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PROCESS FOR CATALYTIC DESULPHURIZATION

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This invention relates to the selective removal of sulphur from hydrocarbon fractions, and refers more particularly to catalysts suitable for this selective sulphur removal from hydrocarbon oils, or their fractions, contaminated with sulphur whether in its elemental form or as organic sulphur compounds, or both. The invention also includes the method of preparation of such catalyst. This is a division of my earlier application Serial No. 252,594 filed January 24, 1939, which has issued as Patent No. 2,369,432.

Most petroleum oils contain greater or lesser quantities of sulphur which is usually present principally in the form of organic sulphur compounds. Also, the greater portion of petroleum oils which are now used in cracking processes for obtaining volatile fractions, such as motor fuels, are of relatively high sulphur content. The resulting motor fuels and other distillates prepared from such oils, as a consequence, contain relatively large quantities of sulphur bodies. The presence of such sulphur compounds in fuels is believed to exert a deleterious effect upon engines since their combustion results in the formation of products having highly corrosive properties. Therefore, the petroleum industry has for many years been concerned with the problem of removing both elemental organic sulphur compounds from hydrocarbon oils and their fractions, and particularly from the more volatile fractions thereof, such as those employed as fuel in internal combustion engines. This has resulted in the development of a number of methods for the treatment of sulphur-contaminated hydrocarbon fractions, most of these methods being well known in the art and therefore requiring no further description. It may be stated, however, that much difficulty has been encountered in developing even a partially satisfactory method for treating these hydrocarbon products to remove the sulphur bodies. Thus, most of the methods known until the present time are only partially effective, since they effect the removal of only a part of the sulphur compounds, such as some of the mercaptans, leaving other organic sulphur compounds, particularly those of the type of thiophenes, unaffected in the hydrocarbon fraction subjected to such desulphurizing treatment. Other well known methods of treatment merely convert the sulphur compounds of a given type into organic sulphur compounds of a different character, such transformation being principally made for the purpose of allowing the treated hydrocarbon material to pass certain arbitrary corrosion tests even though the actual sulphur content of the hydrocarbon fraction is still relatively high. Further, the desulphurizing methods employed until the present time have been of little value in the production of suitable motor fuels from hydrocarbon fractions of relatively high sulphur content.

One of the main objections to the known methods of desulphurization of hydrocarbon fractions resides in the fact that most of these methods attempt to remove the sulphur compounds as such. Such processes involve a large loss of valuable hydrocarbon materials boiling within the motor fuel range, which hydrocarbon materials being chemically combined with sulphur, are removed together therewith. Particularly, this loss of desired hydrocarbons is noticeable when the fraction subjected to treatment contains relatively large percentages of sulphur in the form of complex organic sulphur compounds. For example, a gasoline fraction exhibiting an actual sulphur-content of 3.0% may contain as much as 15% of organic sulphur compounds. By selectively removing only the sulphur, a yield of 97% of sulphur-free gasoline would be obtained. On the other hand, when employing processes designed to remove the sulphur compounds as such, the yield of gasoline would not be more than 85% of the treated hydrocarbon fraction even if such processes could quantitatively remove the organic sulphur compounds.

It is therefore the main object of the present invention to provide a process for treating sulphur containing hydrocarbon fractions to remove the sulphur without the concurrent removal of the hydrocarbon material with which this sulphur is chemically combined. It is a further object of the invention to provide a catalyst and a process suitable for the treatment of sulphur-containing hydrocarbon fractions to lower substantially their sulphur content without any appreciable loss in hydrocarbons chemically combined therewith. A still further object is to provide a catalyst for the catalytic desulphurization of hydrocarbon fractions containing thiophenes and thiophene-type compounds.

It has now been discovered that the above and other objects may be attained by subjecting sulphur-contaminated or sulphur-containing hydrocarbon oils, or their fractions, to a treatment in the presence of certain complex catalysts to be described more fully hereinbelow, and preferably in the presence of hydrogen. It has been further discovered that in such treatment of hydrocarbons containing relatively complex or-

ganic sulphur compounds, with the special catalysts and in the presence of hydrogen and heat, the sulphur compounds are apparently decomposed to yield substantial quantities of hydrocarbons, such as fractions suitable for use in motor fuels, and sulphur in the form of hydrogen sulphide which is readily removed from the treated hydrocarbon material by well known means, such as a simple washing with an alkaline solution.

It has been still further discovered that the chromite and/or molybdate salts of metals selected from the class of iron, cobalt and nickel, as well as mixtures thereof, are excellent catalysts for use in the desulphurization of hydrocarbon fractions, and particularly for the effective decomposition of complex organic sulphur compounds present in sulphur-containing petroleum oils and their fractions. The above catalysts are believed to be complex compounds consisting of oxides of chromium or molybdenum in combination with the oxides of iron, cobalt or nickel. These catalysts do not appear to be mere physical mixtures of the oxides of the two types of metals, since experiments have indicated that such physical mixtures of the two oxides are ineffective in producing the same results as those obtained by the catalytic treatment of the sulphur-bearing oils in the presence of the complex compounds of the present invention. In the preferred embodiment, these complex salts or oxides are admixed with or precipitated on a distending or binding agent, such as bentonite.

The invention further includes the method of preparing these catalyst compounds suitable for the effective desulphurization of hydrocarbon fractions, as well as the process of desulphurization of such sulphur bearing fractions in the presence of the aforementioned catalysts. Broadly stated, the method of preparing the catalysts comprises the steps of commingling an aqueous solution of a salt of iron, cobalt or nickel with a basic salt of chromium or molybdenum (preferably an ammonium salt of said last two metals), rendering the mixture slightly alkaline, thereby precipitating a complex metal salt, separating said salt from the solution, and heating said complex salt to obtain the desired chromite or molybdate salt of iron, cobalt or nickel, or of mixtures thereof. Although other basic salts of chromium or molybdenum may be employed in the preparation of the complex catalysts, it has been found advantageous to employ their ammonium salts. This is especially true of the chromium salts. Thus, the interaction between a water soluble iron, cobalt or nickel salt and ammonium dichromate (when realized in the presence of ammonium hydroxide to render the mixture alkaline) causes the precipitation of a double basic salt which, upon separation, washing and heating, liberate nitrogen and water vapors and leaves a complex iron, cobalt or nickel chromite. On the other hand, the interaction of a basic molybdate (which may be an ammonium, sodium or potassium molybdate) with a water soluble salt of iron, cobalt or nickel, when realized at a pH of greater than seven and preferably at a pH of about nine (as by the addition of concentrated ammonium hydroxide), results in the precipitation of a normal salt, which is a molybdate of iron, cobalt or nickel, and which, as brought out above, may be considered as consisting of a complex of the oxides of molybdenum and of the other metal. Therefore, in this case, the heating of the precipitated and separated salt is purely for the purpose of its desiccation.

As previously stated, the catalyst may be made in the presence of a distending or binding agent of the type of bentonite. In such a case the bentonite, or some other clay, may be commingled with the materials prior to the introduction of the ammonium hydroxide or the like. When operating in this manner the metal-base-chromate or metal-molybdate salts precipitate onto the distending and binding agent, so that the subsequent treatment with heat results in the production of the desired catalyst spread over and held together by such distender and binder.

As a matter of illustration, and in order to describe more fully this phase of the invention, the following illustrating examples of manufacturing two specific desulphurizing catalysts are set forth.

In the first example a catalyst comprising a cobalt molybdate compound distributed on bentonite, was prepared as follows: About 100 grams of Wyoming bentonite was dispersed in approximately 5000 ml. of distilled water containing 350 grams of dissolved $CoSO_4.7H_2O$. Thereafter, a water slurry containing 200 grams of ammonium molybdate was added to the first suspension, and concentrated ammonium hydroxide was then slowly introduced into the mixture over a period of about two hours at the end of which time there was a faint but permanent odor of ammonia. As stated above, this ammonium hydroxide is added to render the mixture alkaline and to cause the precipitation of the normal cobalt molybdate salt. The resulting mixture of cobalt molybdate and bentonite was allowed to stand for a period of thirty-six hours during which it was occasionally stirred. At the end of this time, the mixture was filtered by means of a suction filter. The filter cake produced was then resuspended in about 3000 ml. of water, filtered, and the resulting filter cake subjected to two more washings with water. In order to produce a catalyst of the desired particle size, the washed filter cake was then extruded through a ⅛ inch orifice, thoroughly dried at a temperature of about 150° F., and then broken up into short lengths for use.

In another example, a catalyst suitable for the purpose of the desulphurization of petroleum fractions was prepared by first dissolving one gram molecular weight of nickel nitrate in 1000 ml. of water followed by the addition thereto of 0.5 gram molecular weight of ammonium dichromate dissolved in 1000 grams of water. Thereafter, approximately 140 ml. of concentrated ammonium hydroxide was added to the mixed solution, this amount being sufficient to render the mixture slightly alkaline, and to cause the precipitation of the double base salt. The precipitate thus formed was then filtered off and thoroughly washed. If desired, the washing operations may be repeated to produce a relatively pure double base salt. The filter cake was then heated slowly with stirring. Since the purpose of this heating is to decompose the nickel ammonium chromate salt and to convert it into a nickel chromite, the heating may be realized in an open vessel, over an open flame, and until gas evolution ceases. If desired, the resulting powdered nickel-chromite salt formed by the heating operation may be re-extracted with warm water and then mixed into a paste with

about 75 grams of bentonite. The paste may then be extruded through a ⅛ inch orifice, dried at about 150° F., and then broken into desired lengths suitable for use as a catalyst for the desulphurization of sulphur-contaminated hydrocarbon fractions.

Although the above examples disclosed the production of cobalt molybdate and nickel-chromite salt complexes, the chromite and molybdate salt complexes of the other metals enumerated above may be realized by following the disclosure presented hereinabove, all of these substances being discovered to be excellent catalysts for the catalytic treatment of sulphur-contaminated hydrocarbon fractions, and particularly of hydrocarbons containing organic sulphur compounds.

Having outlined the general principles and examples of the preparation of the chromate and molybdate salts of metals of the type of iron, cobalt and nickel, the following disclosure and examples describe the process of the utilization of these catalysts for the treatment of sulphur-contaminated hydrocarbon fractions and improved results accruing from the utilization of the present invention. Generally speaking, this process comprises bringing a mixture of the sulphur-containing hydrocarbons and hydrogen into contact with a catalyst prepared as described above. Although the desulphurization treatment may be realized in the liquid state it is preferred to practice the invention as a vapor phase process in which the sulphur-contaminated petroleum oils or their fractions are vaporized, and the vapors thus formed in admixture with the hydrogen are contacted with the catalyst. Depending on the stock to be treated as well as on other conditions the desulphurizing reaction may be realized at temperatures between about 600° F. and 900° F. As to the pressure, the reaction may be effectively operated at superatmospheric pressures. However, excellent results have been obtained by conducting the reaction at the aforementioned temperatures and substantially atmospheric pressures. In conducting the reaction in the vapor phase, the catalyst in a granular form may be held stationary in the reaction tube maintained at the desired temperature, the hydrocarbon vapors and hydrogen being conveyed over such catalyst and then passed into a condenser for the liquefaction of the treated hydrocarbons. The invention may also be practiced as a liquid phase process by dispersing the catalyst preferably in powdered form in the liquid medium which is agitated under hydrogen pressure to facilitate contact with the solid catalyst and the hydrogen gas. The liquid phase modification may be carried out as a batch or continuous operation. One satisfactory method of operation is to pump the liquid hydrocarbons to be desulphurized through a heated tower containing the solid catalyst and countercurrent to a stream of hydrogen.

As an example of the utilization of a catalyst of the present invention for vapor phase desulphurization of sulphur containing hydrocarbon fractions, the following may be given:

One hundred milliliters of the nickel chromite catalyst prepared according to the process described above was placed into a reactor tube having a diameter of about one inch. During the reaction the tube was maintained at a temperature of about 650° F. The charging stock consisted of a hydrocarbon fraction boiling within the range of 200° F. to 300° F., and derived from the cracking residuum, said residuum having been prepared by topping Santa Maria Valley, California crude oil. Although the feed stock had an actual sulphur content of 3.02% none of the sulphur was present in elemental form but instead was present in the form of organic sulphur compounds principally of the thiophene type which represented about 15% of the stock. Prior to the passage of this sulphur containing fraction through the reaction tube, it was first conveyed through a vaporizer maintained at a temperature of about 400° F. The vaporizer contained approximately 100 milliliters of fuller's earth for the purpose of removing any high boiling, carbon-forming polymers which might be present in the vapors. Such pretreatment of the vapors was found to be advantageous since it protected the desulphurizing catalyst from being deactivated by carbon-forming polymers. After passing through the vaporizer and the reaction tube, the treated vapors were continuously fed into a condenser from which the condensate was collected.

The hydrocarbon fraction was introduced into the vaporizer at a rate of about 30 ml. of liquid per hour. Simultaneously, hydrogen gas was introduced into the vaporizer at a rate of about 11.7 liters of gas per hour. The reaction was conducted at substantially atmospheric pressure. At the end of a ten hour period of continuous operation, the treated hydrocarbon fraction collected in the condenser amounted to about 95% of that introduced into the system. This fraction was washed with caustic to remove the hydrogen sulphide. An analysis of the washed condensate showed that its sulphur content was reduced to a value of 0.90%. It is thus seen that the operations according to the present process and with the catalyst constituting one phase of said invention resulted in the removal of more than two-thirds of the actual sulphur with the coincidental recovery of most of the valuable hydrocarbons originally chemically combined with the sulphur.

In another experiment the above described hydrocarbon fraction containing organic sulphur compounds was treated in the vapor phase and under the same conditions as described in the first experiment. However, in this case the catalyst comprised a cobalt molybdate catalyst, which as stated above is believed to be a complex inorganic compound consisting of oxides of cobalt and molybdenum. The recovered hydrocarbon fraction, after a continuous operation conducted over a period of twenty-four hours was washed with caustic and showed an average yield of 95% by volume of the material introduced in the reactor. An analysis of this treated hydrocarbon fraction showed that it contained only 0.3% sulphur.

Similar results have been obtained with catalysts prepared from other combinations listed above.

It has been brought out above that the chromate or molybdate complexes precipitated from the aqueous solution are heated to dehydrate them and to form the desired catalyst. In some instances, however, this last heating step employed in the preparation of the catalyst may be eliminated. In such a case, the precipitated complex may be directly introduced into the reaction zone, the heating of such zone being then relied upon to dehydrate the complex salt and to convert it into the desired oxide type catalyst.

When operating at substantially atmospheric

pressures, the catalysts described have been observed to exhibit the desired catalytic activity at temperatures as low as 550° F. or 600° F. Furthermore, these catalysts do not appear to produce any appreciable cracking of the hydrocarbons at temperatures as high as 900° F. mentioned above as being suitable for the desulphurization of the sulphur-containing hydrocarbon oils or their fractions.

It has also been found that further reduction in the sulphur content of the hydrocarbon material may be obtained by recycling the treated materials. Therefore, it is within the scope of the present invention to provide for the continuous recycling of the hydrocarbon fractions through the reaction zone and in contact with the catalyst, thereby producing hydrocarbon fractions which are essentially free from, or at least low in sulphur, even from materials which originally have a relatively high sulphur content. Simultaneously, the conversion of the organic sulphur compounds into hydrogen sulphide and sulphur-free hydrocarbons permits the recovery of such hydrocarbons so that the yield of treated materials is high.

The presence of hydrogen (or of a suitable gas yielding hydrogen) is essential in the catalytic treatment with the catalysts of the present invention. This is due to the fact that the process apparently causes the liberation of the sulphur from the organic sulphur compounds and the chemical combining of this sulphur with the hydrogen to form the easily removable hydrogen sulphide. The amount of hydrogen necessary varies with the stock treated and the conditions of operation. There must be at least enough hydrogen to react with all of the sulphur present (2 atoms of hydrogen per atom of sulphur). However, in order to permit an efficient operation of the desulphurizing process (when operating with the catalyst disclosed), it is preferable to have an excess of hydrogen. The presence of hydrogen in excessive quantities might cause the hydrogenation of the unsaturated hydrocarbon constituents if these hydrocarbons were maintained in the reaction zone for a sufficiently prolonged time. However, the catalyst of the present invention has the selective ability to desulphurize hydrocarbons in preference to the hydrogenation of the unsaturated constituents thereof. Therefore, particularly when operating at the above outlined temperatures and pressures, it is possible to regulate the rate of throughput so as to cause the desulphurization without any substantial hydrogenation. Such operations are within the skill of an operating chemist.

As many apparent and different embodiments of this invention may be made without departing from the spirit and scope thereof, it is understood that there is no intention to be limited to any specific examples or embodiments disclosed herein. Accordingly, all such changes and modifications as come within the terms and spirit of the appended claims are to be embraced within the scope of this invention.

I claim:

1. A process for desulphurizing sulphur contaminated hydrocarbon oils which comprises contacting said sulphur contaminated hydrocarbons in the presence of hydrogen at a temperature above about 600° F. with a catalyst prepared by commingling an aqueous solution of a salt of a metal selected from the class consisting of iron, cobalt and nickel with an aqueous solution of a basic salt of a metal selected from the class consisting of chromium and molybdenum, adding ammonium hydroxide to said solution to render the mixture alkaline, thereby precipitating a complex salt of the metals of said two classes, separating said complex salt from said solution, and heating said complex salt to yield said catalyst.

2. A process for desulphurizing sulphur contaminated hydrocarbon oils which comprises contacting said sulphur contaminated hydrocarbons in the presence of hydrogen at a temperature above 600° F. with a catalyst prepared by commingling an aqueous solution of a salt of a metal selected from the class consisting of iron, cobalt and nickel with an aqueous solution of a salt selected from the class consisting of ammonium chromates and ammonium molybdates, adding ammonium hydroxide to said solution to render the mixture alkaline, thereby precipitating a complex salt from said solution, and heating said complex salt to obtain said catalyst.

3. A process for desulphurizing sulphur contaminated hydrocarbon oils which comprises contacting said sulphur contaminated hydrocarbons in the presence of hydrogen at a temperature above about 600° F. with a catalyst prepared by commingling an aqueous solution of a salt of a metal selected from the class consisting of iron, cobalt and nickel with an aqueous solution of ammonium molybdate, rendering the mixture slightly alkaline with ammonium hydroxide and thereby precipitating a complex metal salt, separating said salt from the solution, and heating said complex salt to obtain said catalyst.

4. A process for desulphurizing sulphur contaminated hydrocarbon oils which comprises contacting said sulphur contaminated hydrocarbons in the presence of hydrogen at a temperature above about 600° F. with a catalyst prepared by commingling an aqueous solution of a salt of a metal selected from the class consisting of iron, cobalt and nickel with an aqueous solution of an ammonium salt of chromium, adding ammonium hydroxide to said solution to render the mixture alkaline, thereby precipitating a complex chromate salt of the metals of said class, separating said complex chromate salt from the solution and heating said complex salt to yield a chromite catalyst of said metal.

5. A process for desulphurizing petroleum oils containing sulphur compounds, which comprises vaporizing said sulphur-contaminated oils, commingling said vapors with hydrogen in a quantity sufficient to combine with all the sulphur in said vapors and to form hydrogen sulphide, and conveying said vapor-hydrogen mixture at substantially atmospheric pressure and at a temperature above about 600° F. over a solid catalyst comprising essentially cobalt molybdate, said catalyst having been prepared by commingling an aqueous solution of a cobalt salt with an ammonium molybdate, rendering the mixture slightly alkaline with ammonium hydroxide and thereby precipitating a complex metal salt, separating said salt from the solution, and heating said complex salt to obtain said catalyst.

6. A process for desulphurizing sulphur-contaminated hydrocarbon oils which comprises contacting said sulphur-contaminated hydrocarbons, in the presence of hydrogen at a temperature above about 600° F. with a catalyst comprising cobalt molybdate, said catalyst having been prepared by commingling an aqueous solution of a

cobalt salt with an ammonium molybdate, rendering the mixture slightly alkaline with ammonium hydroxide and thereby precipitating a complex metal salt, separating said salt from the solution, and heating said complex salt to obtain said catalyst.

7. A process according to claim 3 in which the catalyst is dispersed on a carrier agent.

8. A process according to claim 3 in which the metal of the class consisting of iron, cobalt and nickel is nickel.

9. A process according to claim 2 in which the hydrocarbons and the hydrogen are conveyed over the catalyst at a temperature between about 600° F. and 900° F.

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