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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 containing residual components. More particularly the invention relates to the hydrodesulfurization of petroleum residuum in the presence of a catalyst having a support material prepared in a specific manner.

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 SO_2 and SO_3 upon combustion in industrial furnaces.

Hydrodesulfurization has long been recognized as a means of removing sulfur from petroleum oils and more particularly 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 hydrodesulfurization 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 containing residual components, preferably petroleum residua, at moderate conditions in the presence of a catalyst comprising a mixture of a compound of at least one metal of Group VI (such as an oxide or sulfide of nickel or cobalt and an oxide or sulfide of molybdenum or tungsten) with a compound of at least one Group VIII metal composited with a support material of alumina containing 1–6 wt. % silica, the support material being prepared by forming solutions of oxides or hydrated oxides of aluminum and silicon, preferably containing a specific quantity of Al_2O_3 , and precipitating and drying to obtain the silica-alumina support. During the precipitation of the support, as a slurry, the pH is maintained in the range 5–9.5 and the temperature is maintained in the range 105–120° F., and the resulting slurry is dried to give an apparent density to the support of less than 0.7. In the most preferred embodiment an aldonic acid or an aldonate is included in the starting solution.

The process feedstock is a petroleum oil con-

- 10 taining 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.
- 5 The process is designed to treat the oil without any preprocessing; however, when the metal content of the oil is greater than about 500 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 feedstock 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 materials. Some of these materials or conversion products thereof deposit on the hydrodesulfurization catalyst when hot oil is brought in contact with the catalyst surface.
- 20 Typical feedstocks treated have the following properties and inspections:

TABLE I
Typical Feedstock Properties

	Broad Range	Narrow Range	Feed of Example 3 (Safaniya 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—8	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 procedure followed in the preparation of the support is the most important aspect of the invention.

- 30 The support can be prepared by precipitating the oxides or hydrated oxides of aluminum and silicon from aqueous solutions of water-soluble salts of these elements. For example, suitable proportions of the water soluble salts of aluminum such as the sulfate, chloride or nitrate and suitable proportions of water
- 35 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.

- 40 The 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.

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

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.

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 a mixture of a mineral acid and an aluminum salt of a mineral acid.

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.

The first variable which must be controlled in preparing the support is the alumina concentration. The alumina concentration, expressed as wt. % Al_2O_3 , of the aqueous alkali aluminate solution is preferably between 1.2 and 5.0, more preferably between 1.2 and 3.0 and the most preferred concentration is between 1.2 and 1.7. It is felt that close control of the alumina concentration within the stated ranges is a material factor in producing a support which can be extruded in commercial equipment.

Other important variables include pH and

temperature. The precipitation must be effected at a pH between 5 and 9.5, preferably between 6 and 9. Temperatures ranging between 105—120° F., preferably 110—120° F. must be employed.

In the most preferred embodiment, the silica-alumina support is prepared in the presence of a material selected from the group consisting of an aldonic acid or an aldonate, preferably a gluconate or gluconic acid. Galactonic acid, arabonic acid, xylonic acid, mannoic acid, and salts thereof can be used as well. Suitable aldonates include the sodium potassium, zinc, magnesium, calcium, and lithium salts of gluconic acid or other aldonic acids. This material is used in the initial solution in amounts ranging from 0.5 to 6.0 wt. % based on the Al_2O_3 content of the solution. It appears that the addition of aldonates and aldonic acids in the preparation of the silica alumina base has a beneficial effect on the physical characteristics of the final catalyst and its effectiveness in hydrodesulfurization of petroleum oils, particularly petroleum residua.

In preparing these preferred catalytic materials the following illustrates preferred conditions and concentrations.

TABLE II

Conditions	Broad Range	Preferred Range
I. Concentration of starting aluminate solution, expressed as Al_2O_3	1.2—5 Wt. %	1.2—1.7 Wt. %
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.
V. Aldonate or Alconic Acid	0.5—6 Wt. %	2—3 Wt. %

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—2000° F., preferably 200—500° F. Spray drying, particularly at the stated conditions preserves the catalyst base in the desired form.

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 pilled or otherwise formed into any desired physical form.

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. 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 comprise a Group VI metal compound, specifically a compound of molybdenum or tungsten selected from molybdenum oxide, molybdenum sulfide, tungsten oxide,

tungsten sulfide, or mixtures of these and a Group VIII metal compound, specifically a compound of nickel or cobalt selected from nickel oxide, cobalt oxide, nickel sulfide and cobalt sulfide or mixtures of these. The preferred active metal compounds 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 54	86 to 65

EXAMPLE 1

The following illustrates a typical catalyst preparation.

Three solutions are prepared, A, B, and C.

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

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, spray dried, washed to remove soluble salts, and redried.

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

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 containing 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.

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EXAMPLE 3

For purposes of comparison a conventional hydrodesulfurization catalyst is prepared in the following manner.

10 In a tank containing 6,000 gallons of water at 75° F. are dissolved 300 lbs. of soda ash. When the soda ash has been dissolved, 160 gallons of an 80% concentration aqueous sodium aluminate solution are pumped into the tank over a 15 to 20 minute time and the contents of the tank heated to 80° F. 400 gal-
15 lons of aqueous aluminum sulfate of 7.8% Al_2O_3 concentration are added to the admixture over a one and one-half hour period with water of dilution in conjunction with and in
20 addition thereto diluting the reaction mass at a rate of 18 gallons per minute.

The pH of the resulting aqueous reaction mass is adjusted to 8.5 with about 50 gallons of 82% concentration aqueous sodium alumin-
25 ate solution which, while being added, is also diluted continuously with water at a rate of 35 gallons per minute over a five minute addition period.

30 The contents of the tank are heated to 120° F. and pumped to storage where precipitation of the hydrated aluminum takes place.

The precipitated hydrated alumina is there-
after filtered off in a large gel filter, but not washed. The filtered, slightly gelatinous, pro-
35 duct is spray dried by concurrent drying at 150° F. to 305° F. (max) powder temperature and at 900 lbs. per square inch pressure. 85% to 90% of the collected dried micro-
40 spheres were of a size range to pass through a 200 mesh sieve.

The recovered, dried product was subjected to four plant wash cycles. The first reduced the Na_2O content to 1.20 at 21.8% solids, the second in ammoniacal water of pH 9-10 re-
45 duced the impurities to between 0.13 and 0.28 Na_2O , and the SO_4 content 3.8% at 22%

solids, the third wash product solids contain-
ed 0.04% Na_2O and 1.50% SO_4 at 23.2% solids. The final recovered washed product averaged 0.026% Na_2O and 1.62% SO_4 at
50 24.6% solids. The yield was 66% by weight of the recovered unwashed, spray dried prod-
uct.

4,900 parts by weight of the spray dried product of this Example was reslurried in water. 190 parts of finely divided MoO_3 were first pasted in a small amount of water and sub-
sequently stirred into the catalyst base sus-
55 pension. After about 20 minutes, 90 parts of finely divided prepasted $CoCO_3$ were also in-
60 corporated. The suspension was heated at 180° F. for 1½ hours. During the entire heating period samples were withdrawn at ten minute intervals and microscopically examined. None
65 of the samples examined showed a breakdown of the microspheres of catalyst base. This is contrary to experience where the recovered
precipitate of hydrated alumina catalyst base is washed prior to the spray drying step.

Sample of the impregnated stock were
70 flash dried.

A typical analysis of the product obtained is as follows (on a dry basis):

Percent Volatile	2.9	
Percent Na_2O	0.040	75
Percent SO_4	0.21	
Percent SiO_2	0.20	
Percent MoO_3	12.8	
Percent CoO	3.85	
Percent MgO	0.18	80
Percent CaO	0.30	
Percent Fe	0.038	

The hydrodesulfurization reaction is car-
ried out in a conventional reactor of the fixed
bed, moving bed or fluidized bed type. A
85 slurry of ebullient bed can also be used. Con-
sidering the nature of the feedstock, the re-
action conditions are relatively mild. The oil
is contacted in the liquid phase. Typical con-
90 ditions are as follows:

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

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

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 4

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

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 psig, and 1500 SCF/B of hydrogen. The reactor was held at 500° F. for two hours and then raised to 750° 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 is prepared in the manner shown in Example 3. 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 in Examples 1 and 2.

The temperature increase requirement (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 following 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 an attractive process 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 and 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 was 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.

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 multistep 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.

The catalysts of this invention are sufficiently active that hydrodesulfurization reaction pressures in the range of 800 to 1500 psig. are satisfactory depending upon feedstock. Prior art processes requiring pressures of 2500 to 3000 psig. and a high treat gas recycle because of the low activity of the catalyst, require 25% more investment and higher operating costs to 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 feedstock comprising a petroleum oil containing residual components characterized by contacting said feedstock with hydrogen under hydrodesulfurization conditions in the presence of a hydrodesulfurization catalyst comprising a mixture of a compound of a metal of Group VI and a compound of a Group VIII metal composited with an alumina support containing 1—6 wt.% silica, said support being prepared by the steps of:

(a) forming an aqueous solution of a water soluble alkaline aluminum compound, a water-soluble silicon compound and an acidic precipitating agent.

(b) precipitating a hydrous silica-alumina slurry from said solution at a pH of 5—9.5 and a temperature of 105—120° F., and

(c) drying the slurry to obtain a silica-alumina support having an apparent bulk density of less than 0.7.

2. A process according to claim 1 further characterized in that said hydrodesulfurization conditions include a temperature in the



(14)
With these conditions viscosity reduction of the oil due to processing is not excessive and fuel oil viscosities which meet specifications are easily obtained.

- 5 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.

10 EXAMPLE 4

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

- 15 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 psig, and 1500 SCF/B of hydrogen. The reactor was held at 500° F. for two hours and then raised to 750° 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.

- 30 Catalyst A was selected for comparison because it was effective in hydrodesulfurization of distillate stocks. It is prepared in the manner shown in Example 3. 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 in Examples 1 and 2.

- 40 The temperature increase requirement (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.

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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 and 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 was 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.

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 multistep 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.

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WHAT WE CLAIM IS:—

1. A process for the hydrodesulfurization of a feedstock comprising a petroleum oil containing residual components characterized by contacting said feedstock with hydrogen under hydrodesulfurization conditions in the presence of a hydrodesulfurization catalyst comprising a mixture of a compound of a metal of Group VI and a compound of a Group VIII metal composited with an alumina support containing 1—6 wt. % silica, said support being prepared by the steps of:

(a) forming an aqueous solution of a water soluble alkaline aluminum compound, a water-soluble silicon compound and an acidic precipitating agent.

(b) precipitating a hydrous silica-alumina slurry from said solution at a pH of 5—9.5 and a temperature of 105—120° F., and

(c) drying the slurry to obtain a silica-alumina support having an apparent bulk density of less than 0.7.

2. A process according to claim 1 further characterized in that said hydrodesulfurization conditions include a temperature in the

range of 500—825° F., a pressure in the range of 500—2500 psig., and a space velocity in the range of 0.2—5.0 V/V/Hr.

5. 3. A process according to claim 1 or claim 2 further characterized in that the said aqueous solution of step (a) in the preparation of said support also contains a compound selected from the group consisting of aldonic acids and aldonates.
10. 4. A process according to any of claims 1—3 further characterized in that said water-soluble alkaline aluminum compound is sodium aluminate, said water-soluble silicon compound is sodium silicate and said aqueous solution contains 1.2—5.0 wt.% Al_2O_3 .
15. 5. A process according to any of claims 1—4 further characterized in that said precipitating agent in said aqueous solution of step (a) comprises a mixture of a mineral acid and an aluminum salt of a mineral acid or a mineral acid salt of aluminum or a mineral acid.
20. 6. A process according to claim 5 further characterized in that said aqueous solution contains sodium aluminate, sodium silicate, sulfuric acid, aluminum sulfate and gluconic acid.
25. 7. A process according to any of claims 1—6 further characterized in that said hydrous silica-alumina slurry is dried by spray drying to obtain a silica-alumina support characterized as being opaque and extrudable.
- 30.

8. A process according to any of claims 1—7 further characterized in that the compound of the metal of Group VI is selected from molybdenum oxide, molybdenum sulfide, tungsten oxide, tungsten sulfide or mixtures thereof and said compound of the Group VIII metal is selected from nickel oxide, cobalt oxide, nickel sulfide, cobalt sulfide or mixtures thereof.

9. A process according to any of claims 1—8 further characterized in that said hydrodesulfurization catalyst comprises 10—20 wt.% molybdenum oxide and 2—10 wt.% cobalt oxide or nickel oxide deposited on said support.

10. A process according to claim 9 further characterized in that said metal oxides are sulfided prior to use.

11. A process according to any of claims 1—10 further characterized in that said feedstock contains 30—100 wt.% of materials boiling above 900° F.

12. A process for the hydrodesulfurization of a sulfur-containing petroleum oil containing residual components as claimed in claim 1 and substantially as hereinbefore described.

13. Hydrodesulfurized products obtained by a process in accordance with any preceding claim.

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