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DESULFURIZATION OF HYDROCARBON OILS

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1

This invention relates to an improved procedure for desulfurizing hydrocarbon oils.

Desulfurization of hydrocarbons is in many cases necessary since such sulfur-containing materials corrode equipment in which they are refined, stored or used. It is known to desulfurize hydrocarbons by contacting vapors thereof with hydrogen and a contact agent. The contact agent absorbs the sulfur and is periodically regenerated for reuse in the process. Excessive costs have been encountered due to the destruction of the contact during the desulfurization process. This has been due to rapid powdering of the contact at the high temperatures employed or to loss of activity due to low heat stability.

This invention has for its object to provide improved procedure for desulfurizing hydrocarbon oils and fractions thereof. Another object is to provide a desulfurization process of the type wherein sulfur is absorbed on a contact agent followed by regeneration of the contact to remove the sulfur therefrom. Another object is to provide a desulfurization contact having a relatively low powdering rate and increased stability to heat at the elevated temperatures employed for desulfurization and regeneration. Another object is to provide a desulfurization contact which can be cheaply and easily prepared and which has a long, useful life, thus reducing the over-all cost of the desulfurization procedure. Other objects will appear hereinafter.

These and other objects are accomplished by our invention, which includes contacting sulfur-containing vapors of a hydrocarbon oil with hydrogen in the presence of a contact agent comprising a metal of the iron group or its oxide and a cracking catalyst base. We have found that such a contact agent has a markedly reduced powdering rate, increased heat stability, is easier to prepare by virtue of fewer required impregnations, has a lower density, and a decreased cost in cents per pound.

In the following examples and description we have set forth several of the preferred embodiments of our invention but it is to be understood that they are given by way of illustration and not in limitation thereof.

The invention is applicable to the treatment of sulfur-containing hydrocarbon oils in general such as crude petroleum, reduced crude, topped crude, cracked gasoline distillate, straight run gasoline, naphtha, gas oil, shale oils, coal tar oils and oils from hydrogenation of coal. It is of particular advantage for the treatment of high boiling materials such as total crude petroleum,

2

reduced crude and topped crude. By treating these high boiling materials several advantages are obtained. Thus the sulfur-containing material is desulfurized before it has been subjected to any substantial refining procedure and therefore corrosion of refinery equipment is considerably reduced. Also, the contact agent we employ has a certain amount of cracking activity so that the high boiling petroleum hydrocarbon is simultaneously desulfurized and partially cracked to a more valuable form, such as gasoline. All of the above-mentioned oils may be desulfurized at a temperature between about 600° and 950° F. A temperature of about 700° to 850° F. is advantageous for the high boiling hydrocarbons whereas a temperature of 650° to 800° is preferred for the low boiling hydrocarbons.

The cracking catalyst base acts as a carrier for the iron group metal or iron group metal oxide and it does not of itself absorb the sulfur. However, it improves the desulfurization activity and as mentioned also effects a partial cracking. Any refractory material having a substantial cracking activity can be used. Examples of suitable materials are silica-alumina cracking catalysts such as those prepared synthetically or by acid treatment of natural clays. Silica-zirconia, silica-titania, silica-alumina-titania synthetic cracking catalysts are well known and also can be used as a carrier for the sulfur absorbing iron group metal or metal oxide. In order to be satisfactory the cracking catalyst base should have a conversion index of above about 15. A cracking catalyst that has been used in a conventional cracking operation can be advantageously employed as a carrier for the desulfurizing metal or metal oxide. Such partial use of the cracking catalyst not only removes any of the catalyst particles which are defective in that they break up or powder easily but it also seems to result in an enlargement of the catalyst pores so that such partially used cracking catalyst can take up a larger amount of desulfurizing metal or metal oxide. We have found, furthermore, that all of the cracking catalyst supports have the advantage over other porous types of supports that fewer impregnations are required to incorporate the necessary amount of the desulfurizing iron group metal or metal oxide. This decreased number of impregnations and calcinings of course reduces the initial cost of the contact and thus the cost per barrel of charged stock processed. Examples of suitable cracking catalyst bases are shown in Table I along with conversion index. This table also includes examples of non-active

porous materials which would be less suitable as carriers for the purpose of the present invention since they have conversion index substantially below 15.

TABLE I

Conversion index tests on contact supports

Description of Catalyst	Gasoline Formed, Weight Per Cent of Charge
Synthetic Silica Alumina Beads.....	29.3
Synthetic Silica-Alumina.....	33.0
Do.....	23.3
Do.....	26.8
Natural Silica-Alumina Pellets.....	25.3
Natural Silica-Alumina Pellets (Fines).....	25.0
Natural Silica-Alumina Pellets (Used).....	22.6
Natural Silica-Alumina Pellets (High Density from Shaker).....	8.9
Synthetic Silica-Alumina (Used).....	21.5
"Magnesol" (Commercial Activated Magnesium Silicate).....	8.5
Activated Synthetic Alumina.....	5.4
Silica Gel.....	7.8

¹ Inactive portions of catalyst discarded from a Thermoform cracking unit as described in Litchfield et al. U. S. patent application Serial No. 791,223, filed December 12, 1947.

Conversion index as used in the present specification and in the claims means the amount of gasoline formed when a standard Pennsylvania Diesel fuel oil, topped to an initial boiling point of 450° F. and cut to an end point of 650° F., is passed over 90 cc. of the catalyst to be tested at a temperature of 845° F., a pressure of 1 atmosphere, a liquid space velocity of 1.0 volume of charge oil/hour/volume of catalyst for a throughput of 1.0 volume of oil per volume of catalyst. The vapors are condensed at 55° F. to obtain the "synthetic" product. This product is then distilled in a 10 inch long column packed with ¼ inch glass balls to a cut point of 370° F. The difference in weight between the "synthetic" product and the residual bottoms is the yield in grams of gasoline from which the yield of gasoline as weight per cent of charge can be calculated.

While any iron group metal or metal oxide, i. e. nickel, cobalt, or iron or their oxides can be used, we prefer nickel and especially nickel oxide since these result in a much greater removal of sulfur.

The cracking catalyst base is composited with the iron group metal or metal oxide in any desired manner so long as there is obtained a fairly extensive iron group metal or metal oxide surface supported by the cracking catalyst base. The most convenient method of preparation is to impregnate the cracking catalyst base with a water solution of a water soluble salt of the iron group metal, which salt must be readily convertible into the metal or metal oxide. A suitable salt is, for instance, the nitrate of nickel, iron or cobalt. After such impregnation the material is drained, dried, and calcined at elevated temperature to form the oxide. This oxide may be reduced to the metal if it is desired to use the metal in the desulfurization. Such reduction is accomplished in a well known manner by contact with hydrogen at elevated temperature. The cracking catalyst base also may be impregnated by immersing in the molten salt of the iron group metal. For instance, hydrated nickel nitrate can be melted and the cracking base impregnated with this molten material, followed by calcining, as described above. The amount of iron group metal incorporated may vary considerably and will depend upon the amount of sulfur which is

contained in the petroleum hydrocarbon to be desulfurized. A contact containing about 10 to 80 per cent by weight of iron group metal or metal oxide in general can be used. Amounts of about 20 to 35 per cent nickel in the form of nickel or nickel oxide are quite satisfactory for hydrocarbon oils which are usually desulfurized.

The hydrogen is employed in amounts of about 100 to 6000 cubic feet per barrel of hydrocarbon in the liquid state. 100 to 1000 cubic feet hydrogen per barrel of hydrocarbon is advantageous when desulfurizing low boiling hydrocarbons and 1000 to 6000 cubic feet of hydrogen per barrel of hydrocarbon is advantageous when desulfurizing heavy hydrocarbons such as total crude, topped crude, and reduced crude. The pressure during the desulfurization is advantageously between about 100 and 1000 pounds per square inch gauge.

The contact between the hydrogen and hydrocarbon vapors and the contact agent is conveniently brought about by passing a mixture of the hydrocarbon vapors and hydrogen over the contact agent at the temperatures mentioned above.

The space velocity, i. e., the volume of liquid hydrocarbon charged per hour per volume of contact should in general be between about 0.2 and 6.0. The space velocity is advantageously between about 1 and 6 when treating low boiling hydrocarbons and between about 0.2 and 2.0 when treating heavy hydrocarbons. The hydrocarbon vapors may be diluted with other materials. This is advantageous in connection with the treatment of heavy petroleum hydrocarbons. For instance, steam may be employed as a diluent and may be used to vaporize the heavy hydrocarbon and maintain the vapors thereof in vapor form during passage over the contact. Diluents also are advantageous in certain cases when treating lower boiling hydrocarbons. Other suitable diluents are nitrogen and hydrocarbon vapors and gases such as straight run gasoline or methane.

Vapors of the hydrocarbon are passed over the contact agent with the hydrogen, all as described above, until hydrogen sulfide appears in substantial amounts in the effluent gases and vapors. At this stage the reaction is terminated and the contact agent is regenerated. The point at which such termination takes place will in general correspond to about 50 to 60 per cent conversion, more or less, of the iron group metal or metal oxide into metal sulfide and we accordingly prefer to terminate the desulfurization reaction at about this stage.

The contact agent is preferably regenerated by contact with an oxygen containing gas at elevated temperature in order to convert the iron group metal sulfide into iron group metal oxide. A temperature of between about 1000° and 1400° F. is employed. It is desirable to employ a temperature above 1000° F. since lower temperatures do not result in the complete removal of the iron group sulfide unless uneconomically long periods of regeneration are used. While temperatures above 1400° F. can be used, such temperatures should be employed only with catalysts which are stable to such elevated temperatures. While our desulfurization contact agents are exceedingly stable, we prefer not to employ temperatures above 1400° F. since with repeated regenerations at such high temperatures they will gradually lose their activity. The regeneration is continued until substantially no sulfur dioxide appears in the effluent gases. With repeated re-

5

generations the contact accumulates a small amount of iron group metal sulfate, which is but very slowly decomposed into sulfur dioxide and iron group metal oxide and the regeneration is not necessarily carried to a stage such that iron group metal sulfate is converted into the oxide. All that is necessary is to remove substantially all of the iron group metal sulfide and this is evidenced by the substantial absence of sulfur dioxide in the effluent gases in the final stages of the regeneration. A pressure of 0 to 500 pounds per square inch gauge may be used during the regeneration and, if desired, a diluent gas, such as steam, nitrogen, flue gas, or the like, may be added to the oxygen containing gas in order to control the regeneration temperature. In the event the reduced or free metal is to be employed instead of the oxide, the regeneration includes a final reduction step to convert the oxide into the metal. After regeneration the contact is again employed to remove sulfur from sulfur containing vapors of a hydrocarbon oil as previously described.

Example 1.—Four desulfurization contacts were prepared by impregnating various porous carriers with nickel nitrate followed by calcining to nickel oxide. These four contact agents were employed to desulfurize a West Texas crude oil having the properties shown in Table II. The operating conditions for this desulfurization are shown in Table III and the relative resistance to powdering is given in Table IV.

TABLE II

Inspection on West Texas crude oil charge stock

Gravity, °API	34.1
Sulfur, weight percent	1.48
Viscosity, S. U. S. at 100° F.	42.7
Carbon Residue, weight percent	4.39
Distillation:	
I. B. P., °F.	88
10, percent at °F.	219
50, percent at °F.	548
90, percent at °F.	
Gasoline, 400° F., E. P., vol. percent	33.4

TABLE III

Operating conditions

Charge stock	West Texas Crude Oil
Temperature, °F.	850
Pressure, p. s. i. g.	500
Space velocity, volume of oil/hr./volume of contact	1.0
Throughput, volume of oil/volume of contact	4.0
Hydrogen, cu. ft./bbl.	2,000

TABLE IV

Contact powdering

Contact Support	Per Cent Fines at			Half Life, Months
	1 mo.	2 mos.	3 mos.	
Porocel, 27.6% NiO	32.5			1.5
Activated Alumina, 27.8% NiO	12.5	25.0	37.0	4
Synthetic Silica-Alumina Cracking Catalyst, 28.8% NiO	4.0	8.0	12.0	13
Natural Silica-Alumina Cracking Catalyst, 20.3% NiO	4.0			13

"Porocel" is activated natural alumina obtained by acid treating bauxite. The "activated alumina" in Table IV is an activated synthetic alumina.

It will be noted that carriers such as activated

6

alumina and "Porocel" had an exceedingly short half life and were quickly converted into powders under the desulfurization conditions. It is quite evident from the data in Table IV that the contact agents prepared from cracking catalysts powdered at a much slower rate than non-cracking carriers. Kieselguhr and silica gel supported nickel oxide contacts have also been tested qualitatively and found to powder much more rapidly than the cracking catalyst contacts described herein. In a fixed bed, channeling of the hydrocarbon charge through the contact bed would take place if the contact powdered at a rapid rate and as a consequence the contact time would decrease and result in a decrease in desulfurization.

Example 2.—The heat stability of a desulfurization contact comprising 28.8 per cent nickel oxide on a synthetic silica-alumina cracking catalyst was compared with a contact comprising 27.8 per cent nickel oxide on activated alumina. Both contacts were heated to elevated temperature (1600° F. in the case of synthetic alumina-silica carrier and 1400° F. in the case of the alumina carrier) and the degree of desulfurization activity compared before and after such heating. The material desulfurized in these tests was the same West Texas crude oil described in Example 1 and the operating conditions were the same as described in Example 1. The results are given in Table V.

TABLE V

Heating stability

	Inspection on Product	
	Gravity, °API	Sulfur, Weight Per Cent
Synthetic Silica-Alumina Cracking Catalyst, 28.8% NiO:		
Before heating to 1600° F.	40.8	0.39
After heating to 1600° F.	40.6	0.39
Activated Alumina, 27.8% NiO:		
Before heating to 1400° F.	40.9	0.38
After heating to 1400° F.	40.0	0.65

It will be noted that the high temperature of 1600° F. had practically no effect on the desulfurization efficiency of the cracking catalyst supported contact whereas the non-cracking support type of contact was damaged when subjected to even 1400° F. This is evidenced by higher sulfur content and lower gravity of the product obtained. Powdering of the synthetic silica-alumina cracking support on heating to 1400° F. during regeneration is negligible whereas the activated alumina was nearly completely converted to powder.

It is therefore to be seen that we have provided a desulfurization contact which has exceedingly high stability under the destructive high temperature conditions ordinarily employed in desulfurization and regeneration of desulfurization contacts. Not only are these contacts more stable under desulfurization and regeneration conditions but they also have a lower cost than the non-cracking catalyst type supports.

The density of the contact agent prepared from cracking catalyst type supports is generally about 45 to 50 pounds per cubic foot whereas the contact prepared from non-cracking catalyst type supports has a density of about 55 to 70 pounds per cubic foot. The decreased density of our contact lowers the initial cost on a volume basis and the smaller weight of contact charged to the re-

actors would reduce the required mechanical strength of the supporting screen as well as reactor mounting base.

To summarize the factors which contribute to the contact cost per barrel of charge are: contact life, powdering rate and initial cost of contact per pound. Assuming the initial cost of contact to be the same in all cases it may be calculated that the cracking catalyst type contact would cost about 75 per cent less than the better non-cracking catalyst type contacts and may be as much as 90 per cent less considering lower initial cost of preparation.

What we claim is:

1. The process for desulfurizing a sulfur-containing hydrocarbon oil which comprises treating vapors of said oil with a contact agent comprising a member of the class consisting of metals of the iron group and their oxides composited with a silica-alumina refractory catalytic material capable of promoting, to a substantial extent, the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons and having a conversion index of above about 15, in the presence of hydrogen, at a temperature between about 600° and 950° F., terminating this treatment when a substantial amount of hydrogen sulfide appears in the treated vapors, regenerating the contact agent at a temperature above about 1000° F. to remove substantially all of the sulfur therefrom and employing the regenerated contact agent to treat vapors of a sulfur-containing hydrocarbon oil in the presence of hydrogen under the conditions specified above.

2. The process for desulfurizing a sulfur-containing hydrocarbon oil which comprises treating vapors of said oil with a contact agent comprising a metal of the iron group composited with a silica-alumina refractory catalytic material capable of promoting, to a substantial extent, the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons and having a conversion index of above about 15, in the presence of hydrogen, at a temperature between about 600° and 950° F., terminating this treatment when a substantial amount of hydrogen sulfide appears in the treated vapors, passing an oxygen-containing gas over the contact agent at a temperature between about 1000° and 1400° F. to convert the iron group metal sulfide into iron group oxide, continuing such treatment until substantially no sulfur dioxide appears in the effluent, treating the contact with hydrogen and employing the regenerated contact agent to treat vapors of a sulfur-containing hydrocarbon oil in the presence of hydrogen under the conditions specified above.

3. The process for desulfurizing a sulfur-containing hydrocarbon oil which comprises treating vapors of said oil with a contact agent comprising a member of the class consisting of metals of the iron group and their oxides composited with a silica-alumina refractory catalytic material previously used to promote the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons, in the presence of hydrogen, at a temperature between about 600° and 950° F., terminating this treatment when a substantial amount of hydrogen sulfide appears in the treated vapors, regenerating the contact agent to remove substantially all of the sulfur therefrom and employing the regenerated contact agent to treat vapors of a sulfur-containing hydrocarbon oil in the presence of hydrogen under the conditions specified above.

4. The process for desulfurizing a sulfur-con-

taining high boiling point petroleum oil which comprises treating vapors of said oil with a contact agent comprising an oxide of a metal of the iron group composited with a silica-alumina refractory catalytic material capable of promoting, to a substantial extent, the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons and having a conversion index of above about 15, in the presence of hydrogen, at a temperature between about 750° and 850° F., terminating this treatment when a substantial amount of hydrogen sulfide appears in the treated vapors, passing an oxygen-containing gas over the contact agent at a temperature between about 1000° and 1400° F. to convert the iron group metal sulfide into iron group metal oxide, continuing such treatment until substantially no sulfur dioxide appears in the effluent and employing the regenerated contact agent to treat vapors of a sulfur-containing high boiling point petroleum oil in the presence of hydrogen under the conditions specified above.

5. The process for desulfurizing a sulfur-containing petroleum oil selected from the group consisting of crude, reduced crude and topped crude which comprises treating vapors of said oil with a contact agent comprising nickel oxide composited with a silica-alumina refractory catalytic material capable of promoting, to a substantial extent, the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons and having a conversion index above 15, in the presence of hydrogen, at a temperature between about 750° and 850° F., terminating this treatment when a substantial amount of hydrogen sulfide appears in substantial amounts in the treated vapors, passing an oxygen-containing gas over the contact agent at a temperature between about 1000° and 1400° F. to convert the nickel sulfide into nickel oxide, continuing such treatment until substantially no sulfur dioxide appears in the effluent and employing the regenerated contact agent to treat vapors of a sulfur-containing high boiling point petroleum oil in the presence of hydrogen under the conditions specified above.

6. The process for desulfurizing a sulfur-containing petroleum oil selected from the group consisting of crude, reduced crude and topped crude which comprises treating vapors of said oil with a contact agent comprising nickel oxide composited with a silica-alumina refractory catalytic material capable of promoting, to a substantial extent, the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons and having a conversion index above 15, in the presence of hydrogen, at a temperature between about 750° and 850° F., terminating this treatment when about 50 to 60 per cent of the nickel oxide has been converted into nickel sulfide, passing an oxygen-containing gas over the contact agent at a temperature between about 1000° and 1400° F. to convert the nickel sulfide into nickel oxide by combustion, continuing such treatment until substantially no sulfur dioxide appears in the combustion gases and employing the regenerated contact agent to treat vapors of a sulfur-containing high boiling point petroleum oil in the presence of hydrogen under the conditions specified above.

7. The process for desulfurizing a sulfur-containing petroleum oil selected from the group consisting of crude, reduced crude and topped crude which comprises treating vapors of said oil with a contact agent comprising nickel oxide composited with a silica-alumina refractory catalytic

material capable of promoting, to a substantial extent, the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons and having a conversion index above 15, in the presence of hydrogen, at a temperature between about 750° and 850° F., at a space velocity of between about 0.2 and 2.0, at a pressure of between about 100 and 1000 p. s. i. g. and a hydrogen to oil ratio of between about 1000 and 6000 cubic feet per barrel, terminating this treatment when a substantial amount of hydrogen sulfide appears in the treated vapors, passing an oxygen-containing gas over the contact agent at a temperature between about 1000° and 1400° F. to convert the nickel sulfide into nickel oxide by combustion, continuing such treatment until substantially no sulfur dioxide appears in the combustion gases and employing the regenerated contact agent to treat vapors of a sulfur-containing high boiling point petroleum

oil in the presence of hydrogen under the conditions specified above.

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