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DESULFURIZATION OF HEAVY PETROLEUM
HYDROCARBONS

William A. Horne, Oakmont, and James F. Jungé,
Pittsburgh, Pa., assignors to Gulf Research &
Development Company, Pittsburgh, Pa., a cor-
poration of Delaware

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This invention relates to the desulfurization of heavy petroleum hydrocarbons and more particularly to a method of contacting heavy petroleum hydrocarbons with a reactant to remove the sulfur therefrom.

The efficient processing of high sulfur crudes, such as those from the Permian Basin of West Texas, has long been a problem of utmost importance to the refiner of these sour crudes. The sulfur has been found highly objectionable in petroleum oils for two primary reasons; namely, the problem it presents to the refinery in handling the crude and heavy intermediates, and the undesirable properties of the raw products of refining.

The first of these problems is due to the corrosive action of hydrogen sulfide which is formed in numerous refining stages from the decomposition of the sulfur compounds. Ordinary steels are rapidly corroded by hydrogen sulfide, especially at higher temperatures, so that it has been found necessary to use alloy steels at points of excessive attack, such as heat exchangers, or to use ordinary steel with frequent shut-downs for replacements. A specialized technique has been developed to combat this corrosion by the injection of neutralizers into the stream just prior to the point of attack, but this system has not proved entirely satisfactory.

While acid treating or bauxite desulfurization can be used for straight-run gasolines and naphthas, no efficient method of desulfurizing total crude and topped or reduced crude has previously been developed. A desirable process will substantially reduce the corrosion difficulties in the subsequent refining stages, and at the same time solve the problem of treating the raw products.

An object of the present invention is to remove sulfur from heavy petroleum hydrocarbons.

A further object of the present invention is to remove sulfur in any form including hydrogen sulfide from heavy petroleum hydrocarbons.

These and other objects are achieved by the process of the present invention in which a heavy petroleum hydrocarbon such as total crude, topped, or reduced crude is passed together with hydrogen over a contact agent comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range 750° to 950° F., terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before the available nickel content of the

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contact has been entirely converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and reusing the regenerated contact in the process.

The process generally comprises mixing the charge with hydrogen and passing the mixture over a contact agent containing a reactant consisting initially of nickel oxide. The nickel compound is supported on a carrier such as alumina and by "contact" or "contact agent" as used herein is meant the nickel compound reactant and a carrier. During the reaction the nickel oxide is converted to nickel sulfide and the reaction is discontinued when so much nickel sulfide is present that the end product contains substantial hydrogen sulfide. Hydrogen is present in the range 300 to 4000 cubic feet per barrel of oil charged. The reaction takes place at varying temperatures and pressures depending upon the charge stock, but generally at a temperature in the range 750° to 950° F. and at a pressure in the range 100 to 1000 p. s. i. g. The space velocity is preferably within the range 0.2 to 6.0 volumes of liquid charge per hour per volume of contact agent. It is undesirable to have hydrogen sulfide in the product and for this reason when about 50 to 60 per cent of the original nickel oxide becomes nickel sulfide, the contact agent should be regenerated. The regeneration is accomplished by burning the contact agent with oxygen containing gas to reconvert the reactant to nickel oxide and to burn off the carbonaceous deposit.

Our process begins with nickel oxide and during the course of reaction this is converted to nickel sulfide thereby removing the sulfur from the charge stock and liberating the oxygen of the nickel oxide as water. There may also be simultaneous reduction of some of the nickel oxide to lower nickel oxides, such as Ni_2O , or metallic nickel with concurrent formation of water. Subsequently, part of these lower oxides and/or metallic nickel probably react with the sulfur compounds in the charge stock. It is possible that during the reaction the nickel oxide, nickel sulfide, or nickel metal may act as catalysts but the net result is that of the reaction between nickel oxide and the sulfur. Apparently the use of nickel oxide as the starting material inhibits the cracking activity of the subsequently produced metallic nickel to such an extent that cracking to gas and coke is not excessive. Furthermore, since the total time spent by any of the reactant in the metallic state is limited, rapid loss of activity through sintering is avoided. The maximum processing period is limited to the

interval during which no substantial amount of hydrogen sulfide is liberated from the reactor.

The presence of hydrogen sulfide in the effluent product indicates that essentially all of the readily available nickel oxide and nickel has been converted to nickel sulfide. It is then necessary to regenerate the reactant with an oxygen containing gas which converts the nickel sulfide back to nickel oxide, and simultaneously removes the sulfur as sulfur dioxide in recoverable concentrations. In general 50-60 per cent of the total nickel oxide may be reacted before regeneration is necessary. This percentage is not invariant but depends on the operating conditions, sulfur content of the charge stock and contact. It has also been found that a minor amount of sulfur remains in the contact mass after regeneration as nickel sulfate. However, this nickel sulfate does not accumulate during subsequent cycles under our preferred conditions and apparently is not disadvantageous. The herein proposed theory of the action of the reactant should not be interpreted to limit the claims in any manner.

A flow sheet of the equipment for carrying out our desulfurization process is shown in the attached drawing in which the charge stock enters line 1 and is pumped by means of pump 2 through line 3, product heat exchanger 4 and line 5 into heater 6 where it is heated to reaction temperature either before or after mixing with the hydrogen or hydrogen-rich gas from line 29. The mixture of charge and hydrogen or hydrogen-rich gas at the desired reaction temperature passes through line 7, valve 8 and line 9 into the reaction chamber 10 containing the preferred contact. The desulfurized product leaves the reaction chamber by means of line 11, valve 12, line 13, heat exchanger 4 and line 14 into the high pressure separator 15. The liquid product from the high pressure separator passes through line 16, cooler 17, line 18 and valve 19 into a low pressure separator 20. The desulfurized liquid product from the low pressure separator is withdrawn by means of valve 21 and line 22.

Gases from the low pressure separator are released through valve 23 and line 24. The separated gases contain hydrogen which may be recovered for recycle if desired in any conventional manner such as an oil absorption and stripping system. The hydrogen-rich gas from the high pressure separator may also require some hydrogen enrichment which can also be carried out in a conventional manner. These gases normally pass through line 25, are compressed by pump 26, pass through line 27 and admix with fresh or makeup hydrogen from line 28 and valve 36. This hydrogen-rich gas is preheated either separately or in admixture with the charge stock in heater 6. This mixture then passes through line 7 as described previously.

During this on-stream period valves 30, 31 and 32 remained closed. At the completion of the on-stream period which varies depending on the charge stock and the conditions of reaction, pumps 2 and 26 are turned off and valves 8, 12 and 36 are closed. The pressure is released on contact bed 10 by means of valve 31 and the reactor is vacuum purged in conventional manner. Alternatively valve 31 and valve 32 may both be opened and the contact purged with an inert gas or steam. The purpose of the purge is to recover valuable hydrocarbons which remain in the contact bed. Following the purge, valve 31 is closed and valves 30 and 32 are opened and an oxygen-

containing gas is admitted to the reactor by means of line 34, valve 30 and line 9. The admission of this oxygen-containing gas in controlled amounts regenerates the contact converting the reactant to nickel oxide and simultaneously forms sulfur dioxide which is vented from the reaction chamber by means of line 11, valve 32 and line 35 together with combustion gases from the carbonaceous deposit. This regeneration off-gas contains recoverable quantities of sulfur dioxide in amounts depending upon the quantity of sulfur originally present as nickel sulfide as well as the oxygen content of the regeneration gas. This sulfur dioxide may be recovered in any normal manner such as by solvent absorption and stripping. The sulfur dioxide-free regeneration off-gas may then serve to dilute the fresh regeneration gas admitted to the reaction chamber. Alternatively the sulfur dioxide-containing regeneration off-gas may serve to dilute the fresh regeneration gas. After regeneration is complete, inert gas or steam may again be used to flush the system by closing valve 30 and opening valve 31 or the reaction chamber may be vacuum purged. The unit is then put on-stream again by closing valves 31 and 32, opening valves 8, 12 and 36 and starting pumps 2 and 26.

The foregoing description of the apparatus employed has been used as an example only. Multiple or single beds of fixed contact or fluidized contact as well as systems in which the contact is continuously charged and removed from the reaction zone followed by external regeneration are not excluded.

The following examples using the above described apparatus illustrate the reduction in sulfur and other advantages of the process when using several alternative contacts and charging a West Texas oil.

Example 1

The contact agent employed was an unreduced nickel oxide distributed over kieselguhr. This was prepared by a controlled precipitation of basic nickel carbonate from nickel sulfate in the presence of kieselguhr, followed by controlled washing and drying. The treated mixture of carbonate and kieselguhr was compressed into one-eighth inch diameter pellets, which were then decomposed by heating in an inert gas stream at 750° F. and the temperature maintained for approximately 16 hours. The contact in this form consisted of approximately 75 per cent nickel oxide and 25 per cent kieselguhr.

West Texas Total Crude containing 1.46 per cent sulfur was processed at a temperature of 750° F., a pressure of 250 p. s. i. g., a space velocity of 1 volume of charge per hour per volume of contact and a hydrogen-to-oil ratio of 2000 cubic feet per barrel of liquid charge. The product contained 0.28 per cent sulfur. The gravity of the crude increased from 34.2° to 38.2° API. The total liquid recovery was about 99 volume per cent.

Example 2

The contact agent prepared in Example 1 was used in this example as well as a charge of West Texas Total Crude containing 1.46 per cent sulfur. The temperature used was 850° F., the pressure was 500 p. s. i. g., a liquid space velocity of 1 volume of charge per hour per volume of contact agent was used, and a hydrogen-to-oil ratio of 2000 cubic feet per barrel of liquid charge was used. The product contained 0.18 per cent sulfur. The gravity of the crude increased from

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34.2° to 41.7° API. The volume per cent yield of gasoline increased from 32.6 per cent in the untreated crude to 45.9 per cent in the desulfurized crude. The volume per cent yield of the residuum (everything boiling higher than 700° F.) decreased from 33.5 per cent in the untreated crude to 17.6 per cent in the treated crude. The total liquid recovery was about 98 per cent by volume.

Example 3

The contact agent employed in this example was unreduced nickel oxide distributed on 6 to 20 mesh silica gel. It was prepared by impregnation of the dried silica gel with an aqueous nickel nitrate solution followed by drying at 260° F. and subsequent calcining at 800° F. to decompose the absorbed nickel nitrate to nickel oxide. This sequence of impregnation, drying and calcining was twice repeated so that the final catalyst contained 25 per cent nickel oxide and 75 per cent silica gel. West Texas Total Crude was desulfurized using this contact agent at a temperature of 850° F., a pressure of 500 p. s. i. g., a liquid space velocity of 1.5 volumes of charge per hour per volume of contact agent and a hydrogen-to-oil ratio of 2000 cubic feet per barrel. The sulfur content was reduced from 1.48 per cent to less than 0.3 per cent. The product compared very favorably in sulfur content with typical sweet crudes such as East Texas and Mid-Continent. The API gravity was raised from 33° to 41°, and the gasoline content of the crude was raised from 32.9 volume per cent to 44.9 per cent, based on the original crude. Increase in both clear and leaded octane numbers of the gasoline were also noted. The volume per cent yield of the residuum (everything boiling higher than 700° F.) decreased from 43.4 per cent in the untreated crude to 20.9 per cent in the treated crude. The total liquid recovery was about 98 per cent by volume.

Example 4

The contact agent employed was an unreduced nickel oxide supported on alumina. It was prepared in the same manner as was the contact agent in Example 3 with the exception that three to six mesh alumina was used in place of silica gel. In a run of a series of twenty cycles using a charge of West Texas Total Crude over the above described contact agent a reduction in sulfur content from 1.33 per cent to 0.2 per cent was obtained and the API gravity went from 33.0 to 42.1°. The reactor temperature was 850° F., the pressure 500 p. s. i. g., the hydrogen-to-oil ratio was 1570 cubic feet per barrel, the liquid space velocity was 1 volume of charge per hour per volume of contact agent and the throughput per cycle was 4 liquid volumes of charge per volume of contact. Periodic regeneration of the contact agent was accomplished by passing air over the bed of contact agent and allowing the temperature to rise within the range 1125 to 1175° F. while maintaining the pressure at about 25 p. s. i. g. Gasoline distilled from the product had a substantially increased octane number and the yield was increased from 32.3 volume per cent to 43.3 per cent. The bottoms (boiling above 865° F.) were reduced from approximately 23 volume per cent to approximately 3.0 volume per cent. The average liquid recovery was about 99 volume per cent.

Example 5

Using the same contact agent as in Example 4, a run was made with a charge of West Texas Topped Crude (topped to 450° F.). The reactor

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temperature was 850° F., the pressure 500 p. s. i. g., the hydrogen-to-oil ratio was 3870 cubic feet per barrel, the liquid space velocity was 0.6 volume of charge per hour per volume of contact agent; and the throughput per cycle was 2.5 liquid volumes of charge per volume of contact. Periodic regeneration of the contact agent was accomplished by passing air over the bed of contact agent and allowing the temperature to rise within the range 1125° to 1175° F. while maintaining the pressure at about atmospheric. The sulfur content was reduced from 1.65 per cent to 0.50 per cent. The bottoms (boiling above 580° F.) were reduced from 76 per cent to approximately 50 per cent by volume. The API gravity of the charge was 23° and that of the product was 32°. The total liquid recovery was about 95 per cent by volume.

This invention is concerned with high boiling petroleum hydrocarbon oil such as total crude as well as topped or reduced crude. These terms may be defined as follows: "Total crude" is defined as naturally occurring petroleum oil which has not been processed in any manner but preferably separated from water and sediment and desalted. "Topped or reduced crude" is defined as the residual petroleum oil resulting from removal of all or some of those straight run fractions such as gas, gasoline, kerosene, naphtha, furnace oil, gas oil, etc., which are normally removed from the above defined total crude by the process of atmospheric and/or vacuum topping or distillation.

Charge stocks such as total crude which has been diluted or admixed with lower boiling straight run or cracked petroleum fractions including gases are also included. Diluents of this kind may be required in processing low gravity crudes such as some of those from Mississippi as well as those from Kuwait. Diluents may also be necessary and preferred in desulfurizing topped or reduced crudes. The purpose of this diluent is to assist vaporization of the heavier constituents of the charge stock. In some cases it may be desirable to admix steam with the charge stock to assist vaporization.

Nickel oxide supported on carriers such as kieselguhr, silica gel, alumina, aluminum silicates, Alfrax, Magnesol, Porocel, bauxite and other supports have been tried and found to accomplish desulfurization. The amount of nickel oxide in the total contact agent may be varied considerably. Minor amounts of other chemical substances may be present inadvertently or as impurities. The contact agent may be nickel oxide supported on a carrier or contacts prepared by co-precipitation of nickel oxide and support and precipitation of the nickel oxide in the presence of a support. Impregnation may be employed as a method of preparation by absorbing soluble salts of nickel on the support followed by decomposition of the salt at elevated temperatures. The final contact agent may be prepared by either single or multiple impregnation to attain any suitable concentration of nickel oxide. The preferred contact agents are described in more detail in the examples. Other methods of preparation will be obvious to those versed in the art.

As described above, the preferred operating conditions for the process necessarily vary within certain ranges depending upon the charge stock. In general the conditions are as follows:

Temperature, °F.	750-950
Pressure, p. s. i. g.	100-1000
Space velocity, vol./hr./vol.	0.2-6.0
Hydrogen concentration, cu. ft./bbl.	300-4000

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At temperatures below 750° F. the desulfurizing activity of the contact diminishes, whereas above 950° F. excessive cracking reactions result in decreased product recovery and rapid coke formation which deactivates the contact.

At pressures below 100 p. s. i. g. the partial pressure of hydrogen is not sufficient to maintain desulfurizing activity nor to suppress cracking reactions which result in coke formation. Increasing the pressure above 1000 p. s. i. g. results in only a slight incremental gain in desulfurization and is thus not commercially desirable.

Space velocities below 0.2 vol. of charge per hour per volume of contact agent result in excessive cracking reactions caused by the long contact time, and at space velocities above 6.0 the contact time is too short to allow sufficient desulfurization. Hydrogen concentrations below 300 cu. ft. per barrel of charge stock are not sufficient to maintain desulfurization activity nor to suppress undesirable cracking. Hydrogen concentrations above 4000 cu. ft. per barrel result in only a slight incremental gain in desulfurization. Higher space velocities and hydrogen concentrations than 6.0 vol. charge per hour per volume contact and 4000 cu. ft. per barrel, respectively, result in insufficient contact time and the evolution of hydrogen sulfide from the reactor within a relatively short processing period. The volumes of charge stock passed over one volume of contact during the processing period depends on the per cent sulfur in the charge stock and the per cent nickel oxide in the contact but normally is in the range of 1 to 10 volumes of charge per volume of contact. This throughput is limited by the period during which no substantial hydrogen sulfide is evolved from the contact bed.

The optimum regeneration conditions are approximately:

Temperature, °F-----	1000-1300
Pressure, p. s. i. g-----	0-500
Diluent gas to air ratio, vol./vol-----	0-20

The regeneration temperature is limited to that which does not produce a loss of mechanical strength or activity of the contact agent but at the same time must be sufficiently high to convert nickel sulfide to nickel oxide and burn off any accumulated coke deposit. The regeneration pressure is adjusted within the indicated range to obtain the optimum regeneration time which will depend on charge stock and operating conditions. The diluent gas to air ratio is adjusted to maintain the desired regeneration temperature and obtain the optimum regeneration time. Diluent gases may include steam, flue gas, regeneration off-gas, etc.

The present process provides an efficient and economical process of reducing the sulfur content of heavy petroleum oils. Among the particular advantages is the increased yield of low sulfur content gasoline, naphtha and furnace oil and a reduced yield of tar. In addition the gasoline obtained from the crude treated as herein described has higher clear and leaded octane numbers and higher lead susceptibility than the gasoline from the untreated charge. Further it reduces the equipment requirements for crude fractionation and cracking and the maintenance thereof. There is no substantial hydrogen sulfide evolved thereby reducing maintenance and equipment costs due to corrosion.

All of these advantages accrue by the use of our process due to the fact that the sulfur compounds in the crude are removed and hydrogen

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sulfide is not liberated in the process thereby eliminating the corrosion difficulties as well as the undesirable properties of the products which are caused by the sulfur compounds. The increased yield of the lower boiling fractions and the reduced yield of the residuum or bottoms are important advantages of this process.

The reduction of the sulfur content of the crude substantially eliminates the corrosive action of hydrogen sulfide evolved during conventional processing and makes possible efficient processing of sour crudes by refineries that are at present only able to process low sulfur or sweet crudes.

The process is not to be confused with hydrogenation processes using metallic nickel as a catalyst. We have found that if a nickel oxide is reduced with hydrogen prior to charging the petroleum oil, the efficiency of desulfurization is markedly reduced due to the high cracking activity of reduced nickel which results in excessive gas yields and rapid formation of a coke deposit on the contact.

In the following claims when we speak of absorbing sulfur from the hydrocarbon vapors it is to be understood to mean that the sulfur contained in the vapors, in whatever form that it is present therein, is taken up by the reactant due to the formation of nickel sulfide.

What we claim is:

1. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide on the contact, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

2. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure between about 100 and 1000 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

3. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F., at a pressure above about 100 pounds per square inch gauge, at a space velocity in the range 0.2 to 6.0 liquid volumes of oil per hour per volume of contact and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, ter-

minating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

4. In the process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F., at a pressure between about 100 and 1000 pounds per square inch gauge, at a space velocity in the range 0.2 to 6.0 liquid volumes of oil per hour per volume of contact and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

5. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof with contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure between about 100 and 1000 pounds per square inch gauge, at a space velocity in the range 0.2 to 6.0 liquid volumes of oil per hour per volume of contact and in the presence of hydrogen, said hydrogen being present in a concentration between about 300 and 4000 cubic feet per barrel of oil, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

6. The process for desulfurizing total crude petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapor to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

7. The process for desulfurizing topped crude petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors

and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

8. The process for desulfurizing reduced crude petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

9. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof, in the presence of a diluent, with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

10. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof, in the presence of a low boiling hydrocarbon diluent, with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

11. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof, in the presence of steam, with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact so that it is predominantly in the form of nickel oxide and re-using the regenerated contact in the process.

12. The process for desulfurizing a high boil-

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ing petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapor to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 60 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact by passing an oxygen containing gas over it and re-using the regenerated contact in the process.

13. The process for desulfurizing a high boiling petroleum oil which comprises treating vapors thereof with a contact comprising a support and a nickeliferous reactant initially predominantly in the form of nickel oxide at a temperature in the range of 750° to 950° F. at a pressure above about 100 pounds per square inch gauge and in the presence of hydrogen, absorbing sulfur from the vapors to form nickel sulfide, terminating the treatment before a substantial amount of hydrogen sulfide appears in the treated vapors and before about 50 per cent of the nickel content of the contact has been converted into nickel sulfide, regenerating the contact by passing air over it at a temperature in the range between about

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1000° and 1300° F. at a pressure in the range between about 0 and 500 p. s. i. g. and in the presence of a diluent gas having a ratio to air on a volume to volume basis of between 0 and 20 and re-using the regenerated contact in the process.

WILLIAM A. HORNE.
JAMES F. JUNGÉ.

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