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DESULFURIZATION OF HYDROCARBON
MIXTURES WITH NICKEL CARBONYL

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The present invention relates to the desulfurization of mixtures of hydrocarbons and, more particularly, to the desulfurization of mineral oil and mineral fractions.

The deleterious effect of sulfur compounds present in crude petroleum and various fractions of petroleum is too well known to require detailed discussion. On the other hand, it is becoming more apparent as the supplies of mineral oil from the older fields become less that the desulfurization of petroleum is becoming a greater problem. A review of the problem of producing low-sulfur products from petroleum emphasizes the fact that future supplies of crude petroleum in the main will consist to a very great degree of the so-called high sulfur type. Consequently, it is necessary for the petroleum refining industry to discover more efficient methods for removing sulfur. Many methods have been proposed but each has its deficiencies. Solvent extraction is not sufficiently selective with the present available solvents. Other treating methods involving the use of acids in many instances produce satisfactory results from the standpoint of sulfur removal but because of the relatively low yield of useful oil are industrially impractical.

Other methods of removing sulfur from mixtures of hydrocarbons, especially mineral oil, have been based upon contact between the sulfur containing oil and regeneratable metal oxide catalysts. These methods have been unsatisfactory for industrial purposes because the catalyst could not be reactivated in an industrially satisfactory manner. It is with the latter type of method for desulfurizing mixtures of hydrocarbons, especially mineral oil and analogous mixtures of hydrocarbons that the present invention is concerned.

The use of nickel catalysts for the desulfurization of mixtures of hydrocarbons; e. g., petroleum and petroleum fractions, either with or without hydrogen has been described. In these processes the nickel of the catalyst combines with the sulfur from the sulfur compounds to form nickel sulfide. Considerable amounts of carbon are deposited also on the catalyst. Since nickel is relatively expensive, it is necessary, for economical operation, that the nickel be recovered and re-used. The previously described methods for using nickel on an inert carrier such as kieselguhr to desulfurize mixtures of hydrocarbons involved a regeneration step in which the sulfur and carbon deposited on the catalyst were removed as oxides by treating with air at elevated temperatures. In such a regeneration the nickel, at least in part, theoretically is converted to the oxide and then reduced to metallic nickel by

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treating the oxidized catalyst with hydrogen. These processes have proved to be impractical on a commercial scale because after a few cycles involving, theoretically, deactivation to nickel sulfide, oxidation to the oxide and reduction to metallic nickel, the nickel loses its activity as a desulfurizing agent. Study of the problem has led to the conclusion that the nickel is sintered or that the nickel sulfide during oxidation is converted to other nickel compounds which cannot be reduced to metallic nickel by normal treatment with hydrogen and this change rapidly inactivates the catalyst. This loss of activity on regeneration makes the use of nickel catalysts on a support such as kieselguhr industrially impractical.

However, as early as 1906 a United States Patent No. 809,087 issued to H. S. Blackmore describing the use of nickel carbonyl as a desulfurizing agent. The Blackmore process is made continuous by oxidizing the nickel sulfide formed in the desulfurizing step to nickel oxide and reducing the nickel oxide to metallic nickel with hydrogen and then converting the metallic nickel to nickel carbonyl by treating the reduced nickel with carbon monoxide. The Blackmore process suffers from several disadvantages among which is the fact that when nickel sulfide is treated with oxygen inactivation of the nickel occurs through sintering or the formation of non-reducible compounds such as nickel sulfate. In other words, when nickel sulfide produced by the desulfurization of a mixture of hydrocarbons is treated with oxygen, complete oxidation to the oxide does not occur but only partial oxidation to the sulfate occurs in sufficient amount to seriously reduce the amount of nickel oxide which can be reduced and then re-converted to nickel carbonyl. Furthermore, it has been found that when nickel carbonyl is pumped into a hot reactor or preheater, either in a blend with a mixture of hydrocarbons or separately, the carbonyl decomposes to form metallic nickel and either forms chunks of solid metal or builds up on the walls of the preheater or reactor. Either result soon causes the reactor or preheater to become obstructed. In addition, this form of nickel is a relatively poor desulfurizing agent.

It has now been discovered that the deficiencies of previously disclosed desulfurizing processes involving the use of nickel as the desulfurizing agent can be overcome. First it has been found that nickel carbonyl can be decomposed into an active form in contrast to the inactive form produced in Blackmore's process. Secondly, the nickel sulfide can be converted to nickel car-

bonyl without oxidizing to sulfate, reducing the oxide with hydrogen and converting that portion of the nickel sulfide which has been converted to metallic nickel to nickel carbonyl. Thirdly, in the present method the nickel carbonyl decomposes into a finely divided colloidal state which is very active and does not adhere to the walls of the reactor. After desulfurization of the mixture of hydrocarbons being treated, the nickel-nickel sulfide powder is readily removed from the reactor by conventional means and readily regenerated.

It is an object of the present invention to provide a means for desulfurizing mixtures of hydrocarbons containing sulfur.

It is another object of the present invention to provide a means for the concurrent desulfurizing and cracking of crude petroleum and petroleum fractions.

It is a further object of the present invention to provide a means for desulfurizing mixtures of hydrocarbons wherein nickel carbonyl is employed and the nickel sulfide produced in the desulfurization is converted to nickel carbonyl directly.

Other objects and advantages will become apparent from the following discussion.

Broadly stated the present invention, in contrast to that described by Blackmore, involves spraying nickel carbonyl into hot hydrocarbon vapors, separating the hydrocarbon vapors from the colloidal nickel-nickel sulfide powder, cooling and condensing the hydrocarbon vapors, and regenerating the nickel carbonyl (by treating the nickel-nickel sulfide powder with carbon monoxide).

It is well known that nickel carbonyl is miscible in all proportions with petroleum and petroleum fractions. It is also known that nickel carbonyl begins to decompose at 36° C. and completely decomposes into nickel and carbon monoxide at 180° C. and normal pressure. It is also known that the temperature at which nickel carbonyl decomposes is dependent upon the partial pressure of the carbon monoxide present. Since desulfurization of hydrocarbon mixtures is dependent upon the formation of the highly reactive colloidal form of nickel, it follows that desulfurization of hydrocarbon mixtures can be carried out at any temperature and pressure at which nickel carbonyl is decomposed to the highly active colloidal form of nickel and below the temperature at which the nickel begins to agglomerate and the hydrocarbons begin to crack excessively and form undesirably large amounts of hydrocarbon gases.

In general it is desirable to conduct the desulfurization operation in a cylindrical chamber heated to a temperature between about 400° F. to about 900° F. and preferably about 500° F. to about 750° F. depending on the end point of the charge stock. While pressure has little effect upon the reaction, it has been found that the use of hydrogen and low pressures of about 150 to about 500 pounds per square inch gauge gives improved results.

The use of a cylindrical chamber for desulfurization of mixtures of hydrocarbons is preferred because the walls of a cylindrical chamber can be provided with a blanket of hydrocarbon gases more readily than a chamber of the same volume but of different shape and also because a greater time of contact between the colloidal nickel and the hydrocarbon vapors can be obtained.

In desulfurizing mixtures of hydrocarbons such

as crude petroleum, shale oil and the like or fractions thereof, and preferably having an end boiling point not greater than 750° F., the mixture of hydrocarbons to be desulfurized is preheated to the pre-determined temperature and then introduced into the reactor in a manner to ensure that the walls of the reactor will be provided with a blanket of hydrocarbon vapors. This is most readily accomplished in a cylindrical reactor or desulfurizer by introducing the hydrocarbon vapors tangentially into the reactor at the bottom thereof. The hydrocarbon vapors rise through the reactor providing an efficient blanket for the walls of the reactor because of the swirling action produced by introducing the hydrocarbon vapors tangentially. The nickel carbonyl is sprayed into the center of the reactor preferably at the top or close to the top thereof. The colloidal nickel which is formed by the decomposition of the nickel carbonyl under these conditions settles slowly through the hydrocarbon vapors to the bottom of the reactor from which it is removed in any suitable manner to a receiver. The hydrocarbon vapors and gases are removed from the top of the reactor, cooled and condensed. The nickel-nickel sulfide powder is regenerated; i. e., converted into nickel carbonyl by treating it with carbon monoxide at temperatures and correlated pressures at which nickel carbonyl does not decompose. It has been found advantageous to convert the nickel-nickel sulfide powder to nickel carbonyl in the presence of metallic copper. When desirable the hydrocarbon vapors are not cooled and condensed but treated with more nickel carbonyl in the same or a similar reactor.

The ratio of nickel carbonyl to hydrocarbon (nickel carbonyl expressed as parts by weight nickel) should be from 1:1 to 1:20 parts by weight. The temperature regeneration of the nickel-nickel sulfide powder should be 100° F. to 350° F. and the corresponding pressures from 15 p. s. i. g. to 500 p. s. i. g.

Since the method of the present invention is relatively simple, it is believed that two illustrative but non-limiting examples are sufficient. Thus, 1490 parts by weight of coker gasoline from a California crude were pumped at the rate of about 75 parts by volume (liquid) per minute into a preheater maintained at about 400° F. The gasoline contained 0.98 per cent sulfur. The vaporized hydrocarbons were introduced tangentially into the reactor maintained at about 590° F. Two hundred and fifty-five parts by weight of nickel carbonyl ($\text{Ni}(\text{CO})_4$) were sprayed into the top center of the reactor. Thus, the ratio of nickel carbonyl (expressed as parts by weight nickel) to hydrocarbon was 1 to 17. The products consisted of 1253 parts by weight of desulfurized gasoline containing 0.49 per cent sulfur, 6.3 cubic feet of gas and a black fluffy material which consisted of colloidal nickel and nickel sulfide.

It can be readily calculated that about 50 per cent of the sulfur had been removed from the gasoline.

The nickel carbonyl was regenerated by contacting the black fluffy material with carbon monoxide at 300° F. and 200 p. s. i. g.

Illustrative of concurrent desulfurization and cracking of a hydrocarbon mixture having a boiling range higher than gasoline is the treatment of a Santa Maria gas oil.

About six hundred and eighty parts by weight of Santa Maria gas oil were pumped at the rate

of about 16 parts by volume per minute into a preheater maintained at about 750° F. The vaporized hydrocarbons were introduced tangentially into a cylindrical reactor which was maintained at about 800° F. About 715 parts by weight of nickel carbonyl were sprayed into the top center of the reactor. Thus, the ratio of nickel carbonyl (expressed as parts by weight nickel) to hydrocarbon was 1 to 2.76. The product consisted of about 600 parts by weight of desulfurized and cracked hydrocarbons, about 15.6 cubic feet of gas (containing some C₄ and C₅ hydrocarbons) and a black fluffy material comprising colloidal nickel and nickel sulfide. The properties of the charge stock and the liquid product are compared in the following table:

	Charge Stock	Liquid Product
ASTM Distillation:		
I. B. P. temperature °F.	275	228
10% do.	529	337
24% do.		410
30% do.	584	470
50% do.	624	555
70% do.	670	610
90% do.	737	692
E. P. do.	752	748
Norwood Bromine Number	23.8	45.4
Percent Sulfur	3.24	2.22
Gravity ° A. P. I.	25.6	29.7

As is evident from an inspection of the distillation of the liquid product, the yield of desulfurized gasoline was 24 per cent of the liquid product.

We claim:

1. A method of desulfurizing a mixture of hydrocarbons which comprises heating a mixture of hydrocarbons containing sulfur bearing compounds to at least 400° F., to vaporize said mixture of hydrocarbons, introducing said vaporized hydrocarbons into a cylindrical reaction zone in the region of the bottom thereof in a direction tangential to the inner periphery of said zone thereby causing said vapors to rise in said reaction zone as a swirling column, maintaining said reaction zone at a temperature of 400°-900° F. and at least the vaporization point of said mixture, introducing finely divided nickel carbonyl into the upper portion of said swirling column of vapors of said mixture of hydrocarbons at substantially the center thereof, whereby said nickel carbonyl is decomposed to form finely divided nickel, causing said finely divided nickel to descend through and in contact with said rising swirling column of vapors of said mixture of hydrocarbons containing sulfur bearing compounds thereby converting at least a portion of said finely divided nickel to nickel sulfide, withdrawing treated vapors of said mixture of hydrocarbons having a reduced concentration of sulfur from the top of said reaction zone, withdrawing a mixture of finely divided nickel and nickel sulfide from the bottom of said reaction zone, contacting said mixture of finely divided nickel and nickel sulfide with carbon monoxide, converting said nickel and nickel sulfide to nickel carbonyl, and treating another mixture of hydrocarbons containing sulfur bearing compounds with said nickel carbonyl.

2. The method described and set forth in claim

1 wherein the mixture of hydrocarbons containing sulfur bearing compounds has an end boiling point of about 750° F.

3. The method described and set forth in claim 1 wherein the mixture of hydrocarbons containing sulfur bearing compounds has an end boiling point of about 750° F., nickel carbonyl is introduced into the reaction zone at the rate of 1 part of nickel to 1 to 20 parts of hydrocarbon mixture by weight and the reaction zone is maintained at about 500° to about 750° F.

4. A method of desulfurizing a mixture of hydrocarbons which comprises heating a mixture of hydrocarbons containing sulfur-bearing compounds to at least 400° F., to vaporize said mixture of hydrocarbons, introducing said vaporized hydrocarbons into a cylindrical reaction zone in the region of the bottom thereof in a direction tangential to the inner periphery of said zone, thereby causing said vapors to rise in said reaction zone as a swirling column, maintaining said reaction zone at a temperature of 400°-900° F. and at least the vaporization point of said mixture, introducing finely divided nickel carbonyl into the upper portion of said swirling column of vapors of said mixture of hydrocarbons at substantially the center thereof, whereby said nickel carbonyl is decomposed to form finely divided nickel, causing said finely divided nickel to descend through and in contact with said rising swirling column of vapors of said mixture of hydrocarbons containing sulfur-bearing compounds thereby converting at least a portion of said finely divided nickel to nickel sulfide, withdrawing treated vapors of said mixture of hydrocarbons having a reduced concentration of sulfur from the top of said reaction zone, and withdrawing a mixture of finely divided nickel and nickel sulfide from the bottom of said reaction zone.

5. A method of treating a mixture of finely divided nickel and nickel sulfide produced by desulfurizing a mixture of hydrocarbons with nickel carbonyl to regenerate nickel carbonyl which comprises contacting said mixture of finely divided nickel and nickel sulfide with carbon monoxide, converting said nickel and nickel sulfide to nickel carbonyl and treating another mixture of hydrocarbons containing sulfur-bearing compounds with said nickel carbonyl.

6. A method of regenerating nickel carbonyl as set forth in claim 5 wherein the mixture of metallic nickel and nickel sulfide is contacted with carbon monoxide in the presence of metallic copper.

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