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METHOD OF REFINING KEROSENE WITH BAUXITE AND SULFUR DIOXIDE

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The present invention is concerned with an improved process for the production of high quality kerosenes. The invention is more particularly concerned with the production of kerosenes of low sulphur content, which kerosenes are derived from Near East crudes. In accordance with the present invention, kerosenes of relatively low sulphur content are produced by treating kerosene fractions in an initial stage with bauxite followed by contacting the kerosene fractions in a secondary stage with sulphur dioxide.

It is well known in the art to treat hydrocarbon fractions by various procedures in order to reduce and remove sulphur compounds. For example, it is known to treat hydrocarbon fractions boiling in the kerosene boiling range with sulphuric acid in order to remove objectionable sulphur constituents. It is also known to treat hydrocarbon fractions boiling in the kerosene boiling range with doctor solution in order to convert the sulphur compounds into relatively innocuous disulfides. While these processes have been satisfactory for rteating these fractions boiling in the kerosene range secured from domestic crudes, they have not been entirely satisfactory for treating kerosene fractions secured from crudes having a relatively high sulphur content, particularly from crudes from the Near East.

For example, crudes secured from the Near East, such as Kuwait, Iraq, Iran, and Arabia are of a particular nature, specifically with respect to the fraction boiling in the kerosene boiling range. These crudes have a relatively high sulphur content ranging from about 1% to as high as 7% by weight. On the other hand, the kerosene fractions boiling in the range from about 300° F. to 580° F. secured from domestic crudes generally have a sulphur content, not in excess of about 0.2%. Also, due to the difficulty and expense of reducing the sulphur in a kerosene derived from high sulphur domestic sources, the general practice is to produce kerosenes from relatively sweet crudes which kerosene fractions have sulphur contents of about .04%.

Kerosene fractions derived from Near East crudes have sulphur contents in the range of from .3% to .5%. Furthermore, the sulphur compounds are of two distinct varieties. These compounds seem to have alkyl mercaptans and thiophenic structures. In order to remove or reduce the concentration of the varied and complex sulphur constituents, various procedures have been attempted. Sulfuric acid is not entirely satisfactory for the removal of these complex sulphur compounds nor will a solvent treat reduce them to the desired extent when using limited commercially feasible amounts of solvent. The present process which comprises a vapor phase bauxite treatment, combined with an SO_2 extraction operation, functions satisfactorily to reduce the mercaptanic sulphur and to remove the thiophenic compounds.

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In accordance with the process of the present invention, high sulphur kerosenes derived from Near East crudes are treated with bauxite at a temperature ranging from about 600° to 850° F. and at a pressure ranging from about 0 to 50 pounds per square inch absolute. Operating conditions are generally selected so that substantially no cracking of constituents other than the sulphur compounds results. The treating agent employed is a bauxite, preferably a naturally occurring bauxite, which is preheated at a temperature within the range of about 600° F. to 1150° F. for a period sufficient to remove the water of hydration. In general, it is preferred when treating kerosene fractions of the type under consideration, to employ a temperature in the range from about 700° to 750° F. and to employ atmospheric pressure in the bauxite treating stage.

The bauxite-treated stream is then condensed and treated with liquid sulphur dioxide. The sulphur dioxide stage is operated preferably at a temperature in the range of from about + 20° to −40° F. The quantity of SO_2 employed may vary appreciably, but it is preferred to be within the range from about 35% to 120% by volume. Although batch treatment may be employed, it is preferred that the SO_2 treatment comprises a countercurrent operation.

The present invention may be more fully understood by the following examples illustrating the same:

Example I

A kerosene fraction boiling in the range from about 345° to 514° F. and derived from an Iraq crude was processed as follows:

The Iraq crude had a sulphur content of about 2.0% while the sulphur content of the kerosene fraction was 0.36%. The inspection of the kerosene feed fraction was as follows:

Sulphur, wt. per cent	0.363
Mercaptan sulphur, mg./100 ml	19
Doctor test [1]	DNP

[1] Federal Specification Test Method 520.31.

The kerosene described above in one operation was bauxite-treated at a temperature of about

750° F. and at a pressure of about atmospheric. The kerosene product of this operation had the following specifications:

Sulphur, wt. per cent	0.202
Mercaptan sulphur, mg./100 ml.	Nil
Doctor test	Pass

It is to be noted that the fraction passed the doctor test, but that the sulphur content was relatively high and unsatisfactory. In order to have a satisfactory kerosene product, it is essential that the sulphur content be below 0.05%.

Example II

The feed kerosene employed in Example I in another operation was treated with sulphur dioxide employing 80% by volume of sulphur dioxide treat. The results of this operation were as follows:

Yield, vol. per cent:	
Product	76
Extract	24
Raffinate inspections:	
Sulphur, wt. per cent	0.057
Mercaptan sulphur, mg./100 ml.	8
Doctor test	DNP

It is to be noted from the above data that the yield was relatively low, that the sulphur content of the kerosene was in excess of that considered satisfactory and that furthermore, the kerosene product did not pass the doctor test.

Example III

A kerosene similar to that employed in Example I was treated similarly as described with respect to Example II except that the quantity of sulphur dioxide employed was 120%. The results of this operation were as follows:

Yields, vol. per cent:	
Product	75
Extract	25
Raffinate inspections:	
Sulphur, wt. per cent	0.044
Mercaptan sulphur, mg./100 ml.	7
Doctor test	DNP

It is to be noted that the sulphur content of the kerosene was below .05% but that the finished product did not pass the doctor test. This failure to pass the doctor indicates the presence of mercaptan sulphur which is very undesirable in the finished product.

Example IV

A kerosene similar to that employed in Example I was treated as described with respect to Example II except that the quantity of sulphur dioxide employed was 50% by volume. The results of this operation were as follows:

Yield, vol. per cent:	
Raffinate	82
Extract	18
Raffinate inspections:	
Sulphur, wt. per cent	0.102
Mercaptan sulphur, mg./100 ml.	14
Doctor test	DNP

It is to be observed that although the yield was relatively high, the sulphur content was excessive and the product did not pass the doctor test.

Example V

A kerosene similar to that employed in Example I was acid treated with 20 lbs. per barrel using 98% sulfuric acid. The product was neutralized and rerun. The rerun product showed the following inspections:

Sulphur, wt. per cent	0.163
Mercaptan sulphur, mg./100 ml.	<1
Doctor test	DNP

It is evident that this operation did not produce a satisfactory kerosene.

Example VI

A kerosene similar to that utilized in Example I was treated in the vapor phase with bauxite at a temperature of 750° F. Atmospheric pressure was employed and the feed rate was 1/v./v./hr. The bauxite-treated kerosene was condensed and treated at a temperature of +14° F. with 50% by volume of sulphur dioxide. The results of this operation were as follows:

Yield, vol. per cent:	
Yield	83
Extract	17
Raffinate inspections:	
Sulphur, wt. per cent	0.043
Mercaptan sulphur, mg./100 ml.	Nil
Doctor test	Pass

It is to be noted that the sulphur content was below 0.5%, that the product passed the doctor test and that the yield was high.

As described heretofore, the present invention is adapted particularly for the treatment of hydrocarbon fractions boiling in the kerosene boiling range. It is especially suitable for treating kerosenes derived from crudes having a sulphur content in the range from 1–7% and wherein the sulphur content of the kerosene product is in the range from about .2 to .6% and higher and particularly when the sulphur content of the kerosene is in the range from .3 to .6%. The boiling range of the kerosene fractions is in the general range from about 300° F. to 600° F. and preferably in the range from about 350–500° F. The amount of sulphur dioxide employed in the second stage may vary appreciably, but it is preferred that approximately 40–60% of sulphur dioxide be employed per volume of kerosene, and that the temperature be in the range from about 0° F. to 20° F. However, if it is desired that the final product have a sulphur content below about .03% the amount of sulphur dioxide by volume employed will range from about 80–120%. The bauxite treatment in the initial stage is conducted at temperature and pressure conditions wherein practically no cracking of the kerosene hydrocarbons occur. It is preferred that the kerosene fraction be treated at a temperature in the range from 600–850° F. and preferably in the range from 700–750° F. It is also preferred that the pressure be about atmospheric although pressures up to about 50 lbs. may be used.

Having described the invention, it is claimed:

1. Process for the production of a kerosene of relatively low sulfur content which comprises treating in the vapor phase at a temperature between 600 and 850° F. and at a pressure between 0 and 50 lbs. per square inch a hydrocarbon fraction boiling in the kerosene boiling range in an initial stage with bauxite, withdrawing a bauxite-treated fraction, condensing the same, and contacting it in the liquid phase in a secondary stage with liquid sulfur dioxide and recovering a kerosene fraction of a relatively low sulfur content from said secondary stage.

2. Process for the production of a kerosene fraction boiling in the range between 300 and 600° F. from a crude oil containing in excess of about 1.0% sulfur which comprises segregating from said crude oil a kerosene fraction having a sulfur content above about .2%, passing said kerosene fraction at a temperature between 700 and 750° F. and atmospheric pressure over bauxite, then treating the bauxite-treated kerosene fraction in the liquid phase with liquid sulfur dioxide whereby a kerosene product having a sulfur content below 0.5% and which is substantially completely free from mercaptan sulfur is secured.

3. Process as defined by claim 2 wherein the sulphur content of the feed kerosene fraction is above about .3% and wherein said kerosene is contacted with from about 40–80% of sulphur dioxide by volume, and whereby a kerosene

product having a sulphur content below about .05% is secured.

4. A process as defined by claim 2 wherein said feed kerosene has a sulphur content above about .3%, wherein said kerosene fraction is treated with from about 80–120% by volume of sulphur dioxide and whereby a kerosene product having a sulphur content below about .03% is secured.

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