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PROCESS FOR DESULFURIZING PETROLEUM OILS

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1 Claim. (Cl. 196—28)

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The present invention relates to a process for the refining of petroleum oils. The invention is concerned with an improved process for reducing the sulfur content of petroleum oils having high percentages of sulfur compounds. The process of the present invention is particularly directed to the desulfurization of oils boiling in the kerosene range. In accordance with the present invention, petroleum oils are processed in a two-stage acid and bauxite treatment process, resulting in high yields of purified petroleum oils.

It is well known in the art to remove objectionable sulfur and related compounds from petroleum oils, and particularly from those petroleum oils boiling in the motor fuel boiling range, by treating the same with suitable mineral acids. The acid most generally used in conventional processes for this purpose is sulfuric acid. The acid-treating operation is usually conducted under conditions to secure a maximum removal of the objectionable sulfur compounds and a minimum degradation of the valuable petroleum oil constituents. Generally, the operation is conducted at about room temperatures and pressures although lower temperatures are at times employed. The mixture of petroleum oil and acid, after a sufficient time of contact, is handled in a manner to remove the spent acid as sludge which contains objectionable sulfur compounds as well as other undesirable constituents. The oil freed of the acid solution is then washed in order to remove free acidic constituents. After the removal of the washing solvent, the oil is completely neutralized by treating the same with an alkali metal treating agent such as an aqueous solution of sodium hydroxide. The treated oil is then distilled to give the final product.

It is also known in the art to desulfurize petroleum oils by contacting the oils with bauxite at elevated temperatures. For example, it is known to remove objectionable sulfur compounds from petroleum oils by contacting the same with bauxite at temperatures in the range of about 600–650° F. It is also known to treat distillates boiling in the motor-fuel boiling range secured from various cracking operations with bauxite at temperatures in the range of about 600–800° F.

While these methods of desulfurizing petroleum oils are satisfactory for removing the sulfur from oils having a low sulfur content it has been found

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that poor yields of treated oils are obtained when these processes are applied to high sulfur content petroleum oils. Furthermore, large quantities of acid are required, with the result that these processes are not commercially attractive for desulfurizing petroleum oils having a high sulfur content. It has now been found that by treating petroleum oils by a combination of these two processes improved and unexpected results are obtained. Substantial sulfur removal may be obtained without using prohibitive amounts of the treating agent and at the same time, a high yield of treated oil may be obtained. This improved process is particularly advantageous as applied to the desulfurization of petroleum oils containing so great a quantity of sulfur that a single refining process is not sufficient for producing a satisfactory product without excessive consumption of chemicals and severe treating losses. This is particularly true of certain grades of kerosenes containing as much or more than 0.5% to 0.9% sulfur. The kerosenes to be treated have a boiling point in the range of about 280° F.–550° F.

The process of my invention may generally be used to treat kerosenes having a sulfur content of 0.2% to 0.9%. A particularly effective treatment may be made of kerosenes having a sulfur content of 0.3% to 0.5%.

In accordance with the present invention, the petroleum oil containing sulfur is first treated with dehydrated bauxite and then treated with acid. The bauxite treating may employ pressures of the range between atmospheric and 400 lbs./sq. in., but preferably are between atmospheric and 50 lbs./sq. in. It is preferred that vapor phase bauxite treating be used requiring a temperature in the range between 600° F. and 800° F. The upper range of temperature is critical in that cracking of the petroleum oil will occur above this temperature resulting in decreased yields. Bauxite treating is carried out using a temperature-controlled reactor containing a fixed bed of catalyst through which kerosene vapors are passed downflow at a rate of 0.5 to 2.0 volumes of liquid oil per volume of catalyst per hour.

For subsequently acid treating the petroleum oil, it is preferred that sulfuric acid be used in a temperature range between 40° F. and 80° F. at substantially atmospheric pressures. The sul-

furic acid may have a strength between 88% to 120%. While the quantity of acid required for treatment will depend largely upon the sulfur content of the petroleum being treated, in general, about 5 to 25 pounds of sulfuric acid are used per barrel of oil. The advantages of the process of the present invention will be appreciated from the results presented in the following table of data:

Refining kerosene of high sulfur content

	Sample	Yield, Volume Percent	Doctor Test	Total Sulfur, Weight Per cent	Per cent Reduction in Sulfur
1	Raw Kerosene	100.0	DNP	0.858	
2	Kerosene+10 lbs. 98% H_2SO_4 per bbl.; rerun	97.0	DNP	0.574	33.1
3	Kerosene+20 lbs. 98% H_2SO_4 per bbl.; rerun	96.0	DNP	0.427	50.2
4	Kerosene+30 lbs. 98% H_2SO_4 per bbl.; rerun	95.3	DNP	0.345	59.8
5	Kerosene+60 lbs. 98% H_2SO_4 per bbl.; rerun	93.0	DNP	0.18	79
6	Kerosene+80 lbs. 98% H_2SO_4 per bbl.; rerun	91.9	DNP	0.12	86
7	Kerosene bauxite treated at 770° F. and 30 p. s. i. g.; rerun [1]	98.8	Pass	0.339	60.6
8	Kerosene bauxite treated at 850° F. and 30 p. s. i. g.; rerun [1]	[2] 90.8	Pass	0.339	60.6
9	Kerosene bauxite treated at 770° F. and 30 p. s. i. g.: then treated with 20 lbs. 98% H_2SO_4 and rerun [1]	95.0	Pass	0.129	85.0

[1] 1 vol. kerosene/vol. bauxite/hour.
[2] Low yield caused by cracking.
"DNP" means "did not pass."

The "doctor test" is a sensitive test used in the petroleum field for determining the presence of mercaptans. The test consists of mixing the oil to be treated with a 15% solution of sodium plumbite. Mercaptides present react to form lead mercaptide. Elemental, free sulfur is then mixed with the oil and sodium plumbite. The lead mercaptide then reacts with the sulfur to form lead sulfide which may readily be detected by a dark discoloration on the surface of the sulfur. The total sulfur was determined by standard analytical procedures. It may be noted that in addition to the tests indicated in the table, all samples were tested for corrosive sulfur content, as determined by the copper strip corrosion test. This consists of immersing a bright copper strip in the oil which is maintained at 212° F. for 3 hours. "Corrosive sulfur" is indicated by discoloration and pitting of the copper. It was found all samples except the raw kerosene satisfactorily passed the copper corrosion test.

The table shows raw kerosene which did not pass the doctor test, containing 0.858% sulfur, was used as the petroleum oil to be treated. Samples 2 to 6 show the results of treating the kerosene with varying quantities of sulfuric acid, followed by redistillation. It will be noted that even an acid treat as high as 80 lbs. of sulfuric acid per barrel of oil was not sufficient to cause the kerosene to pass the doctor test for mercaptans. Also notable, is the large quantities of sulfuric acid required to substantially reduce the sulfur content of the kerosene. 30 pounds of sulfuric acid per barrel of kerosene are only effective to reduce the sulfur content 60% while 80 pounds of acid are required to reduce the sulfur content by 86%. Referring to the table, it is apparent that the use of increased quantities of sulfuric acid is decreasingly effective in reducing the sulfur, while at the same time the yield of treated oil drops off appreciably.

Samples 7 and 8 show the results of treating the kerosene with bauxite followed by redistillation. A bauxite treat at 770° F. and 30 lbs./sq. in. (gauge pressure) reduces the sulfur content of the kerosene by 60% giving a high yield (98.8%) and resulting in a kerosene which passes the doctor test. Sample 8 shows further reduction in sulfur cannot be made by increasing the temperature of bauxite treating. The drop in yield at the temperature of 850° F. is due to cracking of the kerosene.

Sample 9 shows the results obtained on treating the kerosene according to the process of the present invention. In the example given, the kerosene was bauxite treated at 770° F. and 30 lbs./sq. in. (gauge pressure), and was then treated with 20 pounds of 98% sulfuric acid per barrel of kerosene. The treated kerosene was redistilled, giving a finished kerosene passing all the tests indicated and having 0.129% sulfur, an 85% reduction in the original sulfur content of the raw kerosene. The yield was 95%.

It is apparent from this data that the combined treating of the kerosene with bauxite and sulfuric acid yields results which are unexpectedly better than could be anticipated from a consideration of the individual treatments. By this combination an 85% reduction in sulfur content is achieved using a quantity of sulfuric acid which is by itself only effective in reducing the sulfur by 50% and using a bauxite treat which by itself is only effective in reducing the sulfur content by 60%. While the chemical explanation for this is not fully understood, it is believed the particular efficacy of the process is due to the removal of different types of organic sulfur compounds by the two treating agents.

In general it is desired to reduce the sulfur content of the kerosene below about 0.1%. This is readily accomplished when treating kerosenes having about 0.3% to 0.5% sulfur. A bauxite treat at the rate of one volume of kerosene per volume of bauxite per hour is effective in reducing the sulfur content of about one half. The subsequent sulfuric acid treat consisting of 20 lbs. of 98% sulfuric acid per barrel of kerosene is thus effective in substantially eliminating the sulfur, resulting in a sulfur content well below 0.1%.

Processes combining the bauxite treating and acid treating of petroleum oils according to this invention may be greatly varied. Temperatures, pressures, contacting methods and types of reactors used, for example, may be modified to accommodate particular exigencies. It is to be understood therefore that the appended claim is to be given a broad interpretation commensurate with the contribution to the prior art.

I claim:

An improved process for the treatment of kerosene containing in excess of 0.2% sulfur, said kerosene boiling in the range of 280° F. to 550° F. which comprises treating said kerosene in the vapor phase in an initial stage with bauxite at

a temperature of about 600° F. to 800° F. and at a pressure between atmospheric and 50 lbs. per sq. in., withdrawing the kerosene and treating it in a second stage at a temperature of about 40° F. to 80° F. and at atmospheric pressure with 5 to 25 pounds of 88% to 120% sulfuric acid per barrel of oil.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,109,446	Kendall	Feb. 22, 1938
2,126,503	Retailliau et al.	Aug. 9, 1938
2,180,372	Shoemaker	Nov. 21, 1939
2,206,921	Schulze	July 9, 1940
2,340,922	Bent et al.	Feb. 8, 1944
2,391,091	Hewlett et al.	Dec. 18, 1945