

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) HYDRODESULFURIZATION OF PETROLEUM RESIDUUM

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, 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:—

This invention relates to a process for the hydrodesulfurization of petroleum oils. More particularly the invention relates to the hydrodesulfurization of petroleum oils containing residual components and having high sulfur contents in the presence of a catalyst having a support material characterized by a critical silica content and pore size distribution.

The process of the invention is applied to a petroleum oil containing residual components and more preferably to a petroleum residuum feedstock. The three major characteristics of residua other than molecular weight which distinguish them from distillates are that residua contain (1) asphaltenes and other high molecular weight, aromatic structures which severely inhibit the rate of hydrodesulfurization, and cause catalyst deactivation; (2) ash forming constituents such as metallo-organic compounds which result in catalyst contamination and interfere with catalyst regeneration; and (3) a relatively large quantity of sulfur which gives rise to objectionable quantities of SO₂ and SO₃ upon combustion in industrial furnaces.

Hydrodesulfurization has long been recognized as a means for removing sulfur from petroleum oils generally and more specifically from residual oils and asphalts. In addition to sulfur removal, hydrodesulfurization processes generally result in improvement in other properties of residual fuels by nitrogen removal and metals removal. In spite of these benefits, the commercial application of hydro-

desulfurization to residua to produce improved residual fuels has been minimal. Low economic incentives for improved fuel oil properties and high operating costs associated with the relatively high pressure required, the high hydrogen consumption and short catalyst life have hindered the utilization of such processes.

The principal object of the present invention is to reduce the sulfur content of petroleum oils containing residual components, preferably petroleum residuum, without significantly changing the properties of the oil. The process is centered on nondestructive hydrodesulfurization as distinguished from destructive hydrogenation or hydrocracking. Thus, conversion to gas and light ends is minimized. Cost studies have shown that the key factors are catalyst activity and catalyst activity maintenance. Therefore the specific object of the invention is to provide a process which is carried out at moderate pressure, temperature and other conditions with a catalyst which features low cost and high activity maintenance.

Summarizing briefly, the object of the invention is attained by hydrodesulfurizing petroleum oils, particularly petroleum residua, at moderate conditions in the presence of a porous catalyst comprising an oxide or sulfide of nickel or cobalt and an oxide or sulfide of molybdenum or tungsten deposited upon a support material consisting essentially of 1 to 6 wt. % silica and 94 to 99 wt. % alumina, the catalyst having a maximum pore volume and surface area in pores 30 to 70Å in diameter.

In the drawings, Figure 1 is a graph comparing the temperature increase requirement of one of the catalysts of the invention compared to that of a typical prior art catalyst and Figure 2 is a graph relating relative catalyst activity to the quantity of silica in the catalyst.

The process feedstock is a petroleum oil,

containing residual components, preferably a petroleum residuum, obtained from distillation or other treating or separation process. From 30 to 100% of the feed may boil above 900°F. The process is designed to treat the petroleum oil without any pre-processing; however, when the metal content of the oil is greater than 500 to 1000 ppm it may be necessary to employ a metals removal step such as HF treatment or solvent precipitation with propane, butane, mixtures of propane and butane, pentane, hexane or naphtha. The petroleum oil can be a blend

of high boiling materials such as atmospheric bottoms, vacuum bottoms, deasphalted oil, visbreaker products, heat soaked materials and gas oil cuts. The feedstocks of the invention contain relatively large amounts of sulfur, asphaltenes, metals and ash-forming constituents. Some of these materials or conversion products thereof deposit on the hydrodesulfurization catalyst when hot oil is brought in contact with the catalyst surface.

The feedstocks treated can suitably have the following properties and inspections:

TABLE I
Typical Feedstock Inspections

	Broad Range	Narrow Range	Feed of Example (Sanfaniya Atmos. Resid.)
% Boiling Above 900°F.	30—100	50—100	60
Gravity, °API	—5 to 25	10—20	15.4
Viscosity, SFS @ 122°F.	50—5000+	100—1000	309
Sulfur, Wt. %	1—3	3—6	4.0
Nitrogen, Wt. %	0—1	0.001—0.5	0.26
Metals (ppm) Total	20—1000	80—500	127
Vanadium (ppm)	10—500	30—300	84
Nickel (ppm)	5—200	10—100	32
Asphaltenes, Wt. %	1—20	2—10	7.2
Pour, °F.	0—200	25—100	45

The composition and characteristics of the support is a most important aspect of the invention and the quantity of silica is critical. Hydrodesulfurization catalyst supports containing silica have been suggested in the past. However, silica was included in the support when the feedstock was gasoline or light gas oil or when a significant amount of hydrocracking was desired. It was felt that the presence of any significant amount of silica in the hydrodesulfurization of heavier oils would cause significant cracking with consequent coke make and catalyst fouling. Thus, it was entirely unexpected that relative catalyst activity could be greatly improved by the presence of a critical quantity of silica in the catalyst support.

The support can be prepared by precipitating the oxides or hydrated oxides of aluminum and silicon from aqueous solutions of water

salts of these metals. For example, suitable proportions of the water soluble salts of aluminum such as the sulfate, chloride or nitrate and suitable proportions of water soluble silicon salts such as sodium silicate are precipitated from solution by adjusting the pH of the solution with acidic or basic material. The precipitate is washed and otherwise treated to remove impurities as necessary. The support can be impregnated with the metals while it is wet or after drying and calcining.

A preferred method of preparing the catalysts is to treat alkaline aqueous aluminate solutions which contain predetermined amounts of silica with acidic reagents to precipitate an aluminosilicate in the hydrous form. A slurry produced by this technique is then dried by known methods to furnish a preferred catalyst support of this invention.

The supports of the types prepared above are then impregnated with metals which promote a hydrodesulfurization reaction.

- 5 The catalyst containing all the active ingredients is then dried and extruded, or the catalyst support is dried to remove excess moisture, impregnated and extruded, or alternatively dried to remove excess moisture, extruded, dried and then impregnated.

- 10 The preferred alkaline aqueous aluminate solution is a solution of sodium aluminate. It is understood that other alkali metal aluminates can be used but they are not preferred from an economic standpoint.

- 15 The acidic reagents which can be used are the mineral acid salts of aluminum, e.g.,

aluminum halides, nitrates, and sulfates. Also useful are the well-known mineral acids themselves, e.g., hydrochloric, nitric, sulfuric acids, and the like.

Preferably, the conditions for preparing the support are so controlled that the finished support has an apparent bulk density of less than 0.70 g./cc. It is further characterized as being opaque as distinguished from glassy in appearance (indicating that a large quantity of the alumina is in a crystalline form). The catalyst is extrudable.

In preparing these preferred catalytic materials the following illustrates preferred conditions:

TABLE II

Conditions	Broad Range	Preferred Range
I. Concentration of starting aluminate solution, expressed as Al_2O_3	1.2—5%	1.2—1.7%
II. Precipitation Temperature	105—120°F.	110—120°F.
III. pH	5—9.5	6—9
IV. Reaction Time	1/4—6 hrs.	1/4—2 Hrs.

- 35 Using the above general reaction conditions, the support resulting from the reaction is in the form of a dilute slurry. This slurry may then be concentrated and subjected to spray-drying operations at temperatures ranging between 200—2,000°F., preferably 200—500°F.

- 40 A method of preparing a catalyst support of this type is described in co-pending Application No. 28369/68 (Serial No. 1,230,143).

- 45 Using conventional techniques known to the catalyst art, the spray-dried material may be subjected to water washing to remove excess alkali metal ions and sulfate ions. The support can then be impregnated with the catalytic metals and extruded or pillled or otherwise formed into any desired physical form.

- 50 The aforementioned silica-alumina hydrogels can be composited with other synthetic and/or semi-synthetic aluminas, silica gels, and/or other silica-alumina-clay hydrogel compositions for the purpose of adjusting the

alumina and/or silica present during impregnation. It is essential that the silica content of the catalyst be maintained in the range of 1—6 weight percent, preferably 1.5—5 weight percent. The resulting catalyst, when calcined, should preferably have a total surface area greater than 150 $M^2/g.$ and the pore volume is preferably greater than 0.25 cc./g. as measured by the BET procedure with nitrogen.

The active metallic components in the finished catalyst are one or more of molybdenum oxide, molybdenum sulfide, tungsten oxide and tungsten sulfide, and one or more of nickel oxide, cobalt oxide, nickel sulfide and cobalt sulfide and mixtures of these. The preferred active metal components are nickel oxide with molybdenum oxide and cobalt oxide with molybdenum oxide. Oxide catalysts are preferably sulfided prior to use.

The final catalyst may contain the following amounts of each component.

TABLE III
Catalyst Composition

	Broad Range (Wt. %)	Preferred Range (Wt. %)
Nickel or Cobalt (as oxide)	1 to 15	2 to 10
Tungsten or Molybdenum (as oxide)	5-25	10-20
Silica	1 to 6	1.5 to 5
Alumina	93 to 52	86 to 64

The structure of the catalyst is also an important aspect of the invention. In the hydrodesulfurization of petroleum oils containing residual components, and particularly petroleum residua, a criticality of pore size has been found with respect to activity maintenance. It has been found that pores having a pore diameter in the 30-70Å range are of critical importance with heavy feeds. Evidently pores of smaller diameter than about 30Å are ineffective in desulfurizing the high molecular weight molecules present in such feeds and pores of larger diameter than about 70Å are rapidly deactivated. Thus a major portion of surface area should be present in pores having a pore diameter in the 30-70Å range and it is preferred that less than 0.25 cc/g. of the catalyst support should have a total pore volume in pores having a diameter exceeding 100Å. Catalysts having good activity and activity maintenance for hydrodesulfurization of heavy feedstocks are characterized by the following relationship between pore diameter in Å, pore volume in cc./g. and surface area in M²/g. for pores over the range of 30-70Å in diameter.

$$\frac{4 \times 10^4 \times \text{Pore Volume (cc./g.)}}{\text{Pore Diameter, Å}} > 100 \text{ M}^2/\text{g. Surface Area}$$

The pore volume distribution of a catalyst as defined by this invention is measured by nitrogen adsorption isotherm where the volume of nitrogen adsorbed is measured at various pressures. This technique is described in Ballou, et al., *Analytical Chemistry*, Vol. 32, April, 1960, pp. 532-536. The pore diameter distributions for the examples of the invention were obtained using a Model No. 4-4680 Adsorptomat manufactured by the American Instrument Company, Silver Springs, Maryland. One skilled in the art can select catalyst manufacturing process steps and process conditions within the specific ranges disclosed herein to prepare catalysts having the required pore diameter, pore size distribution, pore volume, and surface area.

EXAMPLE I

The following illustrates a typical catalyst preparation.

Three solutions are prepared, e.g., A, B, and C:

	Ingredient	Amount
Solution A*	Water	36 gallons
	Sodium Silicate Solution	
	28% SiO ₂	113 cc.
	Sodium Aluminate	
Solution B	23.5% Al ₂ O ₃ Solution	5323 cc.
	48% Gluconic Acid Solution	76 cc.
Solution C	98% H ₂ SO ₄	850 cc. into 4.5 gallons water
	9.5% Alum Solution	3.3 Gallons

* Total Al₂O₃ in solution — 1.3%

Solution B is added to Solution A over a period of 23 minutes. At this point the temperature of the reaction mixture is 118°F.

- 5 Solution C is then added to the mineral acid solution over a 19-minute period. The temperature during addition remains at 118°F. The final pH, after the above additions, is 8.8. The slurry was filtered, reslurried, 10 spray dried, washed to remove soluble salts, and redried.

- 15 The finished silica-alumina support has a pore volume of 2.36 cc./g., a surface area of 310 M²/g., and an apparent bulk density of 0.18 g./cc.

EXAMPLE 2

- 20 A silica-alumina support is prepared in the manner set forth in Example 1 and is composited with suitable quantities of molybdenum oxide and cobalt carbonate by impregnation. The slurry is filtered and dried to provide a catalyst (dry weight basis conditions are as follows:

25 taining 3.5% cobalt oxide, 12.0% molybdenum oxide, 1.7% SiO₂, and the balance alumina). This catalyst is hereinafter referred to as Catalyst B. The support can be impregnated with the other hydrogenation metals of the invention, i.e., nickel and tungsten in the same manner.

30 A commercial catalyst was selected for the purpose of obtaining comparative data. It contained 3.5 weight % cobalt oxide, 12.5 weight % molybdenum oxide, 0.2 weight % SiO₂, and the balance alumina. This catalyst is designated hereinafter as Catalyst A. 35

40 The hydrodesulfurization reaction is carried out in a conventional reactor of the fixed bed, moving bed or fluidized bed type. A slurry or ebullient bed can also be used. Considering the nature of the feedstock, the reaction conditions are relatively mild. The oil is contacted in the liquid phase. Typical con-

TABLE IV
Reaction Conditions

	Broad Range	Preferred Range
Temperature, °F.	500—825	650—800
Pressure, Psig	500—2500	1000—1800
Space Velocity, V/V/Hr.	0.2—5.0	0.5—2.0
Hydrogen Rate, SCF/Bbl.	500—7500	1000—5000

- 45 With these conditions viscosity reduction of the oil due to processing is not excessive and fuel oil viscosities which meet specifications are easily obtained.

- 50 The following comparative examples and tables demonstrate the improvements in hydrodesulfurization of residuum which can be obtained with the catalysts of the invention compared to a group of prior art catalysts.

EXAMPLE 3

55 A pilot plant unit containing 200 cc. of catalyst was used in this example. The oil was passed down through the catalyst bed.

60 The catalyst was calcined overnight at 1200°F. and then sulfided using 5 wt. % carbon disulfide in a light petroleum distillate. Sulfiding was carried out at 1 V/V/Hr., 1500 and 1500 SCF/B of hydrogen. The

reactor was held at 500°F. for two hours and then raised to 750°F. and held there for 16 hours. The temperature was lowered to near 700°F. and feed was cut in. The feedstock was a Safaniya residuum having the properties set forth in Table I. Side-by-side comparative runs were made to give a direct comparison to measure the activity decline of the catalysts. The pressure was 1500 psig., the space velocity was 1 V/V/Hr., and the hydrogen rate was 1500 SCF/Bbl. The reactor temperature was increased as necessary to obtain 55% desulfurization of the residuum. Catalyst A was selected for comparison because it was effective in hydrodesulfurization of distillate stocks. It contained 3.5 wt. % CoO and 12.5 wt. % MoO₃ on a support containing 0.2 wt. % SiO₂ and the balance alumina. Catalyst B is prepared in a manner set forth earlier in this specification. Figure 1 sets forth the temperature increase requirement (TIR) for runs with Catalyst A and Catalyst B. The TIR for Catalyst B is 0.17°F./day, showing a very low activity decline. Catalyst A exhibited the usual initial high activity decline then lined out at a TIR of 1.7°F./day. Thus Catalyst B has an activity maintenance ten times better than that of Catalyst A. This result was completely unexpected because the two catalysts demonstrated no such difference in the hydrodesulfurization of distillates.

Runs with Catalyst B demonstrate the fol-

lowing improvements: (1) greatly improved catalyst life, (2) lower pressure operation (1500 vs. 2200 psig. which was previously considered necessary for good catalyst life), and (3) lower gas rates (1500 vs. 3000 SCF/Bbl. also previously considered necessary for good catalyst life). In addition the new catalyst shows about half the metals laydown usually experienced with petroleum residuum feeds. These improvements make residuum hydrodesulfurization by our process attractive from a cost standpoint.

Kuwait atmospheric residuum (3.8 wt. % S) was desulfurized over Catalysts A and B at 800 psig., 1 V/V/Hr., 1500 SCF H₂ per barrel of feed for Catalyst B and 3000 SCF H₂ per barrel of feed for Catalyst A, the initial temperature of 685°F. The initial desulfurization was 66% for Catalyst B and 42% for Catalyst A in spite of the higher gas rate for Catalyst A. After 50 days the desulfurization with Catalyst B was still 50% at 685°F., whereas it was only 34% for the Catalyst A at 700°F. It is obvious that Catalyst B has higher activity and much better activity maintenance with this feedstock.

EXAMPLE 4

Table V shows the relative activity of a number of hydrodesulfurization catalysts. All runs were carried out on Safaniya atmospheric residuum (4.0% S) at the following conditions: 1500 psig., 725°F., 3000 SCF H₂/Bbl., 1 V/V/Hr., 60 cc. catalyst.

TABLE V

Catalyst	Composition (Alumina plus the following Materials) wt. %	Bulk Density	Rel. Vol. Act.† for Day			
			1	7	14	21
A	3.5 CoO, 12.5 MoO ₃ , 0.2 SiO ₂	0.66	100*	58	43	36
B	3.5 CoO, 12.0 MoO ₃ , 1.7 SiO ₂	0.65	180	140	115	110
C	4.0 NiO, 15.0 MoO ₃ , 3.4 SkO ₂	0.65	150	115	100	90
D	10.0 CoO, 20.0 MoO ₃ , 3.9 SiO ₂	1.0	160	113	105	100
E	10 NiO, 20.0 MoO ₃ , 3.9 SiO ₂	0.88	160	113	105	—
F	7.0 NiO, 23.0 WO ₃ , 3.9 SiO ₂	0.88	94	70	63	60
G	3.5 CoO, 12.5 MoO ₃ , 6.0 SiO ₂	0.59	280	105	65	50
H	3.5 CoO, 12.5 MoO ₃ , 8.6 SiO ₂	0.57	280	80	50	35
I	6.0 NiO, 13.0 MoO ₃ , 14.0 SiO ₂	0.54	160	45	—	—
J	4.0 NiO, 15.0 MoO ₃ , 0.3 SiO ₂	0.59	70	40	—	—

† Relative Volume Activity is the catalytic activity relative to catalyst A which is arbitrarily assigned a value of 100.

* Equivalent to 67% desulfurization or 1.3 wt. % S in product with 4.0 wt. % S in feed.

5 The relative volume activity of the catalysts employed in the process of the invention, i.e., catalysts B, C, D, E, F, and G is far superior to the activity of the prior art catalysts, i.e., A, H, I, and J. It can be seen that silica content is critical. In the drawing, Figure 2 shows the criticality of silica in the range of 1 to 6 in the catalyst base in attaining high activity and activity maintenance.

10 Since catalysts are sold by the pound, we prefer the catalysts having the lowest metals content and bulk density which will give superior activity maintenance, i.e., catalysts like Catalyst B.

15 The catalysts employed in the process of the invention have excellent surface area stability and they are effectively regenerated by

conventional techniques at temperatures ranging from 600—1000°F.

EXAMPLE 5

20 Catalysts A and B of the first two examples have some similar properties as shown by lines 1—5 of Table VI, below. For example, the overall surface areas are nearly equivalent. However, the nature of the surface areas are considerably different. Catalyst A has a surface area in 30 to 70Å pores of 86 square meters per gram. Catalyst B has a surface area in 30 to 70Å pores of 174 square meters per gram. The relatively large number of pores in the 30 to 70Å range of Catalyst B seems to be one of the reasons for its extended life in processing residua.

TABLE VI

	Cat. A	Cat. B	Cat. E
Surface Area, M ² /g.	253	266	271
Pore Volume, cc./g.	0.58	0.50	0.24
Bulk Density, g./cc.	0.63	0.71	0.88
Pellet Density, g./cc.	1.10	1.20	—
Pellet Strength	11.0	16.5	—
SiO ₂ , Wt. %	0.2	2.0	3.9
CoMoO ₄ , Wt. % (by X-ray)	2	0	0
Surface Area in 30—70Å Pores, M ₂ /g.	86	174	136
Relative Wt. Activity at Day 21	36	91	67

After 21 days of operation at the conditions set forth in Examples 4 and 5, Catalyst B has a weight activity of 91 compared to

a weight activity of only 36 for Catalyst A. Weight activity is determined by

$$\text{Relative Vol. Activity} \times \frac{\text{Bulk Density of Reference Catalyst}}{\text{Bulk Density of Test Catalyst}}$$

45 In a series of comparative runs, Catalyst B proved to have at least five times as much catalyst life as Catalyst A. Similarly Catalysts C and E which are nickel-molybdenum type catalysts had a high relative weight activity. Thus a surface area in 30—70Å pores of at least 100 M²/g., preferably 100—300 M²/g. provides excellent activity and activity maintenance.

50 It is well known that hydrodesulfurization of residua can be improved by subjecting the feed to such pretreating steps as deasphalting, deasphalting, dilution and metals removal; however, usually the cost of the multi-

step processes cannot be justified. The process of this invention provides adequate sulfur removal without any other major treating steps unless the feed has a very high metals content.

60 The catalysts of this invention are sufficiently active so that hydrodesulfurization reaction pressures in the range of 800 to 1500 psig are satisfactory depending upon feed-stock. Prior art processes require pressures of 2500 to 3000 psig, and a high treat gas recycle because of the low activity of the catalyst. Furthermore, they require 25% more investment and higher operating costs to

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achieve the same throughput. With respect to temperature, hydrodesulfurization above 825°F. is not practical because of excessive gas make and hydrogen consumption. The process of the invention operates well at lower temperatures. Conversion to light ends, gasoline and other light stocks is less than 15 wt. % based on the feedstock.

WHAT WE CLAIM IS:—

1. A process for the hydrodesulfurization of a sulfur-containing petroleum oil containing residual components characterized by contacting said oil with hydrogen at mild hydrodesulfurization conditions in the presence of a porous hydrodesulfurization catalyst comprising an oxide and/or sulfide of nickel and/or cobalt and an oxide and/or sulfide of molybdenum and/or tungsten deposited on a support material comprising 1—6 weight % silica and 94—99 weight % alumina, the catalyst having a major portion of the pore volume and surface area in pores having diameters in the range 30—70Å.
2. A process according to claim 1 further characterized in that said petroleum oil is a petroleum residuum.
3. A process according to any of claims 1—2 further characterized in that said support material of said hydrodesulfurization catalyst has less than 0.25 cc/g. of its total pore volume in pores having a diameter of more than 100 Å.
4. A process according to any of claims 1—3 further characterized in that said oil is contacted with said hydrodesulfurization catalyst at a temperature of 500—825°F., a pressure of 500—2500 psig and in the presence of 500—7500 SCF/b. of hydrogen.
5. A process according to any of claims

1—4 further characterized in that the active metallic components of the catalyst consist essentially of molybdenum oxide and/or molybdenum sulfide in combination with at least one of nickel oxide, cobalt oxide, nickel sulfide and cobalt sulfide.

6. A process according to any of claims 1—5 further characterized in that said hydrodesulfurization catalyst comprises 10—20 weight % molybdenum oxide and 2—10 weight % cobalt oxide deposited on said support material.

7. A process according to any of claims 1—6 further characterized in that said hydrodesulfurization catalyst is sulfided prior to use.

8. A process according to any of claims 1—7 further characterized in that from 30—100% of the said petroleum oil boils above 900°F.

9. A process according to any of claims 1—10 further characterized in that the said contacting of the said oil with the said hydrodesulfurization catalyst under said reaction conditions is carried out in the liquid phase.

10. A process for the hydrodesulfurization of petroleum oils containing residual components according to claim 1 and substantially as hereinbefore described with particular reference to any of the examples and the drawings.

11. A process according to claim 1 and substantially as hereinbefore described.

12. Hydrodesulfurized petroleum oil products made by a process in accordance with any preceding claim.

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achieve the same throughput. With respect to temperature, hydrodesulfurization above 825°F. is not practical because of excessive gas make and hydrogen consumption. The process of the invention operates well at lower temperatures. Conversion to light ends, gasoline and other light stocks is less than 15 wt. % based on the feedstock.

WHAT WE CLAIM IS:—

1. A process for the hydrodesulfurization of a sulfur-containing petroleum oil containing residual components characterized by contacting said oil with hydrogen at mild hydrodesulfurization conditions in the presence of a porous hydrodesulfurization catalyst comprising an oxide and/or sulfide of nickel and/or cobalt and an oxide and/or sulfide of molybdenum and/or tungsten deposited on a support material comprising 1—6 weight % silica and 94—99 weight % alumina, the catalyst having a major portion of the pore volume and surface area in pores having diameters in the range 30—70Å.
2. A process according to claim 1 further characterized in that said petroleum oil is a petroleum residuum.
3. A process according to any of claims 1—2 further characterized in that said support material of said hydrodesulfurization catalyst has less than 0.25 cc/g. of its total pore volume in pores having a diameter of more than 100 Å.
4. A process according to any of claims 1—3 further characterized in that said oil is contacted with said hydrodesulfurization catalyst at a temperature of 500—825°F., a pressure of 500—2500 psig and in the presence of 500—7500 SCF/b. of hydrogen.
5. A process according to any of claims

1—4 further characterized in that the active metallic components of the catalyst consist essentially of molybdenum oxide and/or molybdenum sulfide in combination with at least one of nickel oxide, cobalt oxide, nickel sulfide and cobalt sulfide.

6. A process according to any of claims 1—5 further characterized in that said hydrodesulfurization catalyst comprises 10—20 weight % molybdenum oxide and 2—10 weight % cobalt oxide deposited on said support material.

7. A process according to any of claims 1—6 further characterized in that said hydrodesulfurization catalyst is sulfided prior to use.

8. A process according to any of claims 1—7 further characterized in that from 30—100% of the said petroleum oil boils above 900°F.

9. A process according to any of claims 1—10 further characterized in that the said contacting of the said oil with the said hydrodesulfurization catalyst under said reaction conditions is carried out in the liquid phase.

10. A process for the hydrodesulfurization of petroleum oils containing residual components according to claim 1 and substantially as hereinbefore described with particular reference to any of the examples and the drawings.

11. A process according to claim 1 and substantially as hereinbefore described.

12. Hydrodesulfurized petroleum oil products made by a process in accordance with any preceding claim.

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