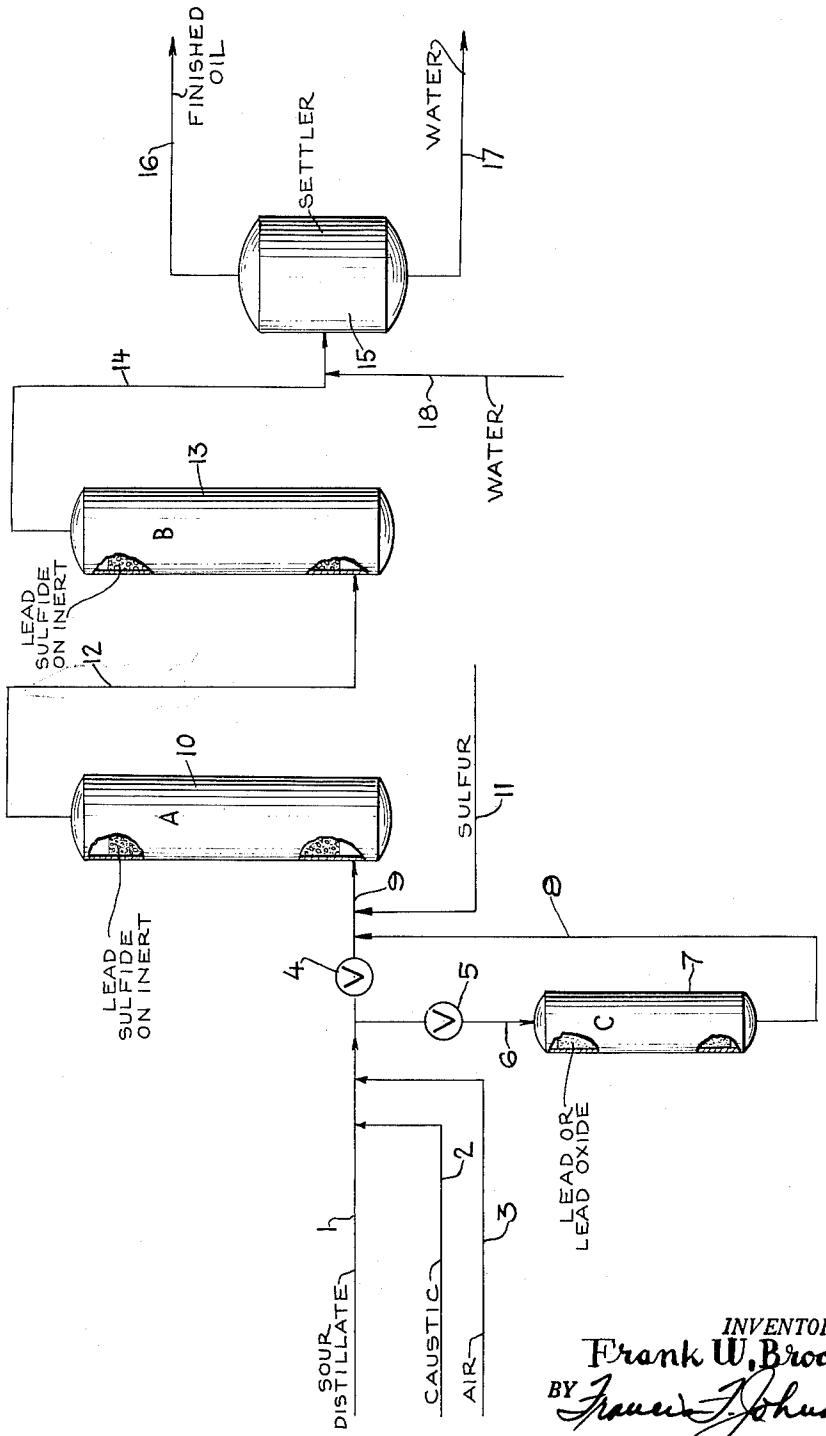
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CONCURRENT DEPOSITION OF LEAD SULFIDE AND MERCAPTAN CONVERSION IN HYDROCARBON OILS

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CONCURRENT DEPOSITION OF LEAD SULFIDE AND MERCAPTAN CONVERSION IN HYDROCARBON OILS

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The present invention relates to the reduction of the mercaptan content of petroleum fractions used as fuels including gasoline, kerosine, and domestic heating oil and, more particularly, to the reduction of the mercaptan content of petroleum fractions, used as fuels, by the addition of sulfur, caustic and air to the sour fuel and contacting the fuel and added caustic, sulfur and free oxygen with a catalyst comprising lead sulfide wherein the lead sulfide is produced in situ in the catalyst bed and/or is substantially continuously or intermittently replaced by lead sulfide introduced in the petroluem fraction to be sweetened.

As previously taught by prior art investigators notably in U.S. Reissue Patent No. 22,135 of U.S. Patent No. 2,272,596 undesirable sulfur compounds can be converted in a petroleum distillate by incorporating in the distillate an amount of elemental sulfur not exceeding the amount of elemental sulfur required to combine with the aforesaid sulfur compounds but sufficient to combine with most of the aforesaid sulfur compounds, an alkaline compound in amount sufficient to render and maintain the distillate alkaline, and finely dispersed oxygen. The resulting alkaline distillate containing elemental sulfur and finely dispersed oxygen is brought into intimate contact with a lead sulfide catalyst in the absence of dispersed water and in the presence of not more than a small amount of added finely dispersed water.

The reduction of the mercaptan content of fuel fractions of petroleum including gasoline, kerosine, and domestic heating oil is promoted by passing the sour oil mixed with air, caustic, and sulfur through a fixed bed of lead sulfide catalyst which coats the surfaces of particles of inert material such as sawdust, ceramic Raschig rings, pumice, etc. The inert catalyst support is coated with approximately 16.2 pounds of lead oxide per cubic foot of support. After varying periods of on-stream time the catalyst is depleted of lead through elution of the lead and other physical and/or chemical actions. When the amount of lead sulfide is reduced to less than 0.10 pound calculated as lead per cubic foot of support or the equivalent 0.11 pound of lead oxide, the catalytic coating on the inert spport must be replaced. This results in interruption of the conversion process or requires a larger inventory of lead sulfide catalyst.

Heretofore it has been the practice to prepare the lead sulfide catalyst by admixing an inert support such as sawdust, pumice, slag, etc., wet with gasoline or other distillate, with lead oxide, e.g., litharge in such proportions that the litharge comprises about 40–50 percent by weight of the mixture. A bed of this mixture is formed in a suitable tower and a charge of alkaline gasoline containing a substantial excess of elemental sulfur passes through the bed until the lead oxide is largely converted to lead sulfide as evidenced by the progressively increased reduction of the mercaptan content of the gasoline discharged from the bed. The catalyst thus produced, comprising about 40–50 percent lead sulfide, can then be used in the normal conversion operation in which the use of excess sulfur in the charge is avoided.

It has now been determined that the lead sulfide catalyst need not be preformed but can be formed simultaneously with the reduction of the mercaptan content of the sour oil. Furthermore, it has also been discovered that, when the catalyst becomes deactivated through loss of lead sulfide, the displaced lead sulfide can be replaced without interrupting the conversion operation. In other words, the mercaptans in a hydrocarbon oil can be converted to sulfides while simultaneously depositing lead sulfide on an inert carrier or while replacing lead sulfide displaced from the inert carrier.

The present invention provides a method for producing the catalytic lead sulfide in situ or replacing the displaced catalytic lead sulfide without interruption of the on-stream period and while reducing the mercaptan content of the fuel fraction. Broadly, the present invention provides for depositing the lead sulfide catalyst while converting the mercaptans of the sour distillate fuel to sulfides. In carrying out the simultaneous conversion of the mercaptans of the sour distillate to sulfides and depositing the lead sulfide coating on the support in the bed in the primary reactor either of two quite similar methods can be used. Preferably, the sour oil, caustic and air are passed through a secondary reactor having a bed of comminuted metallic lead or lead oxide or other lead compound reactive in alkaline medium with the mercaptans in the sour oil. The lead mercaptide thus produced dissolves or is suspended in the oil. The mixture of oil, aqueous caustic, air, and lead mercaptide flows from the secondary reactor to the primary reactor. At a point intermediate to the secondary reactor and to the primary reactor, preferably as close to the primary reactor as local conditions permit, elemental sulfur is admixed with the oil, caustic, air, and lead mercaptide. In the presence of the elemental sulfur the lead mercaptide is converted to lead sulfide which is deposited on the carrier in the primary reactor while the mercaptans of the sour distillate are concurrently converted to sulfides. In this manner, the inert support material in the primary reactor is coated with a very thin layer of the lead sulfide deposited in the primary reactor from the mixture comprising oil, caustic, air, lead mercaptide and sulfur.

The reaction in the secondary reactor can be represented by Equation 1 below and that in the primary reactor by Equation 2 below.

$$(1) \quad 2RSH+Pb(NaO)_2=(RS)_2Pb+2NaOH$$

$$(2) \quad (RS)_2Pb+S=R_2S_2+PbS$$

Alternatively, the elemental sulfur can be added to mixture of sour distillate, aqueous caustic and air prior to the introduction of the mixture into the secondary reactor. This modification, however, can under some circumstances lead to undesirable deposition of lead sulfide within the secondary reactor or in the piping between the secondary reactor and the primary reactor.

In other words, the present invention can be employed as a means of activating a bed of inert packing such as ceramic or glass Raschig rings into an active mercaptan-conversion catalyst by transporting into the primary reactor in the sour oil, lead in the form of lead mercaptide or lead sulfide and depositing a lead sulfide coating on the inert packing surface in the primary reactor. The source of the lead of the lead mercaptide can be metallic lead in the form of sheets or granules, lead oxide, or in general other compounds of lead which in alkaline medium will react with mercaptans and sulfur to form lead mercaptide and/or lead sulfide.

When a sour hydrocarbon oil containing mercaptans is contacted with a source of lead in an alkaline medium lead mercaptide $(RS)_2Pb$ is formed. The lead mercaptide is soluble in the hydrocarbon oil. The lead mercaptide is converted to oil-insoluble lead sulfide in the presence of elemental sulfur usually introduced into the menstruum at the inlet to the primary reactor. By introducing the

sulfur into the oil containing the oil-soluble lead mercaptide at a point contiguous to the inlet of the primary reactor the possibility that oil-insoluble lead sulfide will be deposited in the lead pot or in the conduits leading from the secondary reactor to the primary reactor rather than in the primary reactor is eliminated.

The inert carrier or support for the catalytic lead sulfide is an inert material such as ceramic Raschig rings, quartz particles, pumice, etc. preferably having a minimum surface area of 200 square feet per cubic foot of inert support.

The life of the catalyst is to some extent dependent upon the velocity of the oil through the bed of catalytic lead sulfide supported on the inert carrier. That is to say, it has been found that generally better catalyst life, i.e., less displacement of the catalytic coating of the inert carrier occurs, when the velocity of the oil through the actual void areas within the catalyst bed does not exceed about 2 feet per minute. However, velocities up to about 5 feet per minute through the actual void in the catalyst bed can be used.

In view of the kinetics of the reactions involved it has not been possible to date to determine with absolute surety the particular form in which the lead exists in each step in the process. Basically this is unimportant. However, it is necessary to emphasize that the use of the designation, lead sulfide, is not exclusive of other compounds of lead which may be present at various points in the system. It would appear that lead oxide reacts almost instantaneously after it is formed since none is visible when the process is carried out in glass equipment. It is even possible that the complex reactions involved result in the conversion of the mercaptans of the petroleum fraction to sulfides without the actual formation of lead oxide. Accordingly, it is believed that no appreciable amount of lead oxide is in the treating or primary reactor and that the designation, lead sulfide, is a more accurate descriptive term to use in discussing or designating the form in which the lead is present in the system.

Whether the elemental sulfur be admixed with the sour distillate caustic, air, and small amounts of water prior to introduction into the secondary reactor or prior to introduction into the primary reactor, the oil, caustic, and air is passed through the secondary reactor until the support material in the primary bed is coated with lead sulfide equivalent to about 0.10 to about 1.00, preferably about 0.25 pound of lead per cubic foot (about 0.11 to about 1.10, preferably about 0.27 pound of lead oxide per cubic foot). Thereafter, the secondary bed is bypassed until the mercaptan content of the treated fuel exceeds the required level. On the other hand, the desired lead sulfide coating of the inert support material in the primary bed can be maintained and the required mercaptan content in the treated fuel produced by continuously passing a slip stream of the sour oil and the reagents, caustic, and air, or caustic, sulfur and air through the secondary bed and then into the primary bed.

The following run is exemplary of the preparation in situ of a catalytic bed for the conversion of the mercaptan of a sour hydrocarbon fraction to sulfide. A suitable container is filled with inert support for the lead sulfide catalyst. A suitable inert support is any inert material such as sawdust, pumice, glass, ceramic material, and the like, preferably having a surface area of at least 200 square feet per cubic foot of inert support material.

A lead sulfide coating was deposited on the inert carrier in the primary reactor by passing sour kerosine, caustic, and air through the secondary reactor at the rate of 10,000 barrels of kerosine per day per 4 tons of metallic lead and passing the effluent of the secondary reactor through the primary reactor after injecting elemental sulfur into the effluent of the secondary reactor at a point intermediate the secondary reactor and the primary reactor. A lead sulfide coating also was deposited on the carrier in the primary reactor by passing sour kerosine, caustic, elemental sulfur, and air through the secondary reactor at the rate of 10,000 barrels of oil per day per 4 tons of metallic lead, and passing the effluent of the secondary reactor through the primary reactor. Thereafter, the bed of metallic lead was by-passed and the sour oil was contacted with lead sulfide on Raschig rings at a space velocity of about 8 v./hr./v. 35,000 barrels of sour kerosine were treated by contact only with the lead sulfide catalyst. Conditions for the foregoing for a 10,000 barrel a day unit are as follows:

	Broad	Preferred
100% NaOH, lbs./bbl./0.01 RSH(S)	0.002 to 0.032	.008
Strength of NaOH solution, °Bé	5 to 50	20
Air, cu.ft./bbl./0.01 RSH(S)	0.20 to 0.70	0.50
Elemental Sulfur, lbs./bbl./0.01 RSH(S)	0.014 to 0.028	0.021
Auxiliary lead or lead oxide as lead, tons	0.5 to 24	4
Reactor charge, pounds of lead sulfide calculated as lead/cubic foot of packing	0.1 to 1.0	0.25
Temperature, °F	80 to 200	135

RSH(S) = mercaptan sulfur, weight percent.
Oil circulation rate = 417 bbls./hr., i.e., 10,000 bbls./D.

Accordingly, a sour kerosine containing 0.040 percent by weight mercaptan sulfur [RSH(S)] was pumped from a source not shown through conduit **1** at the rate of about 417 barrels per hour. Caustic soda (20° Bé.) was pumped from a source not shown through pipe **2** into conduit **1** at the rate of 0.0005 barrel of 20° Bé. caustic per barrel of sour kerosine. Air was pumped through conduit **3** into conduit **1** at the rate of about 2.0 cubic feet per barrel of sour kerosine. With valve **4** closed and valve **5** open, the mixture of kerosine, caustic, and air flowed through conduit **1** to conduit **6** and thence to tower **7** containing metallic lead. The reaction mixture, i.e., mixture of kerosine, caustic, and air, flowed downwardly over the metallic lead converting a portion (about 0.055 pound lead per barrel of kerosine containing 0.04 percent by weight mercaptan sulfur) to lead sulfide or mercaptide which was suspended in the mixture. From tower **7** the reaction mixture flowed through conduit **8** to conduit **9** and thence to the bottom of tower **10**. At a point in conduit **9** intermediate to tower **10** and to the junction of conduits **8** and **9** elemental sulfur was injected into the mixture. About 35 pounds per hour of elemental sulfur suspended in treated kerosine was pumped from a source not shown through pipe **11** into conduit **9** at the rate of about 0.084 pound of sulfur per barrel of said sour kerosine. The lead sulfide was deposited in part on the packing in tower **10**. The reaction mixture flows upwardly through tower **10** to conduit **12** and thence to tower **13** likewise filled with inert packing (Raschig rings). The reaction mixture flows upwardly through tower **13**. During passage over the packing in tower **13** the balance of the lead sulfide is deposited on the inert packing.

After the passage of about 10,000 barrels of the aforesaid sour kerosine through the auxiliary bed of metallic lead or lead oxide in secondary tower **7** to provide an amount of lead sulfide equivalent to about 0.1 to about 1.0, preferably about 0.25 pound of lead per cubic foot of support in primary towers **10** and **13**, the flow of sour kerosine through tower **7** is cut off by closing valve **5** and opening valve **4**. It is to be noted that during the first stage of the cycle the mercaptan content of the kerosine flowing from tower **13** had been reduced to the required target level of 0.0004 p.p.m. (by weight).

After the passage of about 10,000 to about 20,000 barrels of sour kerosine containing 0.04 percent by weight of mercaptan sulfur through tower **7**, the flow of reaction mixture is cut off and the reaction mixture flows directly via conduit **9** to tower **10** and, sulfur being injected as described hereinbefore, thence to tower **13**. From tower **13** the treated kerosine in both stages of the cycle is mixed with water, introduced through pipe **18**, and flows through conduit **14** to settler **15**.

In settler **15** the treated kerosine separates from any water. The finished kerosine flows from setler **15** through pipe **16** to storage. The water separated from the treated kerosine in settler **15** flows through pipe **17** to waste.

When replacement of displaced lead is to be carried out contemporaneously with the reduction of the mercaptan content of sour oil containing about 0.04 wt. percent mercaptan sulfur content, valves **4** and **5** are set to divert about 2 to about 4 percent by volume of the reaction mixture through tower **7** while the balance flows directly through conduit **9** to tower **10**. Thus, for a unit treating 10,000 barrels of oil per day (417 barrels/hour) about 2 to about 4 barrels of oil per hour per 0.01 percent by weight of mercaptan sulfur are diverted through conduit **6**, tower **7** and conduit **8** and returned to conduit **9**.

The combined portions of the reaction mixture flow through conduit **9**, sulfur at the rate of about 0.084 pound of sulfur per barrel of sour kerosine feed is injected as before, the mixture flows upwardly through tower **10**, thence through conduit **12** to tower **13** and upwardly through tower **13** to ocnduit **14**. In passage through towers **10** and **13** the suspended lead is deposited on the lead sulfide coated inert packing.

The mixture of treated oil, air and caustic solution, if any, is mixed with water and flows through conduit **14** to settler **15**. In settler **15** the treated oil is separated from any water. The finished treated oil, now having the target mercaptan content, flows from settler **15** through pipe **16** to storage. The separated water flows from settler **15** through pipe **17** to waste.

The phrase "target level" is used to designate the required mercaptan level of the treated petroleum fraction which is usually expressed as weight percent or p.p.m. (parts per million) by weight of mercaptan-sulfur [RSH(S)]. Thus, for example, the specification of some gasoline calls for 40 p.p.m. [RSH(S)] maximum. On the other hand, other specifications call for "doctor sweet" oil, i.e., about 3 to 6 p.p.m. [RSH(S)]. Furthermore, the mercaptan content of the treated oil can be as low as 1 p.p.m. RSH(S).

I claim:

1. In a process for the sweetening of sour hydrocarbon fractions by conversion to polysulfides of mercaptans wherein a mixture of sour hydrocarbon fractions boiling below about 650° F. with caustic, oxidizing gas and sulfur is contacted with a supported lead sulfide catalyst and wherein activity of said catalyst declines with continued operation; the improved method for maintaining activity of said catalyst while sustaining rate of feed of sour hydrocarbon fraction to the process, which improved method comprises admixing caustic and oxidizing gas with a sour hydrocarbon fraction, passing a minor portion of the resultant caustic, oxidizing gas, and hydrocarbon blend in contact with a solid source of lead selected from the group consisting of metallic lead and lead compounds which react in alkaline medium with mercaptans to form lead mercaptide, and passing the total quantity of said resultant lead-containing caustic and hydrocarbon blend, after having mixed said blend with elemental sulfur, in contact with said supported lead sulfide catalyst so as to deposit fresh lead sulfide catalyst on the catalyst support.

2. The improved method of claim 1 wherein said minor portion is a split stream from the major portion of the caustic and hydrocarbon blend, which major portion is mixed with said minor portion for combined contacting with said supported catalyst after said minor portion has been contacted with said solid source of lead.

3. The improved method of claim 1 wherein said minor portion is derived by diverting the total caustic and hydrocarbon blend for passage in contact with said solid source of lead during a minor period of time of operation of said process for the sweetening of a sour hydrocarbon fraction.

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