

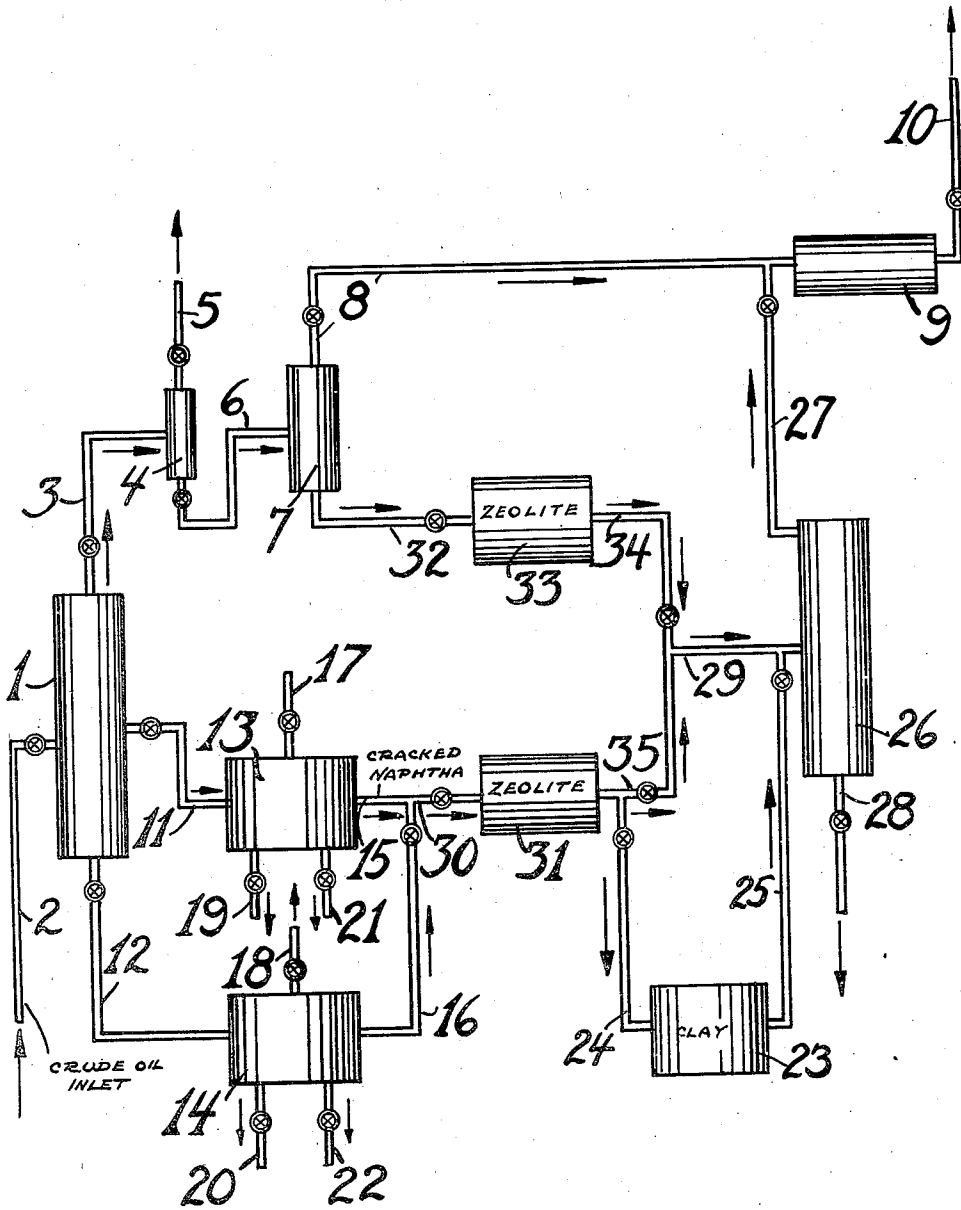
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REFINING OF MINERAL OILS

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REFINING OF MINERAL OILS

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The present invention relates to the refining of mineral oils. The invention is more particularly concerned with the removal of objectionable sulfur compounds from hydrocarbon oils, especially petroleum oils boiling in the motor fuel, kerosene and gas oil boiling ranges. In accordance with the present process, sulfur-containing oils of this character are contacted with a solid material selected from the class of alkali metal aluminum silicates of the zeolite type at elevated temperatures and pressures.

It is known in the art to treat mineral oils, particularly petroleum oil distillates, and the like with various contacting masses such as clay, aluminum oxides and other metallic oxides under various temperature conditions in order to remove objectionable sulfur and related sulfur-containing compounds. For example, a conventional procedure for the removal of sulfur compounds from petroleum oils boiling in the motor fuel boiling range is to pass the oil in the vapor or liquid phase over bauxite under relatively wide varying temperature conditions. The desulfurized oil, after removal from the desulfurization catalyst, is usually treated in a manner to improve its color and color stability. This latter operation is generally accomplished by clay contacting the oil in any desirable manner. It is also known to use various other solid substances for the removal of sulfur compounds from feed oils which, due to their nature, have not been particularly effective for the production of high quality desulfurized products.

I have now discovered a process by which it is possible to substantially completely remove undesirable sulfur compounds from mineral oils containing the same which comprises contacting the sulfur containing petroleum oil with a solid material selected from the class of alkali metal aluminum silicates of the zeolite type at elevated temperatures and pressures. My process not only efficiently and economically removes the undesirable sulfur compounds, but also produces a high quality desulfurized product having improved color, color stability, a relatively low gum content, an improved octane number as well as an improved susceptibility for knock suppressing agents such as tetraethyl lead. I have discovered that if the desulfurization operation be conducted at elevated pressures and temperatures employing these reactants, the effectiveness of the same will be materially unexpectedly increased. The desulfurized product will require a less severe clay treatment and in many instances may entirely by-pass clay treating, thus effecting increased yields and materially reducing manufacturing costs. In accordance with my process, sulfur-containing petroleum oils are desulfurized utilizing zeolites at pressures above about 75 pounds per square inch, preferably

pressures above about 350 pounds per square inch. The temperatures employed are in the range at which substantially no cracking or decomposition of the oil will occur.

The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same. Feed oil which for the purposes of description is taken to be a crude petroleum oil, is introduced into distillation unit 1 by means of feed line 2. Temperature and pressure conditions are regulated in distillation unit 1 which may comprise any number of units arranged in any desirable manner to produce a prime cut fraction boiling in the boiling range below about 400° F., a gas oil fraction and a reduced crude fraction. The prime cut fraction is removed overhead by means of vapor line 3, cooled, and introduced into distillate drum 4. Uncondensed gases are removed from distillate drum 4 by means of line 5 and further processed or disposed of in any desired manner. The condensate is removed by means of line 6 and preferably introduced into a distillation unit 7 in which a separation is made between the relatively lower boiling constituents or light prime cut and the relatively higher boiling constituents or heavy prime cut. The light prime cut is removed overhead by means of line 8, passed to sweetening unit 9, removed by means of line 10, and usually passed to finished motor fuel blending. The gas oil fraction is removed from distillation unit 1 by means of line 11, while the reduced crude fraction is removed by means of line 12. These fractions are passed to cracking coils 13 and 14, respectively. The cracked products boiling in the motor fuel boiling range are removed by means of lines 15 and 16, while the gases, tar and heating oil fractions are removed by means of lines 17, 18, 19, 20, 21, and 22, respectively. The cracked naphtha is introduced by means of line 30 into zeolite treating plant 31 which may comprise any number of zeolite treating units arranged in any suitable manner. Similarly, the heavy prime cut removed from distillation unit 7 is introduced by means of line 32 into zeolite treating plant 33. For purposes of description it is assumed that the zeolite contacting units 31 and 33 are packed with a naturally occurring hydrated sodium aluminum silicate which may be represented by the formula $\text{NaH}_2\text{AlSiO}_7$. Zeolite desulfurization zones 31 and 33 are provided with suitable distributing and contacting means, as well as means adapted for the regeneration or revivification of the zeolite. These desulfurization zones are also provided with means adapted to maintain within said zones the desired temperature and pressure conditions. The zeolite desulfurized oils are removed from the zeolite zones by means of lines 34 and 35, respectively. In general, the de-

sulfurized oil is introduced into clay contacting plant 23 by means of line 24. The clay contacted oil is removed by means of line 25 and introduced into distillation or rerunning unit 26. The zeolite clay contacted oil of the desired end point is removed overhead from distillation unit 26 by means of line 27 and introduced into sweetening unit 9 and passed to motor fuel blending by means of line 10. A heavy residue may be withdrawn from distillation plant 26 by means of line 28 and disposed of as desired. The zeolite desulfurized oil in many instances may be withdrawn from the zeolite contacting units and by-pass clay contacting unit 23 by means of line 29 and handled as a finished product with respect to sulfur concentration, gum content, color and color stability. Clay contacting zone 23 may comprise any number of units arranged in any desirable manner. These units are provided with suitable contacting means as well as means for maintaining a desirable temperature and pressure.

The process of the present invention may be widely varied. Although the process is adapted to the removal of sulfur compounds from any oil by means of zeolites, it is particularly adapted to the removal of mercaptan compounds from the relatively lower boiling petroleum oils boiling in the gas oil, particularly in the motor fuel boiling range.

The solid desulfurizing material employed is a reactant selected from the class of alkali metal aluminum silicates of the zeolite type. The preferred reactants are the naturally occurring alkali metal zeolites. It is also desirable that these naturally occurring alkali metal zeolites be of the hydrated variety. A particularly desirable substance comprises a naturally occurring hydrated sodium aluminum silicate, a species of which may be represented by the following formula: $\text{NaH}_2\text{AlSiO}_7$. Although these desulfurizing reactants may be employed in the naturally occurring state, they are preferably surface conditioned by subjecting the same to a preheat treatment. In general, this preheat treatment is conducted under conditions which will not effect the chemical combination of the substances or which will not produce any substantial hydration of the same. Usually atmospheric pressure is employed and the temperatures are in the range from about 500° F. to 1200° F., preferably in the range from about 800° F. to 900° F.

The desulfurizing operation is conducted at a temperature, pressure and time of contact so regulated that substantially no decomposition or cracking of the feed oil occurs. It is essential that the pressure employed be above about 75 pounds per square inch. The temperature should be in the range above about 600° F., preferably in the range above about 800° F., generally in the range from about 810° F. to 840° F.

The feed rates per volume of desulfurizing reactant employed will be a function of the particular reactant utilized, the character of the feed oil, the type and concentration of the sulfur compounds present, and upon general operation conditions. When employing a naturally occurring hydrated sodium zeolite, the surface of which has been prepared by a suitable pre-heat treatment for the removal of sulfur compounds from petroleum oils boiling in the motor fuel boiling range, the feed rates are preferably from about 0.5 to 2.0 volumes of feed per volume of catalyst per hour.

In order to further illustrate the invention, the

following examples are given which should not be construed as limiting the same in any manner whatsoever.

Example 1

- 5 A cracked petroleum oil boiling in the motor fuel boiling range and produced from a gas oil derived from a Quire crude oil was contacted with a naturally occurring hydrated sodium aluminum zeolite having the formula $\text{NaH}_2\text{AlSiO}_7$, and clay contacted under the following conditions:

Temperature-zeolite stage-----° F. 800
Pressure, lbs./sq. in. gauge, zeolite stage----- 100
15 Feed rate, vol. of oil/vol. of zeolite hour----- 1
Temperature, clay stage-----° F. 500

The treated oil was rerun to a 385° F. E. P. The inspections on the contacted oil, along with the inspections on an identical oil not zeolite and clay contacted, but rerun to a 385° F. E. P., are as follows:

25	Cracked feed oil rerun to 385° F.	Cracked feed oil zeolite and clay contacted and rerun to 385° F.
Color, Saybolt-----	-9	+30
Mg. inh./100 ml.-----	5	5
30 Inhibitor employed (trade name)-----	Du Pont #16	Du Pont #16
Breakdown min. (uninhibited)*-----	50	35
Breakdown Min. (inhibited)-----	80	385
Copper dish gum/100 ml (uninhibited)**-----	44	15
Copper dish gum (inhibited)-----	32	3
Acid heat, A. S. T. M., ° F.-----	141	74
Sulfur-----	0.177	0.104
35 Octane number A. S. T. M. clear-----	77.7	78.3
+3.0 ml. T. E. L.-----	82.7	84.2
Engler distillation:		
I. B. P.-----	90	91
Percent distilled 158° F.-----	13	14
Percent distilled 356° F.-----	90	90
F. B. P. ° F.-----	384	390
40 Percent recovered-----	98.0	97.5

*Test for measuring the stability of an oil. 25 cc. of oil are placed in a bomb at a temperature of 212° F. under oxygen pressure of 100 lbs./sq. in. The time in minutes is measured during which the pressure drops 2 lbs.

45 **Copper dish gum, 100 cc. of oil are placed in a copper dish and the oil evaporated at 212° F. The gum on the dish is measured.

From the above, it is apparent that material substantial benefits are secured by processing the oil in a manner according to the present invention.

50 A portion of the identical feed oil was processed in a similar manner employing bauxite and clay. The inspections on this oil compared with the inspections on the oil secured by contacting with zeolite and clay are as follows:

60	Cracked feed oil, bauxite and clay contacted and rerun to 385° F.	Cracked feed oil, zeolite and clay contacted and rerun to 385° F.
Color, Saybolt-----	+30	+30
Inhibitor employed (trade name)-----	Du Pont #16	Du Pont #16
Mg. inh./100 ml.-----	5	5
65 Breakdown, min. (uninhibited)-----	40	35
Breakdown, min. (inhibited)-----	365	385
Copper dish gum mg./100 ml. (uninhibited)-----	15	15
Copper dish gum mg./100 ml. (inhibited)-----	4	3
Acid heat, A. S. T. M., ° F.-----	88	74
Octane number, A. S. T. M., clear-----	78.9	78.3
+3 cc. of lead-----	84.3	84.2
70 Engler distillation:		
I. B. P.-----	91	91
Percent distilled 158° F.-----	14	14
F. B. P. ° F.-----	388	390

From the above, it is apparent that the zeolite produces a finished product superior to the prod-

uct produced by bauxite, particularly with respect to the breakdown of the inhibited material and as measured by the respective acid heats.

Example 2

A West Texas light prime cut naphtha was contacted with the zeolite employed in Example 1 under the operating conditions employed as described in Example 1. The inspections on the contacted product compared with the inspections on the feed oil are as follows:

	West Texas light P. C. feed oil rerun	West Texas light P. C. zeolite and clay con- tacted and rerun
Color, Saybolt.....	30	30
Copper dish gum.....	11	3
Acid heat, A. S. T. M., °F.....	2.0	4
Sulfur-weight, percent.....	0.138	0.024
Octane number, A. S. T. M., clear.....	61.2	65.0
+3 cc. T. E. L.....	74.6	81.6
Engler distillation:		
I. B. P.....	94.0	109
Percent distillate 158° F.....	15.0	13.5
Percent distillate 302° F.....	88.0	91.5

From the above, it is apparent that, in accordance with the present process, a substantial reduction in sulfur is secured and the quality of the treated product is materially improved.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the treatment of mineral oils containing objectionable sulfur compounds comprising treating said oils with an alkali metal aluminum silicate of the zeolite type at a pressure above about 75 pounds per square inch and at a temperature above about 600° F., said temperature and pressure being in the range at which substantially no cracking or decomposition of the oil occurs.

2. Process in accordance with claim 1, in which said mineral oil is a petroleum oil boiling in the

motor fuel boiling range and in which said oil is contacted in the liquid phase.

3. Process in accordance with claim 1, in which said mineral oil is a petroleum oil boiling in the motor fuel boiling range and in which said oil is treated with a hydrated sodium aluminum silicate at a temperature in excess of about 800° F.

4. Process for the removal of objectionable sulfur compounds from petroleum oils boiling in the motor fuel boiling range which comprises treating said oil in an initial stage with an alkali metal aluminum silicate of the zeolite type at elevated temperatures and pressures under conditions at which substantially no cracking or decomposition of the oil occurs, said pressure being above about 75 pounds per square inch and said temperature being in the range above about 600° F., and then further contacting said oil in a secondary stage with clay.

5. Process in accordance with claim 4, in which said oil is contacted with a naturally occurring hydrated sodium aluminum silicate of the zeolite type in the liquid state.

6. Process in accordance with claim 4 in which said oil is contacted with a naturally occurring hydrated sodium aluminum silicate of the zeolite type at a pressure of about 100 lbs./sq. in. gauge and at a temperature in excess of about 800° F.

7. Process for the removal of objectionable sulfur compounds from petroleum oils boiling in the motor fuel boiling range, which comprises treating said oil in the liquid state in an initial stage with a naturally occurring alkali metal aluminum silicate of the zeolite type at elevated temperatures and pressures at which substantially no cracking or decomposition of the oil occurs, said pressure being in the range above about 75 pounds per square inch and said temperature being in the range above about 600° F.

8. Process as defined by claim 7, in which said pressure is in the range above about 350 pounds per square inch and said temperature is in the range from about 810° F. to 840° F.

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