	5	11	50	37.5	12.5	1200
XV'	F	150	5	—	—	75	25	800
XV''	F	150	5	—	—	100	—	300
XV'''	F	150	5	—	—	—	100	350
XVI	D	150	15	40	40	45	15	1200
XVI'	D	150	15	—	—	75	25	1300
XVI''	D	150	15	—	—	100	—	600
XVI'''	D	150	15	—	—	—	100	800

Of the experiments given in Table D only experiments XIII—XV are demetalization/desulphurization experiments according to the "improved embodiment of the invention". The other experiments have been included in the Table for comparison.

In experiments XIII—XV catalyst combinations were applied in which each of the catalysts satisfied the requirements concerning porosity and particle size; the other requirements according to the "improved embodiment of the invention" were also satisfied in these experiments. Comparison of the lives of each of the catalyst combinations O/I/II given in the last column of Table D and applied in experiments XIII—XV with the lives of the catalyst combinations I/II applied in the associated experiments XIII'—XV' clearly shows the gain in catalyst life which is achieved upon application of catalyst combinations according to the "improved embodiment of the invention".

It is true that a suitable catalyst combination I/II was applied in experiment XVI (and that this experiment therefore falls within the scope of the present patent application), but the quotient $p/(d)^{0.5}$ of the catalyst O applied was too low to meet the requirements of the "improved embodiment of the invention".

Experiments XIII'—XVI' are also experiments within the scope of the present patent application.

It is pointed out that experiments XIII', XIII'' and XIII''' given in Table D are identical with experiments XVI', XVI'' and XVI''', respectively, also in this Table and that experiments XVI'' and XVI''' in Table D are identical with experiments XI' and XI'' in Table B.



WHAT WE CLAIM IS:—

1. A process for the catalytic hydrodesulphurization of vanadium- and nickel-containing residual hydrocarbon oils without catalyst replenishment, which process is carried out in the presence of a quantity of water corresponding with a water vapour partial pressure during the process of 0.5—30 bar and in which process the hydrocarbon oil is consecutively contacted with a catalyst combination comprising a catalyst I and a catalyst II (as defined hereinbefore) which satisfy the following requirements:

- (a) each of the individual catalysts of which the combination of catalyst I and catalyst II is composed has a total pore volume in excess of 0.30 ml/g of which less than 10% is present as pores having a diameter in excess of 100 nm,
 (b) catalyst II has a specific average pore diameter (p) and a specific average particle diameter (d) such that the quotient $p/(d)^{0.9}$ of catalyst II satisfies the requirement:

$$10^{-4} \times (P_H)^2 \leq [p/(d)^{0.9}]_{\text{cat. II}} \leq 4 + 13 \times 10^{-4} \times (P_H)^2$$

wherein P_H is the hydrogen partial pressure applied,

- (c) when the combination of catalyst I and catalyst II is composed of two catalysts, catalyst I has a p and d such that the quotient $p/(d)^{0.9}$ of catalyst I satisfies the requirement:

$$1.2 \times [p/(d)^{0.9}]_{\text{cat. II}} \leq [p/(d)^{0.9}]_{\text{cat. I}} \leq 5 + 30 \times 10^{-4} \times (P_H)^2$$

while when the combination of catalyst I and catalyst II is composed of more than two catalysts, the above requirement in respect of $[p/(d)^{0.9}]_{\text{cat. I}}$ applies to the average $p/(d)^{0.9}$ of catalyst I which is determined as the weight average of the values of $p/(d)^{0.9}$ of each of the individual catalysts of which catalyst I is composed,

- (d) the percentage of the total catalyst volume which is taken up by catalyst II (%vol. of catalyst II) is between 10 and 90% and satisfies the requirement:

$$40 \times \left(\frac{S_F - S_P}{S_F} \times 100 \right)^2 \times (P_H)^{-2} \leq \% \text{vol. cat. II} \leq 300 \times \left(\frac{S_F - S_P}{S_F} \times 100 \right)^2 \times (P_H)^{-2},$$

wherein S_F represents the sulphur content of the feed and S_P the required sulphur content of the desulphurized product, and

- (e) when the combination of catalyst I and catalyst II is composed of more than two catalysts, each of the individual catalysts of which catalyst I is composed has a p and d such that the quotient $p/(d)^{0.9}$ of each of these catalysts is greater than $[p/(d)^{0.9}]_{\text{cat. II}}$ (p in nm, d in mm, P_H in bar, S_F and S_P in percentage by weight).

2. A process as claimed in claim 1, in which the quantity of water used corresponds with a water vapour partial pressure during the process of 1—15 bar.

3. A process as claimed in claim 1 or 2, in which catalyst II has a total pore volume in excess of 0.45 ml/g.

4. A process as claimed in any one of claims 1—3, in which catalyst II has a surface in excess of 100 m²/g.

5. A process as claimed in any one of claims 1—4, in which catalyst II has a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. II}}$ satisfies the requirement:

$$[p/(d)^{0.9}]_{\text{cat. II}} \geq 1.2 \times 10^{-4} \times (P_H)^2.$$

6. A process as claimed in claim 5, in which catalyst II has a total pore volume in excess of 0.45 ml/g of which at least 0.4 ml/g is present in pores having a diameter of at least $0.7 \times p$ and at most $1.7 \times p$ and a sharp pore diameter distribution, in which

- (a) less than 20% of the pore volume is present in pores having a diameter smaller than $0.7 \times p$;
 (b) less than 20% of the pore volume is present in pores having a diameter greater than $1.7 \times p$.



7. A process as claimed in any one of claims 1—6, which is carried out using one catalyst as catalyst I.

8. A process as claimed in claim 7, in which the catalyst used as catalyst I has a total pore volume in excess of 0.40 ml/g.

9. A process as claimed in claim 7 or 8, in which the catalyst used as catalyst I has a p and d such that the quotient $[p/(d)^{0.9}]_{\text{cat. I}}$ satisfies the requirement:

$$[p/(d)^{0.9}]_{\text{cat. I}} \geq 1.4 \times [p/(d)^{0.9}]_{\text{cat. II.}}$$

10. A process as claimed in any one of claims 1—6, which is carried out using two or more catalysts as catalyst I, which catalysts occur in the reactor separated from each other and in such a sequence that the quotient $p/(d)^{0.9}$ of each of the catalysts of which catalyst I is composed is smaller than that of the preceding catalyst.

11. A process as claimed in any one of claims 1—6, which is carried out using two or more catalysts as catalyst I, which catalysts have a total pore volume in excess of 0.40 ml/g.

12. A process as claimed in any one of claims 1—6, which is carried out using two or more catalysts as catalyst I, which catalysts have a p and d such that the average $p/(d)^{0.9}$ of catalyst I, which is determined as the weight average of the values of $p/(d)^{0.9}$ of the individual catalysts of which catalyst I is composed, is at least $1.4 \times [p/(d)^{0.9}]_{\text{cat. II.}}$

13. A process as claimed in any one of claims 1—12, in which catalysts are used which contain 0.5—20 parts by weight of nickel and/or cobalt and 2.5—60 parts by weight of molybdenum and/or tungsten per 100 parts by weight of carrier.

14. A process as claimed in claim 13, in which catalysts are used wherein the atomic ratio between nickel and/or cobalt on the one hand and molybdenum and/or tungsten on the other, is between 0.1 and 5.

15. A process as claimed in any one of claims 1—14, in which the catalysts are used in sulphidic form.

16. A process as claimed in any one of claims 1—15, in which the catalysts contain alumina or silica-alumina as carrier.

17. A process as claimed in any one of claims 13—16, in which catalysts are used which contain the cobalt-molybdenum metal combination supported on alumina or silica-alumina as carrier and which contain 5—10 parts by weight of metal per 100 parts by weight of carrier.

18. A process as claimed in any one of claims 13—17, in which catalysts are used which have been prepared by co-impregnating a carrier in one or more steps with an aqueous solution containing one or more nickel and/or tungsten compounds, followed by drying and calcining of the composition.

19. A process as claimed in any one of claims 1—18, in which the catalysts have a specific average particle diameter of 0.5—2.5 mm.

20. A process as claimed in any one of claims 1—19, which is carried out by passing the hydrocarbon oil to be desulphurized at elevated temperature and pressure and in the presence of hydrogen in an upward, downward or radial direction through two or more vertically arranged fixed catalyst beds, the hydrocarbon oil first coming into contact with one or more catalyst beds which contain catalyst I and subsequently with one or more catalyst beds which contain catalyst II.

21. A process as claimed in any one of claims 1—20, which is carried out at a temperature between 300° C and 475° C, a hydrogen partial pressure of 30—200 bar, a space velocity of 0.1—10 parts by weight of fresh feed per part by volume of catalyst per hour and a hydrogen/feed ratio of 150—2000 NI of H₂/kg of feed.

22. A process as claimed in any one of claims 1—21, in which the desulphurization is preceded by a demetallization treatment.

23. A process as claimed in claim 22, in which the desulphurization is preceded by a catalytic hydrodemetallization treatment.

24. A process as claimed in claim 23, in which, in order to prolong the life of the desulphurization catalyst combination, the desulphurization is preceded by a catalytic hydrodemetallization in which the metal content of the oil is reduced from M₁ to M₂, the degree of demetallization being selected in dependence on the desired extension of the life of the desulphurization catalyst combination in accordance with the equation:

$$M_2 = (1.05 \pm 0.20) \times M_1 \times (L_1/L_2)^{0.5},$$

wherein L₁ and L₂ represent the lives of the desulphurization catalyst combination



* C L M S *

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when it is used for the non-demetalized oil with a metal content M_1 and for the demetalized oil with a metal content M_2 respectively, the following requirements being also satisfied:

- (1) $25 \leq M_1 \leq 1500$
- (2) $2000 \leq L_2 \leq 1600$
- (3) $0.10 \leq M_2/M_1 \leq 0.75$, and
- (4) $2 \times 10^5 \leq M_1 \times L_2 \leq 3 \times 10^6$,
(L_1 and L_2 in hours, M_1 and M_2 in ppmw).

25. A process as claimed in claim 23 or 24, in which the demetallization is carried out by passing the hydrocarbon oil at elevated temperature and pressure and in the presence of hydrogen in an upward, downward or radial direction through one or more vertically arranged reactors containing a fixed or moving catalyst bed.

26. A process as claimed in any one of claims 23—25, in which the demetallization catalyst contains one or more metals with hydrogenating activity, supported on a carrier.

27. A process as claimed in any one of claims 23—26, in which the demetallization of the residual hydrocarbon oil is carried out according to the bunker flow principle or according to the fixed-bed swing principle and that the desulphurization is carried out over two or more conventional fixed catalyst beds.

28. An improved process for the catalytic hydrodesulphurization without catalyst replenishment of vanadium- and nickel-containing residual hydrocarbon oils according to any one of claims 23—27, in which process the hydrocarbon oil is successively contacted with a catalyst I which comprises one catalyst and a catalyst II which comprises one catalyst, which catalysts meet the following requirements:

- (a) both catalysts have a total pore volume larger than 0.30 ml/g of which the percentage (v) that consists of pores with a diameter larger than 100 nm is less than 10;
- (b) catalyst II has such a specific average pore diameter (p) and a specific average particle diameter (d) that the quotient $p/(d)^{0.9}$ meets the requirement

$$10^{-4} \times (P_{H_2})^2 \leq [p/(d)^{0.9}]_{\text{cat. II}} \leq 4 + 13 \times 10^{-4} \times (P_{H_2})^2;$$

(c) the percentage of the joint catalyst volume of catalysts I and II that is occupied by catalyst II (%v cat. II) lies between 10 and 90% and meets the requirement

$$40 \times \left(\frac{S_F - S_P}{S_F} \times 100 \right)^2 \times (P_{H_2})^{-2} \leq \% \text{v cat. II} \leq 300 \times \left(\frac{S_F - S_P}{S_F} \times 100 \right)^2 \times (P_{H_2})^{-2},$$

in which S_F is the sulphur content of the feed and S_P is the desired sulphur content of the desulphurized product (P in nm, d in mm, P_{H_2} in bar, S_F and S_P

in %w).

The improvement consists in the fact that the desulphurization is preceded by a catalytic hydrodemetallization using a demetallization catalyst O, in which the following requirements are met:

- 1) the residual hydrocarbon oil that is used as the feed has a total vanadium and nickel content above 120 ppmw;
- 2) catalyst O meets the following requirements:
 - a) the catalyst comprises one or more metals having hydrogenation activity on a carrier;
 - b) $p/d > 3.5 - 0.02 v$;
 - c) the total pore volume is larger than 0.40 ml/g;
 - d) the specific surface area is larger than 100 m²/g; but in cases where 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:
 - e) the nitrogen pore volume is larger than 0.60 ml/g;
 - f) the specific surface area is larger than 150 m²/g; and
 - g) p is larger than 5 nm;
- 3) catalyst O has a larger total pore volume than catalyst I;
- 4) catalyst O and catalyst I have such a p, d and v that the following relation is met:



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$$[p/(d)^{0.9}]_{cat.O} > 1.2 \{ [p/(d)^{0.9}]_{cat.I} - 0.8(v_0 - v_1) \};$$

5) the percentage of the joint catalyst volume of catalyst O, I and II that is occupied by catalyst O amounts to at least 10%v.

5 29. A process for the catalytic hydrodesulphurization without catalyst replenishment of vanadium- and nickel-containing residual oils as claimed in claim 1 and substantially as described hereinbefore with reference to any of experiments I—XII of Example I and any of experiments XIII'—XVI' of Example II.

10 30. A process for the catalytic hydrodesulphurization without catalyst replenishment of vanadium and nickel-containing residual oils as claimed in claim 23, in which the desulphurization is preceded by a catalytic hydrodemetallization substantially as described hereinbefore with reference to any of experiments XIII—XV of Example II.

31. Hydrodesulphurized residual hydrocarbon oils obtained by a process as claimed in any one of claims 1—30.

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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.