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DESULFURIZATION OF RESIDUAL CRUDES

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The present invention concerns an improved process for removing sulfur from petroleum fractions. The invention relates to an improved process for removing sulfur from hydrocarbon fractions containing sulfur compounds by contacting said fractions with manganese hydroxide or hydrous oxide at elevated temperatures to form the manganese sulfide. The sulfide settles in the treated hydrocarbon fractions, is separated, regenerated, and recycled to the process.

The problem of sulfur removal from petroleum fractions and crudes goes back to the inception of the petrolum industry. For most purposes, it is undesirable to have an appreciable amount of sulfur in any petroleum product. Gasoline should be relatively sulfur free to make it compatible with lead. Motor fuels containing sulfur and mercaptans are undesirable because of odor and gum formation characteristics. Sulfur is objectionable in fuel oils because upon combustion sulfur dioxide, a corrosive gas having an obnoxious odor, is formed. Metropolitan areas have been particularly conscious of air pollution problems caused by sulfur-containing fuels and, in certain instances, have restricted by law the amount of sulfur permissible in the fuel oils utilized in the locale.

Generally, sulfur appears in feedstocks in one of the following forms: mercaptans, hydrogen sulfides, sulfides, disulfides, and as part of complex ring compounds of which thiophene is a prototype. The mercaptans are more reactive and are generally found in the lower boiling fractions, e.g. gasoline, naphtha, kerosene, and light gas oil fractions. Well-known processes for sulfur removal from these lower boiling fractions have been suggested such as doctor sweetening (wherein mercaptans are converted to disulfides), caustic treating (where aqueous solutions of sodium hydroxide are used), solvent extraction, copper chloride treating, etc., all of which give a more or less satisfactory decrease in sulfur or inactivation of mercaptans by conversion into disulfides. When the process results in the formation of disulfides, the disulfides generally remain in the treated product and must be removed by another step if it is desired to obtain a sulfur-free product.

Sulfur removal from higher boiling fractions, however, has been a more difficult problem. Here, sulfur is present for the most part in the less reactive forms as sulfides, disulfides, and as part of the complex ring compounds of which thiophene is a prototype. Such sulfur compounds are not susceptible to conventional chemical treatment found satisfactory for the removal of mercaptans and hydrogen sulfide. Extraction processes employing sulfur selective solvents are usually unsatisfactory because the high boiling petroleum fractions contain such a high percentage of sulfur-containing molecules. For example, even if a residuum contains only 3 wt. percent sulfur, it is possible that substantially all of the molecules may contain sulfur. Thus, if such a residuum were extracted with a solvent selective to sulfur compounds, the bulk of the residuum would be extracted and lost.

Various reagents, such as manganese oxide, iron oxide, and iron hydroxide, as well as cadmium oxide, cadmium hydroxide and cobalt oxide, have been tried in aqueous solutions to desulfurize hydrocarbon streams. These reagents have been substantially ineffective in removing sulfur compounds from the higher boiling fractions.

In accordance with the present invention, manganese hydroxide and/or hydrous manganese oxide is contacted with a sulfur-containing hydrocarbon fraction at mildly elevated temperatures. The sulfur in the hydrocarbon compounds reacts with the metal hydroxide to form metal sulfides which settle from the treated hydrocarbon fraction. The settled sulfides and any unreacted hydroxides are removed from the treated fraction. The metal sulfides are separated and washed and can be regenerated in a number of ways.

The sulfides can be advantageously regenerated by oxidation to the corresponding sulfate which on contact in an aqueous solution with ammonia and air gives the corresponding ammonium sulfate and manganese hydroxide. It is preferable to maintain the hydroxides prepared in this manner in a moist condition to minimize or prevent their conversion to the oxide form before they are recycled to the process.

Many advantages accrue to the process of the present invention in using these particular reagents for carrying out the desulfurization step. Desulfurization can be carried out at temperatures of 500 to 750° F. and can be carried out at about atmospheric or moderately elevated pressure. The degree of desulfurization with these reagents under these mild conditions is sufficient to make the process both practical and economical. One of the primary advantages of using manganese hydroxide, however, is in that this particular reagent is substantially more easily regenerated than other reagents suggested for removing sulfur compounds from residual hydrocarbon fractions.

The desulfurization reagent used in accordance with the present invention is manganese hydroxide ($Mn(OH)_2$) and/or hydrous manganese oxides. The tri and tetra-hydroxides apparently cannot be isolated but hydrated tri- and tetra-valent oxides are readily produced and are especially valuable desulfurizing reagents. Of particular utility are hydrated manganic oxide, $MnO \cdot OH$ (or $Mn_2O_3 \cdot H_2O$), and hydrated MnO_2, $MnO(OH)_2$ (or $MnO_2 \cdot H_2O$), also sometimes referred to as manganous acid (H_2MnO_3). The reagent is used in finely-divided form and may be of an amorphous or crystalline structure. Since the manganous hydroxide tends to oxidize on exposure to air, even at relatively low temperatures, and form Mn_3O_4 or other oxides, it is preferable to store and transfer the regenerated hydroxide reagents as aqueous slurries or in moist powder form to prevent their loss of desulfurizing activity. A preferred form for the hydroxide is a collodial, unflocculated suspension. However, in practice some coagulation takes place during hydroxide preparation, e.g. regeneration. The reagent can be used as an aqueous suspension or the moist hydroxide can be dispersed in light hydrocarbon liquids. The hydroxide is insoluble in both water and petroleum hydrocarbon.

In accordance with the present invention, manganese hydroxide or hydrous manganese oxide is contacted with a sulfur-containing hydrocarbon fraction at temperatures of between about 500 and about 750° F. but below the cracking temperature of the feed. Sufficient pressure is used to maintain most of the hydrocarbon feed in the liquid phase. The sulfur compounds in the hydrocarbon fraction react with the metal hydroxide to form the corresponding metal sulfide. The thus formed metal sulfides settle from the oil and are separated from the oil. The hydroxide is contacted with the oil in a finely-divided form to render the hydroxide readily available for reaction with the sulfur present in the hydrocarbon fraction. The hydroxide is contacted with the hydrocarbon fraction to be treated at hydroxide-to-hydrocarbon weight ratio of 0.1/1. to 2.0/1. The contact between the hy-

droxide and the hydrocarbon fraction is sufficient to substantially reduce the sulfur content in the hydrocarbon fraction. The contacting can be carried out in a cocurrent, countercurrent, or batch technique. The treated hydrocarbon fraction is subsequently fed to a settling zone wherein the metal sulfides are settled and are separated therefrom.

The metal sulfides recovered from the treated oil can suitably be washed and regenerated to the corresponding metal hydroxide. A preferred technique for regenerating the metal sulfides is to air-oxidize the metal sulfides in an aqueous suspension to the metal sulfates and hydrolyze these sulfates with an aqueous ammonium solution to obtain the corresponding ammonium sulfate and metal hydroxide.

The process has particular application to the removal of sulfur from the heterocyclic sulfur ring compounds in heavy residual hydrocarbon fractions, which sulfur is not removable by conventional techniques, e.g. alkali metal caustic treating processes, which processes are suitable for removing H_2S and mercaptan compounds from the lighter gasoline fractions. The process, however, can also be used to remove sulfur from low-boiling hydrocarbons in the gasoline range and intermediate-boiling hydrocarbons in the kerosene and fuel oil range.

Several advantages accrue from carrying out the desulfurization process in accordance with the present invention. The sulfur content of high-boiling residua fractions can be substantially reduced at moderate temperatures and at atmospheric pressure (with higher boiling fractions) by using the manganese hydroxide reagents of the present invention. A distinct advantage of the present process is the ease with which the used manganese sulfide reagent from the desulfurization step can be regenerated to the hydroxides by conventional methods at reasonable temperatures.

A preferred hydrocarbon desulfurization reagent used in accordance with the present invention is manganese hydroxide. The hydroxide is preferably used in the finely-divided form. The hydroxide is preferably contacted with the hydrocarbon feed to be desulfurized as slurry or in colloidal form.

The desulfurization reaction is carried out at mildly elevated temperatures and preferably at about atmospheric pressure. At about atmospheric pressure, water is evaporated from the heated, moist hydroxide or aqueous slurry and the hydroxide may then or during the sulfur removal reaction decompose to release some additional water which is vaporized from the hydrocarbon being treated. Any hydrocarbon fraction containing H_2S, mercaptans, sulfides, or disulfides and/or sulfur ring compounds of which the sulfur atom is a member of the ring can be treated in accordance with the present invention. Therefore, these reagents can be used with light hydrocarbon feeds boiling in the range of 150 to 450° F.; middle distillates, 450° to 650° F.; heavy hydrocarbons, 650° to 900° F.; and residual fractions, 900 to 1200° F. plus. The reagents are particularly useful and are especially preferred to be used in treating residual hydrocarbon fractions containing constituents boiling above 900° F., preferably above 950° F. Particular advantage is obtained in using these reagents with the residual hydrocarbon fractions since the conventional desulfurization agents are not suitable for desulfurizing the heavy residual fractions. The residual fractions boiling above 900° F. will contain up to 2.5 to about 7.0 wt. percent sulfur based on feed. However, feed containing as little as 0.5 to 1 wt. percent sulfur based on feed can also be treated. Specific feeds that can be treated in accordance with the present invention are gasoline fractions, fuel oil fractions, Kuwait residuum fractions boiling above 900° F. and containing about 5.2 wt. percent sulfur, 400° F.+heavy Lake mix fractions containing 2.5 wt. percent sulfur, 700° F.+Kuwait residuum fractions containing 4.2 wt. percent sulfur, 650° F. heavy Lake residuum fractions containing 4.0 wt. percent sulfur, and the like. The desulfurization step can be carried out as a batch process, as continuous, cocurrent, and as a countercurrent process. Preferably, the process is carried out in a slurry mixture of the hydroxide and the feed to be desulfurized. The desulfurization step is carried out at temperatures below the cracking temperature of the hydrocarbon being treated. The desulfurization step can be carried out at temperatures of 500 to 750° F., more generally at 600 to 700° F., and preferably at temperatures of about 600 to 650° F. The hydrocarbon is mixed with the hydroxide at a ratio of 0.1 to 2.0 weight of hydroxide based on dry hydroxide to weight of hydrocarbon, more generally at 0.25 to 1.5 weight, and preferably at 0.50 to 1.0 weight. The weight of hydroxide used can be 1.0 to 3.0 multiples of the stoichiometric amount of manganese needed to remove all of the sulfur present. Contacting is carried out for a sufficient period to substantially reduce the sulfur content of the hydrocarbon being treated. Treating times of ¼ hour to 16 hours can be used, more generally ½ hour to 8 hours, and preferably holding times of 1 to 4 hours are used. The contacting can be carried out at atmospheric pressure up to pressures sufficient to maintain the hydrocarbon in the liquid phase but still allow excess water to vaporize from the hydroxide. However, the pressure at which the contacting is carried out is not particularly critical.

When contacting heavy viscous residual fractions, it may be desirable to add to the hydrocarbon to be treated light diluents such as C_4 to C_8 or a heavier hydrocarbon fraction. Other diluents such as light naphtha fractions boiling in the range of 150 to 450° F. can be used. These fractions are easily separated from the residual fractions by low-temperature distillation. The addition of light diluents substantially lowers the viscosity of the heavy residual fractions and brings about more efficient contact between the finely-divided hydroxides and the hydrocarbon fraction, thereby facilitating desulfurization of the hydrocarbon fraction being treated. The reactor should be provided with a suitable mixing means to obtain adequate contact between the hydroxide and feed.

In accordance with the preferred embodiment of the present invention, a feed such as a 950° F.+Kuwait residua feed having 5.2 wt. percent sulfur is countercurrently contacted with moist, amorphous manganese hydroxide. The hydroxide is dispersed throughout the feed by mechanical mixing with the residua. The hydroxide is added at a ratio of about 1.0 weight of hydroxide per weight of residuum based on dried manganese hydroxide. The temperature of the hydroxide and residuum is then gradually increased from the mixing temperature of about 200° F. to a temperature of about 650° F., at which temperature it is held for a period of about 2 to 4 hours whereby the sulfur concentration of residuum is decreased by about 45%. The sulfur compounds in the residuum react with the manganese hydroxide to form manganese sulfide which separates in finely-divided form. During the heating step from 200 to about 650° F., the moist manganese hydroxide is gradually dehydrated and the water vaporized from the residual fraction being treated leaving manganese hydroxide as the actual desulfurization agent. The reaction effluent containing unreacted hydroxide, manganese oxide, manganese sulfide, and desulfurized oil is fed to a settler wherein the manganese sulfide and unreacted manganese hydroxide and/or oxide settle from the residuum and are separated therefrom.

Settling can be enhanced by the addition, particularly with viscous feeds, of a light hydrocarbon diluent which lowers the viscosity of the oil and increases the settling rates of the manganese sulfide and of the unreacted manganese hydroxide. The separated manganese sulfide and manganese hydroxide can be withdrawn from the bottom of the reactor and/or the treated liquid can be withdrawn from the top of the reactor in a conventional

manner. Settling aids, such as electrical precipitators and baffle plates and centrifuges, etc., can be used to aid in the separation. The thus treated hydrocarbons are cooled to about ambient temperature and can be further treated to remove any residual amounts of hydroxides and/or sulfides if needed. The withdrawn manganese sulfide and manganese hydroxide are washed to remove residual hydrocarbons and are then treated to regenerate the manganese sulfide to manganese hydroxide.

The recovered hydrocarbon fraction is reduced in sulfur content from about 5.2 wt. percent to about 2.9 wt. percent based on feed. This treated hydrocarbon could be subjected to a second desulfurization step or it could be blended with hydrocarbon fractions containing substantially no sulfur to obtain a blended hydrocarbon fraction of less than about 2.5 wt. percent sulfur which is acceptable for most uses.

In an embodiment of the present invention, the manganese sulfide separated from the treated hydrocarbon is washed with a light hydrocarbon solvent stream, for example, light naphtha, steam stripped, and then dispersed in water. The suspended sulfides are oxidized by bubbling air through the water to obtain water-soluble manganese sulfate. This step can be carried out in an autoclave at temperatures of 200 to 300° F. and at pressures of 100 to 200 p.s.i.g. The oxidation step is carried out for a period of 1 to 2 hours. The solution of manganese sulfate obtained is then cooled and contacted with an aqueous solution of ammonia and air is bubbled through the aqueous solution, and the manganese sulfate is hydrolyzed to manganese hydroxide. In this manner a fluffy metal hydroxide reagent containing occluded water is produced. The metal hydroxide slurry may be uncoagulated and partly colloidal in form. This hydroxide produced is separated from the ammonia solution, water washed to remove residual ammonia and/or ammonium sulfate, and it is then recycled to the process and contacted with the hydrocarbon feed at the prescribed dosage rate at a temperature of about 100 to 200° F. The manganese hydroxide is dispersed throughout the oil by mixing the moist hydroxide in the oil.

Another technique for removing the ammonium sulfate from the regenerated hydroxide is to mix the aqueous ammonia solution containing the manganese hydroxide and ammonium sulfate directly with the residuum feed to be treated. The hydroxide is colloidally dispersed in the residuum and the residuum retains the hydroxide, whereas the aqueous solution of ammonium sulfate separates into an aqueous phase and can be easily withdrawn from the oil. After separation of the aqueous solution of ammonium sulfate, the residuum containing the dispersed manganese hydroxide is gradually heated to the treating temperature as heretofore stated. Water can be removed from the decanted aqueous ammonium sulfate solution and the recovered ammonium sulfate can then be heated to a temperature of about 535° F. or above, at which temperature the ammonium sulfate decomposes and gaseous ammonia is recovered and can be recycled to the regeneration process.

Another technique for regeneration of the manganese sulfide is to mix the manganese sulfide with manganic chloride at elevated temperatures and pressures to obtain manganous chloride and free sulfur, separating the manganous chloride from the free sulfur, and hydrolyzing it in the presence of water and oxygen to obtain manganese hydroxide and manganic chloride. Manganese hydroxide is separated from the manganic chloride and recycled to the desulfurization process.

This technique for regenerating the manganese sulfide is illustrated by the following reactions:

(1) $MnCl_2+H_2O+O_2 \rightarrow MnO\cdot OH+MnCl_3$

(2) $MnO\cdot OH+S(\text{desulfurization}) \rightarrow MnS$

(3) $MnS+MnCl_3 \rightarrow MnCl_2+S$

The $MnCl_3$ formed in (3) is separated from the sulfur and reconverted as in (1).

Other means of converting sulfide to manganese hydroxide are known in the art.

The following examples are given to illustrate the preferred embodiments of the present invention.

Example 1

In order to show the effectiveness of the present manganese hydroxide reagent for desulfurization of a residuum fraction, the following tests were carried out. These tests also compare manganese hydroxide with other reagents, such as manganese oxide, iron hydroxide, and iron oxide. The hydrocarbon feed used consisted of a 950° F.+Kuwait residuum which contained 5.2 wt. percent sulfur. The desulfurization step was carried out at temperatures of 600 to 650° F. for periods of contact of 2 to 4 hours. The contacting was carried out at atmospheric pressure. The hydroxide was added in the form of moist hydroxide. In carrying out the process, the prescribed amount of reagent (dry weight of hydroxide) based on weight of oil was admixed in a slurry and heated for the indicated amount of time at the indicated temperature. The results of the tests are indicated below in Table I.

TABLE I.—DESULFURIZATION OF RESIDUA WITH MANGANESE HYDROXIDE

Reagent	Wt. Percent Reagent on Oil	Temp., °F.	Time, Hrs.	Percent Sulfur Removed
$Mn(OH)_2$	121	600	4	32
$Mn(OH)_2$	120	650	2	45
$MnO\cdot OH$	120	600	4	55
Mn_3O_4	82	650	2	19
$Fe(OH)_3$	64	600	4	7
Fe_2O_3	100	600	4	9

The above data clearly show that manganese hydroxide and hydrated manganic oxide are unexpectedly superior metal desulfurization agents and that they may be used to effectively desulfurize the heavy residuum fraction. The above data also show that manganese oxide, iron hydroxide, and iron oxide are relatively inefficient desulfurization agents.

In carrying out the above desulfurization step, the manganese sulfides are settled from the treated oil, are separated from the treated oil, and are regenerated in accordance with one of the above-described techniques. A residuum of decreased sulfur concentration is recovered.

Example 2

To further illustrate the unique properties of manganese hydroxide, several additional tests were carried out wherein other metals, such as iron, copper, barium, calcium, strontium, and hydroxides and/or their oxides, were used in the same manner as the manganese hydroxide of the present invention to carry out a desulfurization process. In this example, a 950° F.+Kuwait residuum containing 5.2 wt. percent sulfur was treated for 2 to 4 hours at temperatures of 600 to 700° F. In each case the hydroxide or oxide was added as finely-divided material to the hydrocarbon to be treated to form a slurry of the hydrocarbon and the hydroxide or oxide reagent. After the period of time indicated for the treatment, the metal sulfide and unreacted hydroxide or oxide were separated from the hydrocarbon, and the amount of sulfur removed was determined. In each case the moist hydroxide reagent was added to the oil being treated. The oxides were added as finely-divided material.

TABLE II.—DESULFURIZATION OF 950° F.+KUWAIT RESIDUUM WITH MANGANESE AND OTHER METAL COMPOUNDS

Reagent	Wt. Percent Reagent on Oil	Metal Equiv. on Oil	Temp., ° F.	Time, hrs.	Percent Sulfur Removed
$Mn(OH)_2$	121	8	600	4	32
$Mn(OH)_2$	120	8	650	2	45
$Mn(OH)_2$	82	7	650	2	19
Mn_3O_4	64	4	600	4	7
$Fe(OH)_2$	100	8	600	4	9
Fe_2O_3	100	6	600	4	[1] 38
$Cu(OH)_2$	100	3	700	3	11
$Ba(OH)_2$	38	3	600	4	<5
$Ca(OH)_2$	100	10	600	4	12
CaO	70	3	600–700	4	8

[1] Excessive coke formation.

The above data clearly show the unique desulfurization properties of manganese hydroxide in desulfurizing a heavy residuum fraction. The manganese hydroxide is far superior to the other metal oxides and hydroxides. The copper hydroxide, though efficient in desulfurization, resulted in the formation of excessive coke which makes for a substantial loss of the product. The barium and calcium hydroxides, as well as strontium hydroxide, are relatively inefficient in removing sulfur from the residuum fraction.

Applicants have unexpectedly found that the manganese hydroxide and hydrous manganese oxides of the present invention are uniquely suitable for removing sulfur from sulfur compounds in residuum fractions. These sulfur compounds are more difficult to remove than mercaptans, hydrogen sulfides, sulfides, or disulfides from the lighter fractions. Though the examples specifically illustrate removal of sulfur from heavy fractions and though manganese has particular advantages in removing sulfur from heavy fractions, the same reagent can also be used to remove sulfur from lighter fractions.

The invention is not to be limited by any theory regarding its operation nor is it to be limited by the specific examples herein presented nor the specific embodiments herein described. The scope of the invention is to be determined by the appended claims.

What is claimed is:

1. The process for removing sulfur impurities from a hydrocarbon fraction containing from 0.5 to 7.0 wt. percent sulfur which comprises contacting said fraction in the liquid phase at a temperature of 500–700° F. with a reagent consisting essentially of manganese hydroxide and recovering a fraction of substantially reduced sulfur content.

2. The process of claim 1 wherein the hydroxide reagent is contacted with said hydrocarbon at a hydroxide-to-hydrocarbon weight ratio of 0.1/1. to 2.0/1.

3. The process of claim 1 wherein said hydroxide comprises $Mn(OH)_2$.

4. A process for removing sulfur impurities from a hydrocarbon stream containing constituents boiling above about 950° F. which comprises mixing said hydrocarbon stream in a liquid phase at about atmospheric pressure with a reagent consisting essentially of manganese hydroxide at a temperature of 100 to 300° F., gradually increasing the temperature of the mixture to about 600 to 700° F., maintaining said latter temperature until the sulfur concentration of said stream is substantially reduced by conversion of the manganese hydroxide to manganese sulfide and subsequently separating the manganese sulfide from said stream.

5. The process for removing sulfur impurities from a hydrocarbon stream consisting essentially of the steps of contacting said hydrocarbon stream in the liquid phase with a hydrated manganese oxide reagent, said contacting being carried out in a liquid phase at a temperature of 600 to 800° F. and wherein the weight ratio of said hydrated oxide reagent to said hydrocarbon is 0.1/1. to 2.0/1.

6. The process of claim 5 wherein said hydrated oxide comprises $MnO \cdot OH$.

7. The process of claim 5 wherein said hydrated oxide comprises $MnO(OH)_2$.

8. A process for removing sulfur impurities from a hydrocarbon stream containing constituents boiling above about 950° F. consisting essentially of the steps of mixing said hydrocarbon stream in a liquid phase at about atmospheric pressure with a reagent consisting essentially of hydrated tri or tetra-valent manganese oxide at a temperature of 100 to 300° F., gradually increasing the temperature of the mixture to about 600 to 700° F., maintaining said latter temperature until the sulfur concentration of said stream is substantially reduced by conversion of the hydrated manganese oxide to manganese sulfide and subsequently separating the manganese sulfide from said stream.

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