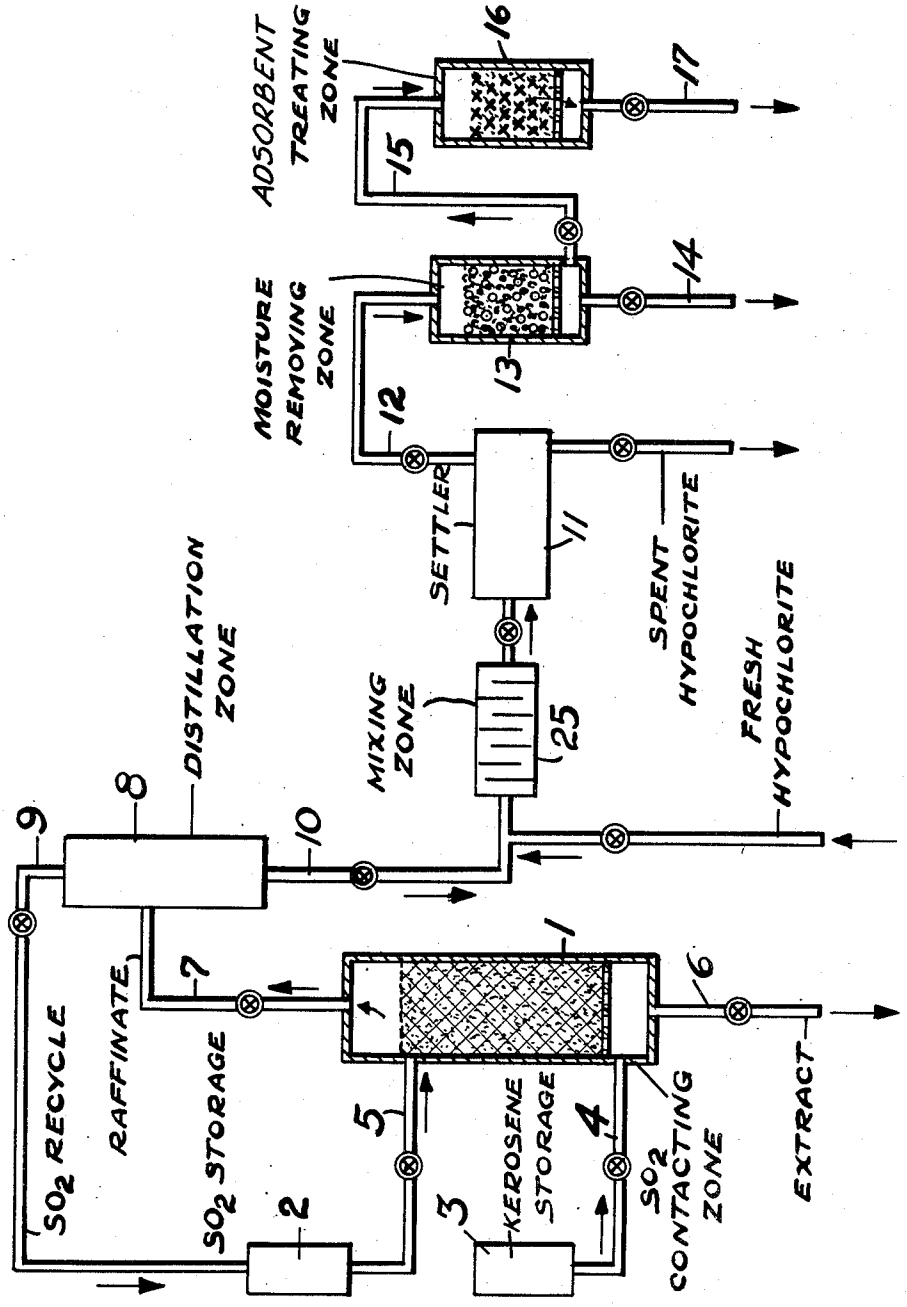
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KEROSENE FINISHING PROCESS

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## KEROSENE FINISHING PROCESS

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1

This invention relates to a process adapted for providing superior quality kerosene. The process of this invention is of application to the finishing of kerosenes so as to improve their tendency to form wick char on burning and so as to improve their color characteristics. To attain these objectives in accordance with this invention, kerosenes are subjected to a first stage treatment with sulfur dioxide and a second stage treatment with a solid adsorbent.

At the present time a great deal of the kerosene produced is utilized in a variety of appliances equipped with a wick. Thus, even at the present, a considerable quantity of kerosene is used for lighting and for heating purposes. Many kerosenes as obtained from the conventional refining of petroleum oils tend to deposit hard, carbonaceous material on the wick during burning. This material tends to clog the pores of the wick and consequently to reduce the size of the flame; concomitantly the light and heat output of the flame are reduced. In addition this carbonaceous material tends to cause smoking. Consequently, an important characteristic of kerosene is a low char forming tendency, so that the indicated difficulties may be minimized. It is the particular object of this invention to provide a kerosene refining process yielding kerosenes having substantially reduced tendencies towards forming wick char.

At the same time it is the broader object of this invention to provide a kerosene finishing process which will similarly improve other characteristics of kerosene. For example, the process of this invention is also adapted to reduce the sulfur content of the kerosene, to increase the smoke point of the kerosene and to improve the color of the kerosene. In connection with these characteristics, the process of this invention is particularly efficacious in improving the color of kerosene.

The kerosenes to which this invention has application are clearly those kerosenes which are not of suitable characteristics as obtained by the conventional refining of crude oils. For example, the Middle East crude oils are of such a nature that the kerosenes obtained by fractionation of these crudes are not of desirable characteristics, particularly with regard to wick charring tendency, sulfur content, and color characteristics. While the particular constituents of these crude oils, which result in the production of unsatisfactory kerosenes, cannot be successfully identified, it is believed that a correlation exists between the sulfur content of the crude oil, and the quality of the kerosene obtained therefrom.

2

Thus typical Middle East crude oils from which, as indicated, high quality kerosene can not readily be obtained, have sulfur contents of 1.4%, or greater. It is, therefore, contemplated that the invention is of particular application to kerosenes obtained by the fractionation of crude oil having a sulfur content above about 1.4%, and particularly to the Middle East crude oils.

Alternatively, the feed stocks to be subjected to the process of this invention may be defined as kerosenes having undesirable wick char, and color characteristics. Thus at the present time it is generally considered that to be of competitive quality in wick char critical marketing areas kerosene should have a wick char value of 10 or less, as determined by the test method 10–44 of the Institute of Petroleum. In this test a sample of the kerosene is burned in a standardized type of lamp, under specified conditions. The char is then recovered from the wick, measured quantitatively, and the result expressed as milligrams of char per kilogram of oil burned. Consequently, it may be stated that the process of this invention is applicable to the treatment of kerosenes having a wick char value of 10, or higher.

While attempts have been made to determine which constituents of kerosene result in a high char value, these attempts have not been successful. At the present time the constituents which result in a high char value have not been successfully identified. In this connection it has been determined that the inorganic content of the kerosene is apparently not a factor, as a series of kerosenes having substantially the same ash content can have widely varying wick char values. Data of this nature clearly shows a lack of any consistency between the amount of ash, or inorganic material and the char forming tendency. Similarly by considering the effect of blending a wide variety of compounds in kerosene as regards their effect on the wick char value of the kerosene, no definite conclusions could be formed. Aromatic compounds vary widely in their tendency to form char without any apparent correlation between char formation and aromatic structure. Olefinic compounds again appear to have some undesirable influence on char formation, while sulfur and nitrogen compounds also appear to be at least in part causative of wick charring. In any case, the reason for wick charring has not been sufficiently identified to permit application of any of the conventional methods for removing particular constituents from the kerosene, or to enable the prediction of the effect of a particular process on the wick char value of a kerosene.

However, in accordance with this invention it has been discovered that the properties of a kerosene, and particularly the wick char characteristics of the kerosene may be markedly improved by a two step treatment, involving a first stage treatment with sulfur dioxide followed by a second stage treatment with a solid adsorbent. In general the conventional methods of sulfur dioxide treatment, and solid adsorbent treatment may be adapted to this process. Thus, any suitable means of contacting the kerosene to be treated with sulfur dioxide and subsequently with a suitable solid adsorbent may be used.

As indicated, the treatment of kerosenes with sulfur dioxide in the first step of the process of this invention may be conducted according to conventional sulfur dioxide treating techniques. It is preferred, however, that the sulfur dioxide treatment be carried out by a liquid phase contacting of the kerosene in a counter-current type of extraction tower. In such a process, liquid sulfur dioxide may be charged to the top of a treating zone, while the kerosene to be treated may be introduced to the bottom of the treating zone. The sulfur dioxide will then drop downwardly through the less dense kerosene which will move upwardly through the sulfur dioxide. Unpacked towers may be used as the contacting environment, or packing of a wide variety of types can be employed, or perforated plates can be utilized. The conditions of temperature and pressure under which the sulfur dioxide contacting is carried out are generally about −40 to +25° F. and 0 to 100 p. s. i. While the ratio of the sulfur dioxide to oil is clearly a function of the extent of kerosene improvement desired, it is preferred that treats of about 25% to 100% be used. The kerosene rich phase separating after treatment with the sulfur dioxide, called the raffinate, may then be subjected to treatment with a solid adsorbent to secure the finished kerosene.

Suitable solid adsorbents which may be used are bauxite, silica gel, charcoal, iron oxide or adsorbent clay. However, it is preferred that adsorbent clay, such as fuller's earth, or bauxite be used as the solid adsorbent in the process of this invention, as materially better results are obtained by using either of these two specific solid adsorbents. Again, any suitable method for contacting the solid adsorbent with the kerosene may be used. One of the simplest manners of conduting this operation is to contain the adsorbent in granular form as a bed in a suitable vessel through which the kerosene to be treated may be passed. Alternatively, if desired, the solid adsorbent in finely divided form may be mixed as a slurry with the kerosene. In general it is suitable to utilize ambient temperature and atmospheric pressures for the treatment, although elevated temperatures and pressures may be used if desired or convenient due to process conditions encountered. While the quantity of adsorbent used to treat the kerosene is determined largely by the improvement desired, it is preferred to utilize a quantity of about 0.1 to 4 lbs. absorbent per barrel of oil and preferably about one pound of adsorbent per barrel of oil treated, at feed rates of about 0.25 to 4 volumes of oil per volume of adsorbent per hour. While no part of this invention, the adsorbent used may be regenerated for continued use in the process by steaming, drying, and roasting, or by washing with quantities of a wide variety of



washing agents as in conventional adsorbent regeneration systems.

While, as heretofore described the process of this invention comprises the combination treatment of the kerosene with sulfur dioxide followed by treatment with a solid adsorbent, it is apparent that many modifications of this process may be made. Thus, for example, in the case of extremely high sulfur kerosenes it may be desirable to subject the kerosene to additional treating steps to further reduce the sulfur content. For example, acid treating, hypochlorite sweetening, or Doctor sweetening, as these processes are identified in the petroleum industry, may be utilized, in addition to the particular processing steps of this invention. In the preferred embodiment of this invention, after the kerosene has been treated with sulfur dioxide it is subjected to a process for conversion or removal of mercaptans to improve odor, and thereafter the kerosene is treated with a solid adsorbent. Again, minor alterations of the process may be made involving for example particular washing techniques for the kerosene. In this connection it is generally preferred that the raffinate obtained from the sulfur dioxide treatment be subjected to a water wash followed by a caustic wash, and followed by a second water wash, although other washing techniques may be used if desired. Apparently, the particular technique used for washing the kerosene during, or after the processing steps of this invention does not materially affect the wick char value of the kerosene. As an operating expedient, the kerosene should be free of moisture prior to contacting the adsorbent material.

The process of this invention may be understood by reference to the accompanying drawing indicating a diagrammatic flow plan of one embodiment of this invention. Referring to this drawing, the numeral 1 designates a treating zone in which kerosene may be contacted with sulfur dioxide. Zone 1 may consist of a counter-current liquid-liquid extraction tower as illustrated in the drawing. In this case liquid sulfur dioxide will be withdrawn from a reservoir 2 and will be introduced near the top of tower 1, while kerosene may be removed from reservoir 3 for introduction near the bottom of zone 1. In the embodiment illustrated in the drawing, extraction tower 1 is shown as containing a packing material such as Raschig rings, or similar packing. This packing ordinarily does not extend completely to the top or bottom of the tower, as free space is maintained near the top and bottom of the tower for phase separation. In the operation of an extraction tower, such as that illustrated, the oil introduced through line 4 flows upwardly through the tower counter-currently to a flow of sulfur dioxide introduced at the top of the tower through line 5. The material reaching the top of the tower is permitted to separate into two phases in the portion of the tower above line 5, to yield a raffinate phase consisting substantially of kerosene. Similarly, the material at the bottom of the tower is permitted to settle in the free area of the tower below line 4 to yield a lowermost phase consisting principally of sulfur dioxide and identified as the extract phase. The extract phase may be withdrawn from the bottom of zone 1 through line 6 for disposal as desired. Generally, the extract phase is subjected to distillation to permit recovery of sulfur dioxide which may be recycled into the process. The extract product obtained

from this distillation is rich in aromatics and sulfur compounds and may be profitably used after desulfurization as a superior blending agent for tractor fuel. Similarly, the raffinate phase obtained through line 7 at the top of tower 1 may be conducted to a distillation zone 8 operated so as to remove sulfur dioxide overhead through line 9 for recycle after liquefaction and cooling to zone 2. The treated kerosene, or the raffinate product is then withdrawn as a bottoms product from still 8 through line 10. While an optional feature of the process of this invention, as applied to many kerosenes it is preferred that the raffinate product of line 10 be subjected to a hypochlorite treatment in zone 11 in the event that the kerosene being treated contains noxious odored mercaptans. Thus, if the kerosene raffinate contains over about 1 mg. of mercaptan sulfur per 100 ml., it is preferred that the raffinate product of line 10 be subjected to hypochlorite sweetening in zone 11. Again, any of the conventional methods of conducting the hypochlorite treatment may be used. It is presently contemplated that a preferential treatment may be obtained by treating the raffinate product of line 10 in zone 11 with about 1–10 volume percent of hypochlorite solution containing about 2–30 grams per liter of sodium hypochlorite, and more than about two grams per liter of free caustic. As diagrammatically illustrated in the drawing, the kerosene may be hypochlorite treated in a mixing and settling system comprising the orifice mixer 25 and settler 11. The hypochlorite sweetened kerosene may then be removed from the upper portion of zone 11 through line 12 for treatment with a moisture removing or coalescing agent such as sand, in vessel 13; coalesced water being withdrawn through line 14, and dried kerosene passing through line 15 to treatment with a solid adsorbent in zone 16. Zone 16 may consist of a tower, or vessel substantially filled with a solid adsorbent through which the kerosene is passed at flow rates of about 0.25 to 4 volumes of kerosene per volume of adsorbent per hour and at existing temperatures and pressures. As indicated, it is preferred that the adsorbent consist of either bauxite or fuller's earth. The finished kerosene is then obtained from the process through line 17 leading from the solid adsorbent treating zone.

The treatment of the kerosene by the two stage process disclosed will improve the wick char value of the kerosene, and will improve the color and other properties of the kerosene.

As examples of the effectiveness of the process of this invention, and to aid in a more thorough understanding of the invention, data will be given relative to the treating steps of the process.

## EXAMPLE I

A kerosene distillate boiling in the range of 300 to 525° F. as obtained from a Bradford crude oil had a wick char value of 20 mg./kg. In this example and all other examples the wick char value reported is that obtained by test method 10–44 of the Institute of Petroleum.

After subjecting this kerosene to treatment with fuller's earth at a temperature of about 80° F. atmospheric pressure and at a rate of 1.0 v./v./Hr., the kerosene had a wick char value of 19 mg./kg.

It will be noted from this example that substantially no improvement of the wick char value of the kerosene resulted from the solid adsorbent treatment. It is apparent that the kerosene could not be materially improved by the single step treatment of clay treating as indicated by this data.



## EXAMPLE II

A kerosene having a boiling range of 320 to 550° F. obtained from the distillation of mixed sweet crude oils and subjected to the Doctor sweetening process had a wick char value of 36 mg./kg. This feed stock was then filtered through Attapulgus clay or fuller's earth under identical conditions to those given under Example I. The kerosene was then found to have a wick char value of 33 mg./kg.

It will be noted from this example, as in the case of Example I, that clay, or adsorbent treatment alone does not significantly improve the wick char characteristics of kerosene.

## EXAMPLE III

A kerosene having a boiling range of 355 to 518° F., obtained from the distillation of a Middle East Kuwait crude oil had a wick char value of 36. After treatment of this kerosene with 108% by volume of sulfur dioxide at 14° F. and 85 p. s. i. g. pressure in a counter-currently operated packed tower 10 ft. high and 2 in. in diameter, the wick char value was found to be 20. As indicated by this example, sulfur dioxide treatment alone is not suitable for reducing the wick char value to a value of less than 10.

## EXAMPLE 4

A kerosene having a boiling range of 357 to 512° F. obtained from an Iraq crude oil initially had a wick char value of 46. After treatment with fuller's earth, employing the conditions indicated in Example I, the wick char value was reduced to 32. This same kerosene when treated with 150% by volume of sulfur dioxide at 15° F., according to the conditions of Example III, had a wick char value of 25. However, when this kerosene was treated with sulfur dioxide, and subsequently treated with Attapulgus clay, according to the same treating conditions, it was found that the wick char value had been reduced to 6. Again, it will be noted from this example that while neither clay treatment alone, or sulfur dioxide treatment alone were suitable to reduce the wick char value to a low value, the combination treatment of sulfur dioxide extraction and adsorbent percolation was successful in producing a kerosene of low wick char value.

As further examples of the process of this invention, kerosenes obtained from a variety of Middle East crude oils were subjected to sulfur dioxide extraction and then treated with a variety of solid adsorbents. The inspections of the crude oils employed in these tests, and the kerosenes obtained from these crude oils, are given in Table I, below.

These kerosenes were then treated as indicated in Table II, wherein the operating conditions are given together with the inspections of both the feed and the raffinate product. Again, it will be noted from Table II, that the sulfur dioxide extraction, while resulting in some improvement of the kerosene characteristics did not lower the wick char value below 10.

The raffinate products identified in Table II, and obtained as indicated in Table II, were then subjected to treatment with a variety of solid adsorbents. The results of these tests are indicated in Table III below.

It will be observed from Table III, that the

adsorbent treatment following the initial sulfur dioxide treatment was successful in lowering the wick char value of the kerosene very materially. In the case of the fuller's earth, bauxite, char coal and iron oxide, it was possible to obtain wick char values below 10.

*Table I.—Inspections of Middle East crudes and kerosenes therefrom*

| Country<br>Producing Area | Iraq<br>Kirkuk | Kuwait.<br>Burghan. |
|---|---|---|
| Crude: | | |
| Gravity, °API | 36.1 | 32.7. |
| Sulfur, percent | 2.00 | 2.55. |
| Maximum Kerosene Fraction (300° F.-580° F.): | | |
| Yield, percent (Vol.) | 29.9 | 26.1. |
| Gravity, °API | 44.3 | 44.3. |
| Sulfur, percent | 0.42 | 0.41. |
| Smoke Point, mm | 24 | 25. |

*Table II*

| Feed Stock | Kuwait Kerosene | | Iraq Kerosene | |
|---|---|---|---|---|
| Operation Conditions: | | | | |
| Percent $SO_2$ Treat [1] | | 108 | | 106 |
| Extraction Temp., °F | | +13 | | +14 |
| Raffinate Yield, Percent | | 79 | | 80 |
| Raffinate Inspections | (Feed) | | (Feed) | |
| Gravity, °API | 44.7 | 49.7 | 44.5 | 49.1 |
| Sulfur, Wt. percent | 0.33 | 0.02 | 0.34 | 0.02 |
| Smoke point, mm | 23 | 44 | 24 | 42 |
| Wick Char, Mg./Kg. | 36 | 19 | 46 | 20 |
| Color (Saybolt) | +21 | +13 | +18 | +4 |

[1] Treating carried out in counter-current packed tower GS in Example III.

*Table III.—Reduction of wick char by adsorbent percolation at room temp.*

[Feed stocks represent raffinates from 100% counter-current $SO_2$ extraction of respective crude.]

| Sample | Sample Period | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Kuwait thru Fuller's earth:[1] | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 215 | 434 | 655 | 870 | 1,092 |
| Wick Char | 16 | 7 | 4 | 5 | 6 | 7 |
| Saybolt Color | +13 | +30 | +30 | +30 | +30 | +30 |
| Iraq thru Fuller's earth:[1] | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 201 | 435 | 673 | 862 | 1,032 |
| Wick Char | 17 | 9 | 9 | 7 | 10 | 6 |
| Saybolt Color | +4 | +30 | +30 | +30 | +30 | +30 |
| Kuwait thru Bauxite:[1] | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 147 | 304 | 450 | 609 | 794 |
| Wick Char | 16 | 7 | 5 | 5 | 5 | 3 |
| Saybolt Color | +13 | +30 | +30 | +30 | +30 | +30 |
| Iraq thru Bauxite:[1] | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 150 | 303 | 464 | 616 | 766 |
| Wick Char | 17 | 6 | 3 | 9 | 5 | 8 |
| Saybolt Color | +4 | +30 | +30 | +30 | +30 | +30 |
| Kuwait thru Silica Gel (20/40 mesh): | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 304 | 571 | 827 | 1,092 | ------ |
| Wick Char | 16 | 11 | 11 | 15 | 9 | ------ |
| Saybolt Color | +13 | +18 | +13 | +13 | +12 | ------ |
| Kuwait thru Charcoal (10/20 mesh): | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 407 | 842 | 1,174 | 1,476 | ------ |
| Wick Char | 16 | 7 | 9 | 13 | 10 | ------ |
| Saybolt Color | +13 | +30 | +28 | +24 | +23 | ------ |
| Kuwait thru Iron Oxide (10/20 mesh): | | | | | | |
| Yield at end of period, B/T | 0 (Feed) | 261 | 525 | 791 | ------ | ------ |
| Wick Char | 16 | 9 | 6 | 7 | ------ | ------ |
| Saybolt Color | +13 | +30 | +30 | +25 | ------ | ------ |

[1] 30/60 mesh fresh clay or bauxite used in all cases; dehydrated at 800° F. for one hour prior to usage.

What is claimed is:

1. The process for providing a kerosene of satisfactory burning quality derived from a Middle East crude oil having a sulfur content of 1.4% or greater, comprising the steps of contacting said kerosene in liquid phase with about 25% to 100% by volume of sulfur dioxide at a temperature of about −40 to +25° F., and a pressure of about 0 to 100 p. s. i. to obtain a raffinate product characterized by a wick char value greater than about 10, and thereafter contacting the said raffinate product with about 0.1 to 4 pounds of a solid adsorbent per barrel of oil.



2. The process for producing kerosene comprising the steps of fractionating a Middle East crude oil containing more than about 1.4% sulfur and segregating a kerosene fraction boiling in the range of about 300° to 580° F., contacting said kerosene fraction in liquid phase with about 25% to 100% by volume of sulfur dioxide at a temperature of about −40 to +25° F., and a pressure of about 0 to 100 p. s. i. to obtain a raffinate product, characterized by a wick char value greater than about 10, and thereafter contacting the said raffinate product in liquid phase with about 0.1 to 4 pounds of adsorbent clay per barrel of oil.

3. The process of providing high quality kerosene in which a kerosene boiling in the range of about 300° to 580° F. derived from a Middle East crude oil having a sulfur content greater than about 1.4 is contacted with sulfur dioxide in liquid phase at a temperature of about −40 to +25° F., and a pressure of about 0 to 100 p. s. i. to obtain a raffinate product characterized by a wick char value above about 10, and a mercaptan content greater than about 1 mg. of mercaptan sulfur per 100 ml., contacting said raffinate product with about 1 to 10 volume percent of an alkali metal hypochlorite, and thereafter contacting the said treated raffinate product with about 0.1 to 4 pounds of a solid adsorbent per barrel of oil.

4. The process for providing a kerosene of satisfactory burning quality derived from a Middle East crude oil having a sulfur content of 1.4% or greater, comprising the steps of contacting said kerosene in liquid phase with about 25% to 100% by volume of sulfur dioxide at a temperature of about −40 to +25° F., and a pressure of about 0 to 100 p. s. i. to obtain a raffinate product characterized by a wick char value greater than about 10, and thereafter contacting the said

raffinate product with about one pound of a solid adsorbent per barrel of oil at ambient temperatures.

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