

PATENT SPECIFICATION

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(54) PROCESS AND CATALYST FOR THE DESULPHURIZATION
 OF RESIDUAL HYDROCARBON OILS

(71) We, SHELL INTERNATIONAL-
 ALE, RESEARCH MAATSCHAPPIJ N.V.,
 a company organised under the laws of The
 Netherlands, of 30 Carel van Bylandtlaan,
 The Hague, The Netherlands, do hereby de-
 5 clare 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 par-
 ticularly described in and by the following
 10 statement:—

The invention relates to a process and a
 catalyst for the catalytic hydrosulphurization
 of residual hydrocarbon oils or oil fractions,
 in which during the operation continuous or
 15 periodic replenishment of the catalyst present
 in the desulphurization reactor is carried out.

Residual hydrocarbon oils generally contain
 a considerable quantity of sulphur compounds.
 When these oils are used as fuel, the sulphur
 20 present in the sulphur compounds is converted
 into sulphur dioxide which is discharged to
 the atmosphere. In order to restrict air pol-
 lution as much as possible in the combustion
 of these oils, it is desirable for the sulphur
 25 content to be reduced. The sulphur content
 of the hydrocarbon oils can be reduced by
 the catalytic hydrosulphurization of the oils.
 For this purpose processes can be used in
 which during the operation continuous or
 30 periodic replenishment of the catalyst present
 in the desulphurization reactor takes place,
 or processes in which during operation no
 continuous or periodic replenishment of the
 catalyst present in the desulphurization re-
 35 actor takes place. For the sake of brevity the
 former processes will be referred to in this
 patent application as "catalytic hydrosulphur-
 ization with catalyst replenishment" and the
 latter processes as "catalytic hydrosulphur-
 40 ization without catalyst replenishment".

The catalytic hydrosulphurization of re-
 sidual hydrocarbon oils or oil fractions in-
 volves certain problems which do not arise
 when this process is used for hydrocarbon
 45 oil distillates. These problems result from the
 fact that most residual hydrocarbon oils, such
 as residues obtained in the distillation of

crude oils under atmospheric or reduced pres-
 sure, comprise high-molecular non-distillable
 compounds, such as asphaltenes, resins, poly- 50
 aromatics and metal compounds. When the
 residual hydrocarbon oils are exposed to high
 temperatures, as is usual in hydrosulphuriz-
 ation, the asphaltenes which are colloiddally
 55 dispersed therein tend to flocculate and de-
 posit on the catalyst particles. The flocculation
 of the asphaltenes during catalytic hydrosulphur-
 ization is further promoted by the fact
 that the aromaticity of the liquid phase in
 which the asphaltenes are colloiddally dis- 60
 persed falls as a result of hydrogenation and
 hydrocracking. The principal high-molecular
 metal compounds present in residual hydro-
 carbon oils are nickel and vanadium com- 65
 pounds. The metal compounds are present
 in the oils as, among others, organometallic
 complexes, such as metalloporphyrines, and
 are for a considerable part bound to the as- 70
 phaltenes, the high-molecular metal com-
 pounds tend to deposit on the catalyst par-
 ticles during hydrosulphurization. A portion
 of the high-molecular compounds which de-
 75 posit on the catalyst particles are converted
 into coke. As a result of the increasing con-
 centration of heavy metals and coke on the
 active sites of the catalyst, a very rapid de-
 80 activation of the catalyst occurs in the catalytic
 hydrosulphurization of residual hydrocarbon
 oils. According as the activity of the catalyst
 decreases, a higher temperature must be ap-
 85 plied in order to maintain the desired degree
 of desulphurization. In practice, this pro-
 cedure is often followed, the process being
 started at the lowest possible temperature at
 90 which the desired degree of desulphurization
 can just be obtained. Although this procedure
 results in a product having a constant sulphur
 content, other properties of the product, such
 as viscosity, change continuously as a result
 of the rising temperature. According as higher
 temperatures are used, hydrocracking reactions
 begin to play a more important part and the
 oil to be desulphurized is increasingly con-

verted to gas and low-boiling fractions, such as gasoline, naphtha and kerosine. Consequently, a fuel oil is obtained the quality of which is not constant. Moreover, catalyst life is relatively short in this mode of operation, since the deposition of asphaltenes and other high-molecular compounds on the catalyst is highest at the low temperatures which are used at the beginning of the process.

It has already been considered carrying out desulphurization at the highest possible temperature. In this case, however, the excessive catalyst activity results in too high a degree of desulphurization, and the fuel oil yield is only poor as a result of drastic hydrocracking. Moreover, such a process is very difficult to control, since hydrogen consumption is not constant as a result of the fact that during operation the degree of desulphurization falls as catalyst activity decreases.

In order to prolong catalyst life it has also been suggested removing the asphaltenes from the feed before desulphurizing it and subsequently remixing the separated asphaltenes with the desulphurized product. Apart from the fact that this mode of operation requires an additional process step, namely de-asphaltinizing, this method of desulphurization involves another drawback, which is particularly important if a product with a very low sulphur content is desired. Since asphaltenes generally have a fairly high sulphur content, mixing of the desulphurized product with the separated asphaltenes may result in a final product having an unacceptably high sulphur content. If the separated asphaltenes are only partly mixed with the desulphurized product or if mixing is entirely omitted to avoid the said drawback, the final product yield may consequently be so adversely affected that the process is no longer economically attractive. In connection with the foregoing, preference is given to a method of carrying out the catalytic hydrodesulphurization in which the feed as such, i.e. including the asphaltenes, is processed. However, this embodiment of the process requires catalysts having an improved resistance to deactivation than those which are now generally recommended for this purpose.

An investigation into the catalytic hydrodesulphurization of residual hydrocarbon oils with catalyst replenishment has revealed that optimum catalysts for this purpose must comply with a number of specific requirements with regard to their particle diameter and porosity. Moreover, the total vanadium and nickel content and the C_{10} -asphaltene content of the hydrocarbon oil to be desulphurized play an important part. By an optimum catalyst for the hydrodesulphurization of residual hydrocarbon oils with catalyst replenishment is meant a catalyst which shows as high as possible a degree of equilibrium activity during its residence time in the reactor.

It has now been found that for the catalytic hydrodesulphurization with catalyst replenishment of residual hydrocarbon oils having a total vanadium and nickel content above 30 ppmw (parts, by weight, per million) and a C_{10} -asphaltene content above 0.5%, by weight, the above specific requirements with respect to particle diameter and porosity of the catalyst are as follows. In the first place the catalyst particles must have a pore volume above 0.30 ml/g, while less than 10% of this pore volume must be present in pores with a diameter above 1000 Å. Further, the catalyst particles must have a specific pore diameter (p), expressed in Å, of $45 \times d^{0.6}$ to $140 \times d^{0.6}$, in which d is the specific particle diameter in mm. The above-mentioned values d and p are determined by the following method, which is referred to hereinafter as "the determination method here defined".

After a complete sieve analysis of a catalyst sample has been carried out d is read off from a graph in which for every successive sieve fraction the percentage by weight, based on the total weight of the catalyst sample, has been cumulatively plotted as a function of the linear average particle diameter of the relevant sieve fraction; d is the particle diameter corresponding with 50% of the total weight.

After a complete determination of the pore radius distribution of a catalyst sample, p is read off from a graph in which for the pore diameter range of 0–1000 Å, for every successive pore volume increment smaller than 10% of the pore volume, the quotient of the pore volume increment and the corresponding pore diameter interval has been cumulatively plotted as a function of the linear average pore diameter over the relevant pore diameter interval; p is the pore diameter corresponding with 50% of the total quotient at 1000 Å.

For determining the pore radius distribution of the catalyst nitrogen adsorption/desorption combined with porosity determination by mercury displacement is very suitable.

According to the present invention a process for the catalytic hydrodesulphurization of a residual hydrocarbon oil or oil fraction having a total vanadium and nickel content above 30 ppmw and a C_{10} -asphaltene content above 0.5%, by weight, is provided, in which during the operation the catalyst present in the desulphurization reactor is continuously or periodically replenished, in which process a catalyst is used the particles of which have a pore volume above 0.30 ml/g, less than 10% of which pore volume being present in pores with a diameter above 1000 Å and in which the catalyst particles have a specific pore diameter (p), expressed in Å, of from $45 \times d^{0.6}$ to $140 \times d^{0.6}$, in which d is the specific particle diameter in mm. and in which d and p are

determined by the determination method herein defined.

The relationship found between specific particle diameter and specific pore diameter makes it possible at a certain specific particle diameter of the catalyst particles to determine the range within which the specific pore diameter of the catalyst particles must be selected to obtain an optimum catalyst. Conversely, it is also possible to derive from the relationship found the range within which the specific particle diameter of catalyst particles having a certain specific pore diameter must be selected to obtain an optimum catalyst. The most suitable values for the specific pore diameter and the specific particle diameter respectively within the ranges found are mainly determined by the composition of the hydrocarbon oil to be desulphurized.

If in the application of the above relationship for determining the range of the optimum specific pore diameter and optimum specific particle diameter respectively, values are substituted for the particle diameter respectively, which values have been determined by a method other than that specified above for the specific particle diameter and specific pore diameter respectively (for example the particle diameter calculated as linear average or the pore diameter calculated as the quotient of four times the pore volume and the surface), completely different results may be obtained.

The catalytic hydrodesulphurization of residual hydrocarbon oils with catalyst replenishment may be carried out in various ways. Hydrogen may be passed with or without the hydrocarbon oil to be desulphurized in the upward direction through a vertically disposed reactor containing a suspension of the catalyst in oil. The hydrogen may be introduced into the bottom end of the reactor at such a rate as to cause recycling of the oil, together with the catalyst suspended therein. The process may also be carried out with the aid of a moving catalyst bed which moves in the vertical direction through the reactor during the operation.

Below are given some attractive embodiments of the process for the catalytic hydrodesulphurization of residual hydrocarbon oils, according to the invention.

1. Desulphurization is carried out by recycling a suspension of the catalyst particles in the hydrocarbon oil to be desulphurized by the action of a driving force generated by a gas lift installation present in the reactor, the gas which provides the gas lift action and which substantially consists of hydrogen, being introduced from outside into the lower part of the gas lift installation, while gas that is still present in the liquid in the form of bubbles at the upper end of the gas lift installation is separated from the suspension and passed outside the reactor, liquid product being passed outside the reactor after catalyst par-

ticles have been separated from the suspension in one or more hydrocyclones, which separated particles are returned to the reactor through a long stand pipe (stand pipes) connected to that hydrocyclone (those hydrocyclones), and the recycled/supplied liquid stream ratio being between 4:1 and 20:1.

2. Desulphurization is carried out by passing the hydrocarbon oil to be desulphurized together with hydrogen through a vertically disposed catalyst bed in the upward direction, the liquid and gas velocity used being such that the catalyst bed expands and occupies a volume which is at least 10% larger than the volume of the non-expanded catalyst bed when it is out of operation.

3. Desulphurization is carried out with the use of a moving catalyst bed, in which case the catalyst bed moves through a vertically disposed reactor in the upward or downward direction, fresh catalyst being periodically supplied to the one side of the reactor, for example at the point where the desulphurized product is discharged, a substantially deactivated catalyst being periodically discharged on the other side of the reactor, for example, at the point where the hydrocarbon oil to be desulphurized is introduced into the reactor.

In the catalytic hydrodesulphurization of residual hydrocarbon oils with catalyst replenishment, use is generally made of catalyst particles having a specific particle diameter of 0.05—2.5 mm. If the desulphurization is performed with the use of the catalyst in the form of a suspension in an expanded bed, use is preferably made of catalyst particles with a specific particle diameter of 0.05—1.0 mm. If the desulphurization is carried out with the use of the catalyst in the form of a moving bed, catalyst particles with a specific particle diameter of 1.0—2.0 mm are preferably used.

As already stated, the catalyst particles should have a specific pore diameter of from $45 \times d^{0.6}$ to $140 \times d^{0.6}$. If catalyst particles with a specific particle diameter of from 0.05 to 1.0 mm are used, particles having a specific pore diameter of from $45 \times d^{0.6}$ to $130 \times d^{0.6}$ are preferred; if catalyst particles with a specific particle diameter of from 1.0 to 2.0 mm are employed preference is given to particles having a specific pore diameter of from $45 \times d^{0.6}$ to $120 \times d^{0.6}$.

The catalyst particles preferably have a pore volume above 0.40 ml/g, in particular a pore volume above 0.50 ml/g.

The defined relationship between specific particle diameter and specific pore diameter of the catalysts used in the process of the present invention provides catalysts for the hydrodesulphurization of residual hydrocarbon oils, which possess optimum properties. If a catalyst or catalyst carrier which does not comply with this relationship is available, it

is possible to prepare therefrom an optimum catalyst or a catalyst carrier by adapting the specific particle diameter to the specific pore diameter. This can be effected in a simple way by increasing or reducing the particle size of the catalyst or catalyst carrier (for example by bonding the particles with or without the use of a binding agent or by grinding the particles respectively).

In the preparation of optimum desulphurization catalysts according to the invention starting from a certain catalyst or catalyst carrier material the following problem may arise. The optimum specific particle diameter corresponding with the specific pore diameter of material from which the catalyst must be prepared may be so small that difficulties arise when such small catalyst particles are used for catalytic hydrodesulphurization. In this case it is preferred that agglomerates be formed from the small particles the specific particle diameter of which is optimum in relation to the specific pore diameter, which agglomerates are composed of a number of the small particles, more than 10% of the pore volume of these agglomerates being present in pores with a diameter above 1000 Å. It is preferred that from the small particles agglomerates be formed having more than 25% of its pore volume in pores with a diameter above 1000 Å. The use of these porous catalyst agglomerates in the hydrodesulphurization of residual hydrocarbon oils offers the same advantages as the use of the small optimum catalyst particles without the drawbacks inherent in the use of these small particles being encountered. The porous catalyst or catalyst agglomerates may very suitably be prepared from small optimum particles by bonding them with or without the use of a binding agent in the presence of a material which is incorporated in the agglomerates and subsequently removed therefrom by evaporation, combustion, solution, leaching or otherwise, leaving pores with a diameter above 1000 Å in the agglomerates. Suitable compounds for this purpose are cellulose-containing materials, polymers and compounds soluble in organic or inorganic solvents.

Catalysts suitable for the hydrodesulphurization of residual hydrocarbon oils according to the invention generally possess a chemical composition substantially corresponding with that of the known desulphurization catalysts. Preference is given to sulphur-resistant catalysts containing one or more metals of Group VIB, VIIB and/or VIII, their sulphides and/or oxides, supported on an inorganic oxide of the elements of Group II, III or IV, or on mixtures of the said oxides. Examples of suitable catalysts are catalysts containing nickel/tungsten, nickel/molybdenum, cobalt/molybdenum or nickel/cobalt/molybdenum supported on silica, alumina, magnesia, zirconia, thoria, boria, hafnia, silica-alumina,

silica-magnesia or alumina-magnesia as carriers.

The said catalyst may also contain additives, such as phosphates or phosphorus and/or halogens, such as fluorine and chlorine. The phosphates may be present in a quantity of 10–40% by weight, more particularly of 15–30%, by weight, based on the total catalyst weight, the halogens and phosphorus generally being used in a quantity smaller than 10%, by weight.

Although in principle the metal components may be present in the catalyst in any quantity, preference is given to catalysts containing 2–35%, by weight, and more particularly 5–25%, by weight, of metal. A group VIII metal or metals is or are generally used in quantities of from 0.1 to 10%, by weight, and a Group VIB metal or metals in a quantity of from 2.5 to 30%, by weight. The atomic ratio of the said Group VIII and Group VIB metals may vary widely, but is preferably between 0.1:1 and 5:1.

Alumina and silica-alumina are preferred as carrier materials for the present desulphurization catalysts.

If the hydrodesulphurization of residual hydrocarbon oils according to the invention is carried out in the presence of a silica-alumina based catalyst, preference is given to a catalyst which has been prepared by calcining a silica-alumina hydrogel, neutralizing the xerogel, thus obtained with a nitrogen base and recalcining the neutralized xerogel after one or more catalytically active metals have been deposited thereon.

The Groups mentioned above are the Groups of the Periodic Table of the Elements printed in the Handbook of Chemistry and Physics (43rd edition) published by The Chemical Rubber Co.

The reaction conditions in hydrodesulphurization according to the invention may vary widely dependent on the nature of the residual hydrocarbon oil to be desulphurized. Desulphurization is preferably carried out at a temperature of 350–475°C, and preferably at a temperature of 385–445°C. The total pressure is preferably 50–350 kg/cm², more preferably 75–225 kg/cm². The space velocity is preferably 0.1–10 parts, by weight, of fresh feed per part by volume of catalyst per hour and more preferably 0.5–5 parts, by weight, of fresh feed per part by volume of catalyst per hour.

The hydrodesulphurization according to the invention may be applied to any residual hydrocarbon oil or oil fraction, provided that it has a total nickel and vanadium content exceeding 30 ppm, by weight, and a C₆-asphaltene content exceeding 0.5%, by weight. Examples of feeds to which the desulphurization process according to the invention may be applied are crude oils and residues obtained by distilling crude oils at atmospheric and re-

duced pressure. It is preferable that the feed to be desulphurized should contain less than 50 ppm, by weight, and preferably less than 25 ppm, by weight, of alkali metal and/or alkaline earth metal. If the alkali and/or alkaline earth metal content in the feed is excessive, it may be reduced, for example, by washing the feed.

The invention also relates to the catalyst particles and agglomerates described herein.

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

EXAMPLE.

A residual hydrocarbon oil having a total nickel and vanadium content of 245 ppmw, a C_{50} -asphaltene content of 7.2% by weight and a sulphur content of 2.1%, by weight, which oil had been obtained as residue in the atmospheric distillation of a Caribbean crude oil was catalytically hydrodesulphurized with catalyst replenishment and with the use of different catalysts. To this end the oil together with hydrogen was passed through a stirred reactor containing the oil saturated with hydrogen and the catalyst at a temperature of

420°C, a total pressure of 150 kg/cm², an exit gas rate of 250 NI/kg of fresh feed and a space velocity of 4.35 kg of oil/kg of catalyst per hour.

The alumina-based catalysts contain 10.9 g of molybdenum and 4.3 g of nickel or cobalt supported on 100 g of alumina. The silica-alumina based catalysts contain 16 g of molybdenum and 2 g of nickel supported on 100 g of carrier consisting of 87 g of silica and 13 g of alumina. The metals had been deposited on the carriers by co-impregnation with a monoethanolamine solution containing ammonium heptamolybdate and nickel formate or cobalt acetate. The silica-alumina carriers had been prepared by calcining a silica-alumina hydrogel and neutralizing the xerogel thus obtained with ammonia.

The results of the desulphurization experiments are shown in Table A.

In this Table k_s is the reaction rate constant for desulphurization in the stationary state in a reactor wherein continuous catalyst replenishment is effected at a rate of 0.3 kg of catalyst/ton of fresh feed.

TABLE A

Catalyst No.	Catalyst	Total pore volume, ml/g	% of the pore volume present in pores with a diameter above 1000 Å	specific pore diameter, Å	specific particle diameter, mm	k, kg of feed/kg of catalyst hour. (% by weight. of S) [†]
1	Ni/Mo/Al ₂ O ₃	1.09	3.7	88	1.5	2.7
2	"	1.09	3.7	88	0.76	2.6
3	"	0.98	3.6	228	1.5	1.9
4	"	0.78	22.2	76	1.5	1.0
5	"	0.63	11.1	136	0.9	0.7
8	Co/Mo/Al ₂ O ₃	0.51	5.9	46	1.5	1.3
9	"	0.51	5.9	46	0.76	4.1
10	"	0.51	5.9	46	0.2	3.4
11	Ni/Mo/SiO ₂ -Al ₂ O ₃	1.08	4.6	100	0.76	3.0
12	Co/Mo/Al ₂ O ₃	0.51	5.9	46	0.07	1.5
13	Ni/Mo/SiO ₂ /Al ₂ O ₃	0.95	<3	78	0.5	3.6
14	"	0.95	<3	78	0.76	3.0
15	"	0.95	<3	78	1.5	2.3

The criterion for an optimum catalyst for the hydrodesulphurization, with catalyst replenishment, of residual hydrocarbon oils having a total vanadium and nickel content above 30 ppmw and a C_{50} -asphaltene content above 0.5%, by weight, is that the equilibrium activity of the catalyst in the stationary state (k_s) must exceed 2.0.

The catalysts 1, 2, 9, 10, 11, 13, 14 and 15 (with $k_s > 2.0$) are catalysts according to the invention for the catalytic hydrodesulphurization with catalyst replenishment. They comply with the relationship $45 \times d^{0.6} < p < 140 \times d^{0.6}$. The catalysts 3, 4, 5, 8, and

12 (with $k_s < 2.0$) are less suitable for the catalytic hydrodesulphurization with catalyst replenishment. The catalysts 3, 5, 8 and 12 do not comply with the relationship $45 \times d^{0.6} < p < 140 \times d^{0.6}$. Moreover, more than 10% of the pore volume of catalyst 5 is present in pores having a diameter above 1000 Å. Catalyst 4 does comply with the relationship, but more than 10% of the total pore volume in this catalyst is present in pores having a diameter above 1000 Å.

Catalyst 3 which is less suitable for the catalytic hydrodesulphurization with catalyst regeneration has proved very suitable for the catalytic hydrodesulphurization without catalyst replenishment. Such a process forms the subject of our co-pending U.K. Patent Application No. 32596/71. (Serial no. 1,356,272). Conversely, catalysts 1, 9 and 15 which are very suitable for the catalytic hydrodesulphurization with catalytic replenishment, have proved less suitable for catalytic hydrodesulphurization without catalyst replenishment.

The following information is provided to show why the determination method herein defined is adopted for determining the values of p and d :—

(a) By means of nitrogen adsorption and porosity determination by mercury displacement a complete pore radius distribution of the catalysts 4 and 5 was determined. Tables B and C show the percentage of the pore volume present in the pores with a given pore radius.

Table B

Catalyst 4

pore radius, Å	% of the pore volume
0—20	19.2
20—30	7.0
30—40	6.4
40—50	5.7
50—60	5.7
60—70	5.1
70—80	5.1
80—100	7.0
100—200	12.8
200—500	3.8
500	22.2

pore volume: 0.78 ml/g
surface: 238 m²/g

Table C

Catalyst 5

pore radius, Å	% of pore volume
0—10	6.4
10—20	6.4
20—30	7.2
30—40	5.6
40—50	3.1
50—60	3.1
60—70	7.9
70—80	12.7
80—90	12.7
90—100	11.1
100—150	7.9
150—200	1.6
200—500	3.2
500	11.1

pore volume: 0.63 ml/g
surface: 133 m²/g

Of the catalysts 4 and 5 the pore diameters

were determined by three different methods, each used as such in practice.

Method 1: Calculated by means of the formula

$$\text{pore diameter} = \frac{4 \times \text{pore volume}}{\text{surface}} \times 10^4$$

Method 2: Read off from a graph composed by means of a complete pore radius distribution and in which for the pore diameter range of from 0 to 1000 Å, for each pore volume increment smaller than 10% of the pore volume, the quotient of the pore volume increment and the corresponding pore diameter interval has been plotted as a function of the linear average pore diameter over the relevant pore diameter interval; the pore diameter is read off at the point where the curve reaches a maximum.

Method 3: Read off from a graph composed by means of a complete pore radius distribution and in which for the pore diameter range from 0 to 1000 Å, for each pore volume increment smaller than 10% of the pore volume, the quotient of the pore volume increment and

the corresponding pore diameter interval has been cumulatively plotted as a function of the linear average pore diameter over the relevant pore diameter interval; the pore diameter is read off at the point corresponding with 50% of the total quotient at 1000 Å.

For catalyst 4 the following pore diameter values are found by the different methods.

By method 1: 131 Å.

By method 2: Undeterminable, since there is no distinct maximum in the curve.

By method 3: 76 Å.

For catalyst 5 the following pore diameter values are found by the different methods.

By method 1: 189 Å.

By method 2: 160 Å.

By method 3: 136 Å.

It is seen that the different methods for determining the pore diameter of the catalyst particles lead to widely varying results. For determining the specific pore diameter (p) of the particles of catalysts for use in carrying out the process of the present invention method 3 is used.

(b) A complete sieve analysis was carried out of a Ni/Mo/Al₂O₃ catalyst having a particle diameter between 0.115 and 1.10. The results of this sieve analysis are shown in Table D.

TABLE D

Sieve No. (US mesh)	Particle diameter, mm	%, byweight	Average particle size, mm	Cumulative %, by weight
16— 18	1.00 —1.19	1.0	1.10	100.0
18— 20	0.84 —1.00	2.3	0.92	99.0
20— 25	0.71 —0.84	3.5	0.77	96.7
25— 30	0.59 —0.71	5.2	0.65	93.2
30— 3	0.50 —0.59	5.5	0.55	88.0
35— 40	0.42 —0.50	6.6	0.46	82.5
40— 45	0.35 —0.42	8.1	0.38	75.9
45— 50	0.297—0.35	7.1	0.32	67.8
50— 60	0.250—0.297	9.3	0.27	60.7
60— 70	0.210—0.250	8.9	0.23	51.4
70— 80	0.177—0.210	8.5	0.19	42.5
80—100	0.149—0.177	9.9	0.165	34.0
100—120	0.125—0.149	10.8	0.13	24.1
120—140	0.105—0.125	13.3	0.115	13.3

Of this catalyst the particle diameter was determined by two different methods which are both used in practice.

- Method 1: calculated as linear average by means of the formula

$$\text{particle diameter} = \frac{d_1 + d_2}{2}$$

in which d_1 and d_2 represent the particle diameter of the largest and the smallest particle respectively.

Method 2: read off from a graph composed by means of a complete sieve analysis and in which for every successive sieve fraction the percentage, by weight, based on the total weight of the catalyst sample, has been plotted cumulatively as a function of the linear average diameter of the relevant sieve fraction; the particle diameter is read off at the point corresponding with 50% of the total weight.

For this catalyst the following particle diameter values are found by the different methods.

By method 1: 0.61 mm

By method 2: 0.225 mm.

It is seen that the different methods for determining the particle diameter of the catalyst lead to widely varying results. For determining the specific particle diameter (d) of the particles of catalysts for use in carrying out the process of the present invention method 2 is used.

WHAT WE CLAIM IS:—

1. A process for the catalytic hydrodesulphurization of a residual hydrocarbon oil or oil fraction having a total vanadium and nickel content above 30 ppmw and a C_{10} -asphaltene content above 0.5% by weight, in which during the operation the catalyst present in the desulphurization reactor is continuously or periodically replenished, in which process a catalyst is used the particles of which have a pore volume above 0.30 ml/g less than 10% of which pore volume being present in pores with a diameter above 1000 Å, and in which the catalyst particles have a specific pore diameter (p), expressed in Å, of from $45 \times d^{0.6}$ to $140 \times d^{0.6}$, in which d is the specific particle diameter in mm., and in which d and p are determined by the determination method herein defined.

2. A process as claimed in claim 1, in which a catalyst is used the particles of which have a specific particle diameter of 0.05—2.5 mm.

3. A process as claimed in claim 1 or 2, in which a catalyst is used the particles of which have a specific particle diameter of

0.05—1.0 mm and a specific pore diameter of from $45 \times d^{0.6}$ to $130 \times d^{0.6}$.

4. A process as claimed in claim 1 or 2, in which a catalyst is used the particles of which have a specific particle diameter of 1.0—2.0 mm and a specific pore diameter of from $45 \times d^{0.6}$ to $120 \times d^{0.6}$.

5. A process as claimed in any one of claims 1—4, in which the desulphurization is carried out with the use of the catalyst in the form of a suspension or an expanded bed.

6. A process as claimed in any one of claims 1—3, in which the desulphurization is carried out with the use of the catalyst in the form of a suspension or an expanded bed, the catalyst particles having a specific diameter of 0.05—1.0 mm.

7. A process as claimed in claim 5 or 6, in which the desulphurization is carried out by recycling a suspension, of the catalyst particles and the hydrocarbon oil to be desulphurized by the action of a driving force generated by a gas lift installation present in the reactor, the gas which provides the gas lift action and which substantially consists of hydrogen, being introduced from outside into the lower part of the gas lift installation, while gas that is still present in the liquid in the form of bubbles at the upper end of the gas lift installation is separated from the suspension and passed outside the reactor, liquid product being passed outside the reactor after the catalyst particles have been separated from the suspension in one or more hydrocyclones, which separated particles are turned to the reactor through a long stand pipe (stand pipes) connected to that hydrocyclone (those hydrocyclones), and the recycled/supplied liquid stream ratio being between 4:1 and 20:1.

8. A process as claimed in claim 5 or 6, in which the desulphurization is carried out by passing the hydrocarbon oil to be desulphurized together with hydrogen through a vertically disposed catalyst bed in the upward direction, the liquid and gas velocity used being such that the catalyst bed expands and occupies a volume which is at least 10% larger than the volume of the non-expanded catalyst bed.

9. A process as claimed in any one of claims 1—4, in which the desulphurization is carried out with the use of the catalyst in the form of a moving bed.

10. A process as claimed in any one of claims 1, 2 or 4, in which that the desulphurization is carried out with the use of the catalyst in the form of a moving bed, the catalyst particles having a specific particle diameter of 1.0—2.0 mm.

11. A process as claimed in claim 9 or 10, in which the desulphurization is carried out with the use of a moving catalyst bed, in which case the catalyst bed moves through a vertically disposed reactor in the upward or



Of this catalyst the particle diameter was determined by two different methods which are both used in practice.

Method 1: calculated as linear average by means of the formula

$$\text{particle diameter} = \frac{d_1 + d_2}{2},$$

in which d_1 and d_2 represent the particle diameter of the largest and the smallest particle respectively.

Method 2: read off from a graph composed by means of a complete sieve analysis and in which for every successive sieve fraction the percentage, by weight, based on the total weight of the catalyst sample, has been plotted cumulatively as a function of the linear average diameter of the relevant sieve fraction; the particle diameter is read off at the point corresponding with 50% of the total weight.

For this catalyst the following particle diameter values are found by the different methods.

By method 1: 0.61 mm

By method 2: 0.225 mm.

It is seen that the different methods for determining the particle diameter of the catalyst lead to widely varying results. For determining the specific particle diameter (d) of the particles of catalysts for use in carrying out the process of the present invention method 2 is used.

WHAT WE CLAIM IS:—

1. A process for the catalytic hydrodesulphurization of a residual hydrocarbon oil or oil fraction having a total vanadium and nickel content above 30 ppmw and a C_{50} -asphaltene content above 0.5% by weight, in which during the operation the catalyst present in the desulphurization reactor is continuously or periodically replenished, in which process a catalyst is used the particles of which have a pore volume above 0.30 ml/g less than 10% of which pore volume being present in pores with a diameter above 1000 Å, and in which the catalyst particles have a specific pore diameter (p), expressed in Å, of from $45 \times d^{0.8}$ to $140 \times d^{0.6}$, in which d is the specific particle diameter in mm., and in which d and p are determined by the determination method herein defined.

2. A process as claimed in claim 1, in which a catalyst is used the particles of which have a specific particle diameter of 0.05—2.5 mm.

3. A process as claimed in claim 1 or 2, in which a catalyst is used the particles of which have a specific particle diameter of

0.05—1.0 mm and a specific pore diameter of from $45 \times d^{0.8}$ to $130 \times d^{0.6}$.

4. A process as claimed in claim 1 or 2, in which a catalyst is used the particles of which have a specific particle diameter of 1.0—2.0 mm and a specific pore diameter of from $45 \times d^{0.6}$ to $120 \times d^{0.4}$.

5. A process as claimed in any one of claims 1—4, in which the desulphurization is carried out with the use of the catalyst in the form of a suspension or an expanded bed.

6. A process as claimed in any one of claims 1—3, in which the desulphurization is carried out with the use of the catalyst in the form of a suspension or an expanded bed, the catalyst particles having a specific diameter of 0.05—1.0 mm.

7. A process as claimed in claim 5 or 6, in which the desulphurization is carried out by recycling a suspension, of the catalyst particles and the hydrocarbon oil to be desulphurized by the action of a driving force generated by a gas lift installation present in the reactor, the gas which provides the gas lift action and which substantially consists of hydrogen, being introduced from outside into the lower part of the gas lift installation, while gas that is still present in the liquid in the form of bubbles at the upper end of the gas lift installation is separated from the suspension and passed outside the reactor, liquid product being passed outside the reactor after the catalyst particles have been separated from the suspension in one or more hydrocyclones, which separated particles are turned to the reactor through a long stand pipe (stand pipes) connected to that hydrocyclone (those hydrocyclones), and the recycled/supplied liquid stream ratio being between 4:1 and 20:1.

8. A process as claimed in claim 5 or 6, in which the desulphurization is carried out by passing the hydrocarbon oil to be desulphurized together with hydrogen through a vertically disposed catalyst bed in the upward direction, the liquid and gas velocity used being such that the catalyst bed expands and occupies a volume which is at least 10% larger than the volume of the non-expanded catalyst bed.

9. A process as claimed in any one of claims 1—4, in which the desulphurization is carried out with the use of the catalyst in the form of a moving bed.

10. A process as claimed in any one of claims 1, 2 or 4, in which that the desulphurization is carried out with the use of the catalyst in the form of a moving bed, the catalyst particles having a specific particle diameter of 1.0—2.0 mm.

11. A process as claimed in claim 9 or 10, in which the desulphurization is carried out with the use of a moving catalyst bed, in which case the catalyst bed moves through a vertically disposed reactor in the upward or



downward direction, fresh catalyst being periodically supplied to the one side of the reactor and a substantially deactivated catalyst being periodically discharged on the other side of the reactor.

12. A process as claimed in any one of claims 1—11, in which a catalyst is used the particles of which have a pore volume above 0.40 ml/g.

13. A process as claimed in any one of claims 1—12, in which the catalyst is used in the form of agglomerates each of which is made up of particles having a pore volume above 0.30 ml/g, less than 10% of which pore volume being present in pores with a diameter above 1000 Å, and which particles have a specific pore diameter (p), expressed in Å, of from $45 \times d^{0.6}$ to $140 \times d^{0.6}$, in which d is the specific particle diameter in mm, and d and p are determined by the determination method herein defined, and more than 10% of the total pore volume of the agglomerates being present in pores with a diameter above 1000 Å.

14. A process as claimed in claim 13, in which more than 25% of the total pore volume of the agglomerates is present in pores with a diameter above 1000 Å.

15. A process as claimed in claim 13 or 14, in which the agglomerates are prepared by bonding said particles, with or without the use of a binding agent, in the presence of a substance which is incorporated in the agglomerates and subsequently removed therefrom by evaporation, combustion, solution, leaching or otherwise, leaving pores with a diameter above 1000 Å, in the agglomerates.

16. A process as claimed in any one of claims 1—15, in which the desulphurization is carried out in the presence of a sulphur-resistant catalyst containing one or more metals of Group VIB, VIIB and/or VIII, their sulphides and/or oxides, supported on an inorganic oxide of elements of Group II, III or IV, or on mixtures of the said oxides.

17. A process as claimed in claim 16, in which the catalyst contains 2—35%, by weight, of metal.

18. A process as claimed in claim 16 or 17, in which the catalyst contains 0.1—10%, by weight, of one or more metals of Group VIII and 2.5—30%, by weight, of one or more metals of Group VIB, in such quantities that the atomic ratio of the said Group VIII and VIB metals is between 0.1:1 and 5:1.

19. A process as claimed in any one of claims 16—18, in which the catalyst contains as carrier material alumina or silica-alumina.

20. A process as claimed in claim 19, in which a silica-alumina supported catalyst is used which has been prepared by calcining silica-alumina hydrogel and neutralizing the resultant xerogel with a nitrogen base and recalcining the neutralized xerogel after one or more catalytically active metals have been deposited thereon.

21. A process as claimed in any one of claims 1—20, in which the desulphurization is carried out at a temperature of 350°C—475°C, a total pressure of 50—350 kg/cm² and a space velocity of 0.1—10 parts, by weight, of fresh feed per part by volume of catalyst per hour.

22. A process as claimed in claim 21, in which the desulphurization is carried out at a temperature of 385°C—445°C, a total pressure of 75—225 kg/cm² and a space velocity of 0.5—5 parts by weight, of fresh feed per part by volume of catalyst per hour.

23. A process for the catalytic hydrodesulphurization of a residual hydrocarbon oil or oil fraction, substantially as described hereinbefore with reference to the Example in so far as relating to desulphurization with the use of catalysts 1, 2, 9, 10, 11, 13, 14 and 15 thereof.

24. A residual hydrocarbon oil or oil fraction desulphurized by the process claimed in any one of claims 1—23.

25. Catalyst particles suitable for the catalytic hydrodesulphurization of a residual hydrocarbon oil, which have a pore volume above 0.30 ml/g, less than 10% of which pore volume being present in pores with a diameter above 1000 Å, and a specific pore diameter (p), expressed in Å, of from $45 \times d^{0.6}$ to $140 \times d^{0.6}$, in which d is the specific particle diameter in mm., and in which d and p are determined by the determination method herein defined.

26. Catalyst agglomerates suitable for the catalytic hydrodesulphurization of a residual hydrocarbon oil, which are made up of particles as claimed in claim 25 and in which more than 10% of the total pore volume of the agglomerates is present in pores with a diameter above 1000 Å.

27. Catalyst particles as claimed in claim 25 and substantially as described hereinbefore.

28. Catalyst agglomerates as claimed in claim 26 and substantially as described hereinbefore.

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