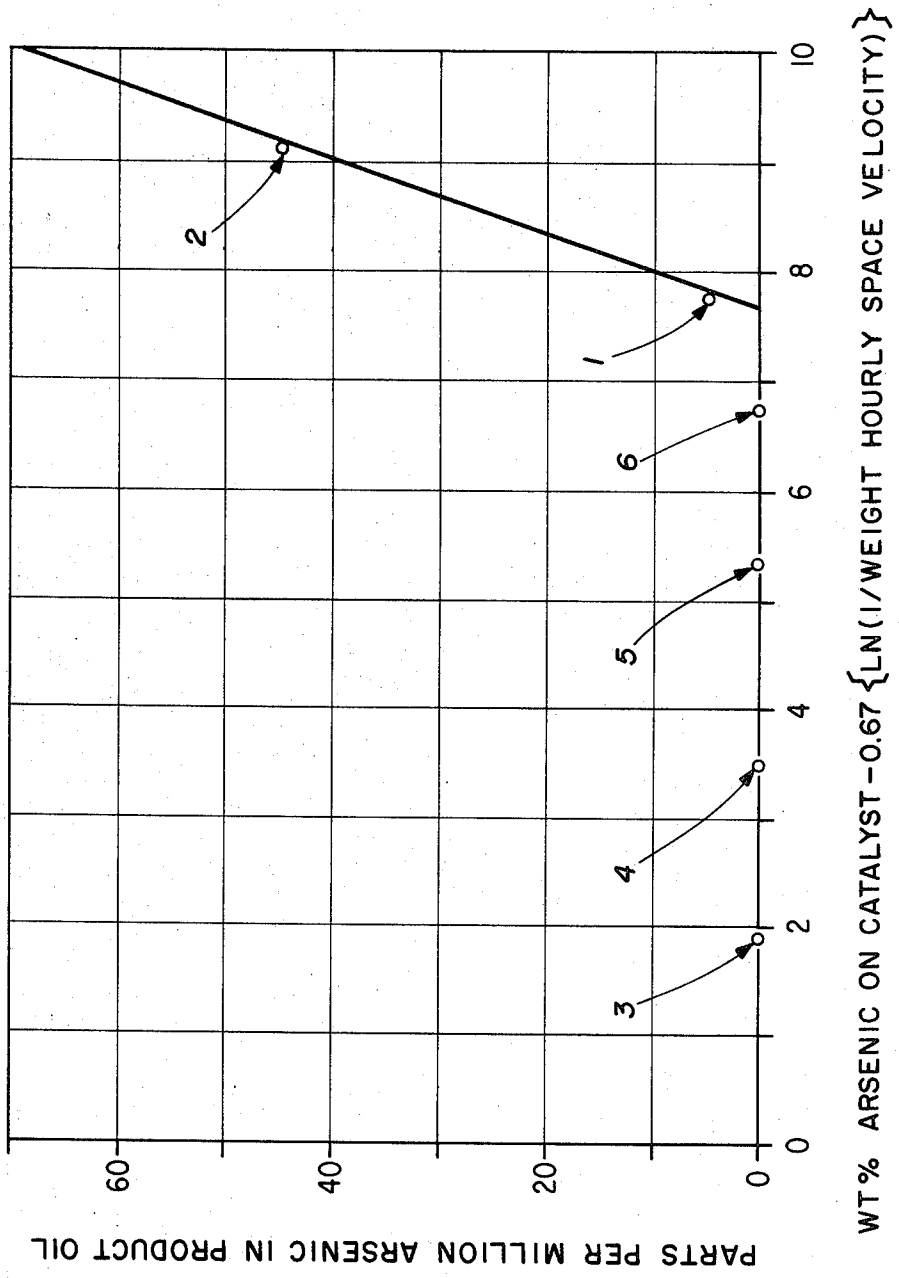
SHALE OIL TREATMENT

Filed Dec. 22, 1972



United States Patent Office 3,804,750
Patented Apr. 16, 1974

3,804,750

SHALE OIL TREATMENT

Gary A. Myers, Plano, and Donald K. Wunderlich, Richardson, Tex., assignors to Atlantic Richfield Company, New York, N.Y.

Filed Dec. 22, 1972, Ser. No. 317,625
Int. Cl. C10g 17/00
U.S. Cl. 208—253 12 Claims

ABSTRACT OF THE DISCLOSURE

A method for removing arsenic from shale oil by contacting the oil with a mixture of nickel sulfide and molybdenum sulfide, employing an elevated temperature and reducing atmosphere for said contacting, and terminating the contacting at least by the time that the equivalent of about 7.7 weight percent arsenic at one weight hourly space velocity (WHSV) has been deposited on the sulfide mixture.

BACKGROUND OF THE INVENTION

Heretofore, various metal oxides including mixtures thereof have been employed to remove arsenic from hydrocarbon charge stocks such as naphtha, all such charge stocks having been obtained from naturally occurring crude oil. For example, in U.S. Pat. 3.069,350, the disclosure of which is incorporated herein by reference, the removal of arsenic from naphthas obtained from naturally occurring crude oil in a conventional refining process, can have arsenic removed therefrom when contacted with a mixture of cobalt oxide and molybdenum oxide on an alumina carrier. It is taught in this patent that the cobalt-molybdenum catalyst must be discarded when the catalyst has been contacted with the hydrocarbon a sufficient time to deposit on the catalyst about 1.5 lbs. of arsenic per 2000 lbs. of catalyst, i.e., when 0.07 weight percent arsenic is deposited on the cobalt oxide-molybdenum oxide mixture, using a weight hourly space velocity in the range of from one to ten.

BRIEF DESCRIPTION OF THE INVENTION

It has now been discovered that with shale oil which is obtained from normally solid oil shale and which is not derived from naturally occurring crude oil, arsenic can be removed therefrom by contacting same with a mixture of nickel sulfide and molybdenum sulfide and that if this particular mixture of sulfides is employed at an elevated temperature and under a reducing atmosphere, contacting of the shale oil with the sulfide mixture to remove arsenic need not be terminated until the equivalent of about 7.7 weight percent arsenic at one WHSV has been deposited on the sulfide mixture.

This is a substantially higher amount of arsenic deposition on the sulfide mixture of this invention before termination of the process than is suggested by the prior art for oxide mixtures and was a surprising discovery. Further, this discovery is of substantial economic advantage in that it means that with shale oil the sulfide mixture can be employed for arsenic removal for substantially longer periods of time and for greater volumes of shale oil than would be obvious from the prior art.

Accordingly, it is an object of this invention to provide a new and improved method for purifying shale oil. It is another object to provide a new and improved method for removing arsenic from shale oil. It is another object to provide a new and improved method for employing certain metal sulfides for the removal of impurities from shale oil. It is another object to provide a new and improved method for treating shale oil to improve the quality thereof.

Other aspects, object and advantages of this invention will be apparent to those skilled in the art from this disclosure and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

According to this invention non-naturally occurring shale oil is contacted with a mixture of nickel sulfide and molybdenum sulfide, the nickel sulfide being nickelous or nickelic (Ni_2S_3 and/or Ni_3S_4) and the molybdenum being of any valence from 2 through 6, preferably NiS and MoS_3. The contacting is carried out at an elevated temperature, preferably at least about 300° F., still more preferably from about 300 to about 850° F., and under a reducing atmosphere, preferably containing some molecular hydrogen, still more preferably being essentially molecular hydrogen. The contacting is terminated at least by the time that the equivalent of about 7.7 weight percent arsenic at one WHSV has been deposited on the sulfide mixture. Thus, this invention applies to WHSV values which are different from unity, the 7.7 value at one WHSV being chosen for sake of clarity. Any WHSV value can be used and the percent arsenic deposition at the chosen WHSV value translated to the equivalent percent arsenic deposition for one WHSV.

The drawing is a graph of data obtained by carrying out the process of this invention up to and beyond the 7.7 weight percent arsenic deposition limit at one WHSV, and clearly shows that above the 7.7 weight percent cutoff line or its equivalent if a WHSV different from one is used, the amount of arsenic in the iol product, i.e., the shale oil after it has passed over the sulfide mixture, increases very dramatically, but that below the 7.7 weight percent limit and above the 0.07 weight percent limit described in the above-identified U.S. patent, the amount of arsenic in the oil product is substantially nil.

The nickel sulfide-molybdenum sulfide mixture can contain the various sulfides in varying weight ratios but preferably in the weight ratio range of nickel sulfide to molybdenum sulfide of from about 1/99 to about 99/1. The sulfide mixture can be supported or unsupported and any conventional support such as silica, alumina, magnesia, zirconia, thoria, zinc oxide, naturally occurring supports such as clays, kieselguhr, fuller's earth, pumice, bauxite, and the like, and combinations of two or more thereof whether naturally occurring or synthetically prepared can be employed. The sulfide mixture, whether supported or unsupported, should be in particulate form, the particle size not being critical although the greater the surface area the better from a point of view of completeness of contacting between the shale oil and the sulfides. Generally, the material should be in a particulate form such that at least about 50 weight percent thereof has a large cross-sectional dimension (i.e., the diameter of a particle if it is round or the longest dimension through the center of a particle if it is not round) of no larger than about one-quater inch. The sulfides, supported or unsupported still more preferably will have a surface area of at least one square meter per gram and can have a surface area of at least fifty square meters per gram depending upon the intimacy of contacting desired between the shale oil and sulfides. The sulfides, supported or unsupported, can be in any physical form including powders, pellets, granules, spheres, flakes, cylinders, and the like. When the sulfides are supported, the nickel sulfide is preferably present in an amount of from about 1 to about 7, still more preferably from about 2 to about 5, weight percent, and the molybdenum sulfide is present in an amount of from about 10 to about 30, still more preferably from about 15 to about 25, weight percent, all weight percents being based upon the total weight of the supported sulfide mixture.

The sulfide mixture can be made in any conventional manner, e.g., impregnating a porous support material such

as alumina with an aqueous solution of nickel nitrate and molybdenum nitrate, calcining the nitrate containing support to form nickel oxide and molybdenum oxide on said support, followed by sulfiding to convert the oxides to sulfides. This is all well-known in the art and therefore will not be described in greater detail.

In the discussion of this invention, reference to arsenic is intended to include arsenic in the free or elemental form as well as arsenic in any combined form.

The time of contacting of the sulfide mixture and shale oil will vary widely but it will generally be for a time sufficient to achieve the desired degree of arsenic removal, and will generally be at least about one minute. The pressure of contacting can vary widely from atmospheric and on to an elevated pressure as desired. When molecular hydrogen is employed as part or all of the reducing atmosphere, the hydrogen partial pressure is preferably at least 500 p.s.i.g., still more preferably at least 1500 p.s.i.g.

Either before, after, or before and after the shale oil is contacted with the above-described sulfide mixture for arsenic removal, the oil can be treated in other ways for removal of arsenic. The liquid can be pretreated for partial removal of arsenic before treatment in accordance with this invention. After treatment in accordance with this invention, the oil can be further treated for cleanup removal of arsenic if desired.

One suitable method that can be practiced in conjunction with this invention is conventional caustic washing. For example, one way for carrying out caustic washing is to contact the shale oil with an aqueous solution of at least one alkali metal hydroxide such as sodium hydroxide and potassium hydroxide, the hydroxide or combination of hydroxides being present in an amount of from about 1 to about 20 weight percent based on the total weight of the aqueous solution. The caustic solution is contacted with the oil in a solution/liquid weight ratio of from about 1/1 to about 1/10, the contacting being carried out at a temperature of at least 200° F., preferably at least 300° F., with the pressure being maintained sufficient to prevent substantial vaporization of solution or oil, e.g., at least about 300 p.s.i.g. The atmosphere present during the contacting with caustic solution can be ambient, although if desired, neutral or reducing atmospheres can be employed but are not necessary.

After treatment, the aqueous solution is separated from the oil by a conventional method such as employing a settling tank followed by a centrifuge and the like. The shale oil after treatment with the caustic solution can be washed with water or other suitable solvent to remove residual caustic solution and any arsenic associated with that solution.

EXAMPLE

A nominal 400 to 800° F. cut of shale oil obtained by retorting normally solid Colorado oil shale and containing 82 parts per million of arsenic was contacted with a commercial nickel-molybdenum hydrotreating catalyst that had been sulfided which contained 3.2 weight percent NiO and 15.1 weight percent MoO_3 and the remainder essentially alpha alumina prior to sulfiding. The catalyst had a surface area of 180 square meters per gram, a particle size of 0.07 inch in diameter and 0.18 inch in length, and a bulk density of 40 pounds per cubic foot.

Seventy-five grams of the oxide mixture were charged to a one-inch diameter reactor after which the reactor was purged first with nitrogen, and then with hydrogen, and then heated to 400° F. The catalyst was treated at 400° F. with a gas mixture of 10 volume percent hydrogen sulfide in hydrogen for four hours to convert the nickel and molybdenum oxides to sulfides. The reactor was then pressured with molecular hydrogen to 2000 p.s.i.g. Thereafter, the shale oil was charged to the reactor at the rate of 750 grams per hour, 10 weight hourly space velocity (10 WHSV), the temperature raised to 720° F., and the hydrogen pressure maintained at 2000 p.s.i.g. with a hydrogen flow rate of 10 standard cubic feet per hour.

Samples of product oil, after passing over the sulfide mixture (catalyst), were taken and analyzed by conventional X-ray spectroscopy using triphenylarsine in mineral oil as the arsenic standard to determine the arsenic content in the product oil. The arsenic removed from the oil was deposited on the catalyst. Thus, the arsenic deposition at various points were used to determine how much arsenic had been deposited on the catalyst. Analysis of the catalyst following the competion of the test showed that the arsenic had deposited on the catalyst in the amounts previously determined. The data showed that below 6.1 weight percent arsenic on the catalyst substantially no arsenic was present in the shale oil product whereas above 6.1 weight percent arsenic on the catalyst the amount of arsenic in the shale oil product increased dramatically. To convert this 6.1 weight percent value obtained at 10 WHSV to a value of one WHSV the formula; wt. percent—0.67 [Ln 1/WHSV]; was used and gave a curve as shown in the drawing.

When the experiment was repeated in all respects except that a 1.5 weight hourly space velocity was established for the shale oil feed to the reactor, substantial amounts of arsenic in the oil product did not appear until about 7.2 weight percent arsenic was deposited on the catalyst. For example, with the 1.5 weight hourly space velocity feed rate, with about 7.4 weight percent arsenic on the catalyst (refeernce numeral **1** in the drawing) the amount of arsenic in the oil product was about 4 parts per million. As greater amounts of arsenic were deposited on the catalyst the amount of arsenic in the oil product increased dramatically along the slope as shown in the drawing so that at at about 8.8 weight percent arsenic on the catalyst (reference numeral **2** in the drawing) the amount of arsenic in the oil product was 44 parts per million. In contrast, at the 1.5 WHSV value and at 1.6, 3.1, 5.0, and 6.4 weight percent arsenic on the catalyst the amount of arsenic in the oil product was less than 5 parts per billion (p.p.b.), 5 p.p.b., 15 p.p.b., and 35 p.p.b., respectively. Converting all these values to a value for one WHSV by using the above formula, the points shown on the drawing by reference numerals **3** through **6**, respectively, were obtained.

Reasonable variations and modifications are possible within the scope of this disclosure without departing from the spirit and scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for removing arsenic from shale oil comprising contacting said oil with a mixture of nickel sulfide and molybdenum sulfide at an elevated temperature and under a reducing atmosphere, and terminating said contacting at least by the time that the equivalent of about 7.7 weight percent arsenic at one weight hourly space velocity has been deposited on said mixture.

2. A process according to claim **1** wherein said nickel sulfide is essentially NiS and said molybdenum sulfide is essentially MoS_3, said sulfides being present in said mixture in the weight ratio range of NiS/MoS_3 of from about 1/99 to about 99/1.

3. A process according to claim **2** wherein said mixture of sulfides is supported on alumina.

4. A process according to claim **3** wherein said NiS is present in an amount of from about 1 to about 7 weight percent and said MoS_3 is present in an amount of from about 10 to about 30 weight percent, both weight percents being based on the total weight of the alumina supported mixture.

5. A process according to claim **4** wherein said alumina is alpha alumina.

6. A process according to claim **1** wherein said mixture is in a particulate form such that at least about 50 weight percent thereof has a largest cross-sectional di-

mension of no larger than about one-quarter inch, said elevated temperature is at least about 300° F., and said reducing atmosphere contains molecular hydrogen.

7. A process according to claim **2** wherein said mixture has a surface area of at least about one square meter per gram, said elevated temperature is from about 300 to about 850° F., and said reducing atmosphere is essentially molecular hydrogen.

8. A process according to claim **3** wherein said NiS is present in an amount of from about 2 to about 5 weight percent, and said MoS_3 is present in an amount of from about 15 to about 25 weight percent, both wegiht percents being based upon the total weight of the alumina supported mixture.

9. A process according to claim **2** wherein said NiS is present in an amount of from about 1 to about 7 weight percent and said MoS_3 is present in an amount of from about 10 to about 30 weight percent, both weight percents being based on the total weight of the mixture.

10. A process according to claim **9** wherein said mixture is in particulate form such that it has a surface area of at least about one square meter per gram, said elevated temperature is from about 300 to about 850° F., and said reducing atmosphere is essentially molecular hydrogen.

11. A process according to claim **1** wherein one of prior to, after, or both said contacting of said shale oil and said sulfides, said oil is contacted with at least one alkali metal hydroxide to remove part of the arsenic present in said oil.

12. A process according to claim **11** wherein said alkali metal hydroxide is at least one of NaOH and KOH and is employed in an aqueous solution containing from about 1 to about 20 weight percent alkali metal hydroxide, said caustic solution being employed in a solution/shale oil weight ratio of from about 1/1 to about 1/10, contacting of said solution and oil being at a temperature of at least 200° F. and a pressure sufficient to prevent substantial vaporization of said solution and oil.

References Cited

UNITED STATES PATENTS

3,367,861	2/1968	Aldridge et al.	208—251
3,496,099	2/1970	Bridge	208—251 H
2,897,131	7/1959	Berger	208—253
3,069,350	12/1962	Ramella	208—89

FOREIGN PATENTS

797,857	7/1958	Great Britain	208—251 H

DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

U.S. Cl. X.R.

208—89, 251 H