

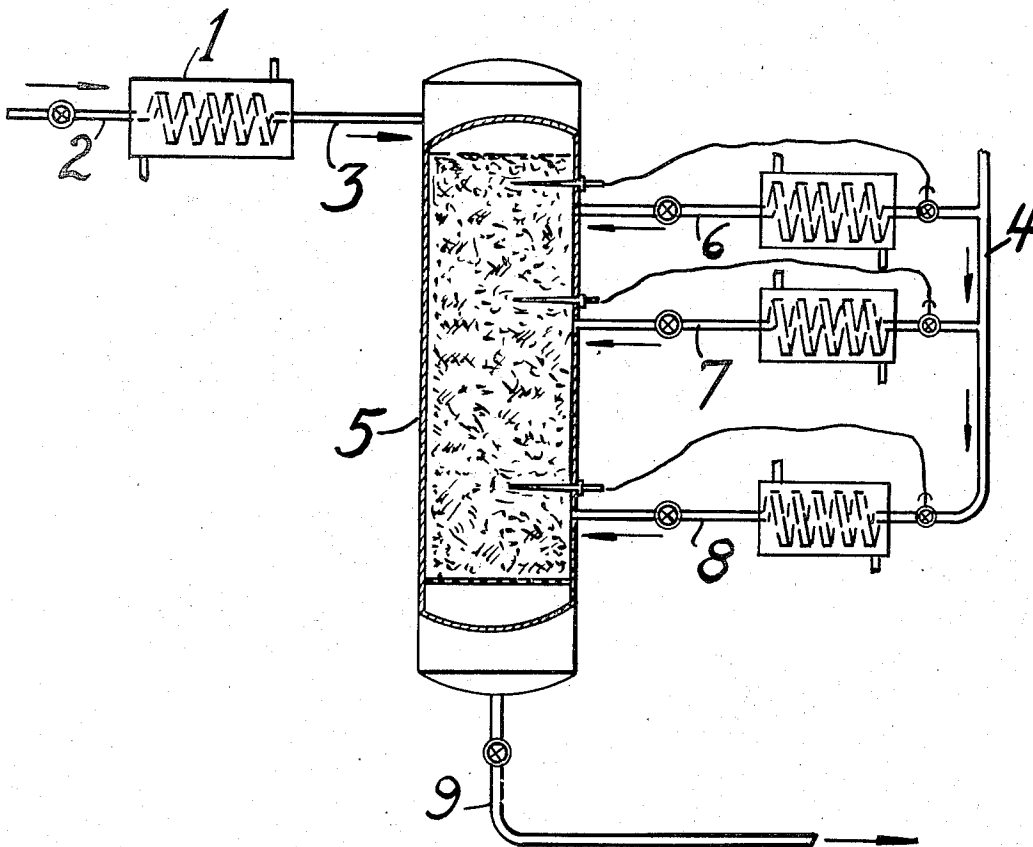
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REFINING OF MINERAL OILS

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REFINING OF MINERAL OILS

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9 Claims. (Cl. 196—28)

The present invention relates to a process for refining mineral oils. The invention is more particularly concerned with the production of improved motor fuels having high anti-knocking characteristics as measured by a high octane number, by an operation which comprises bauxite-treating petroleum feed oils under carefully controlled conditions. In accordance with the present invention, petroleum oils are processed under conditions adapted to produce products boiling in the motor fuel boiling range, which are characterized by having relatively high octane numbers and relatively low sulfur concentrations. These products are produced by passing a suitable feed oil through a bauxite bed within a critical temperature range which is controlled by introducing, preferably at a plurality of stages, a liquid, preferably water, in relatively small amounts.

It is known in the art to subject various petroleum oil feed stocks, such as heavy naphthas, gas oils, reduced crudes, and the like, to temperature and pressure conditions adapted to produce relatively lower boiling constituents and relatively higher boiling constituents. It is also known in the art to refine the resulting products by treating the same with various acids, clays, metallic oxides, such as bauxite, and the like. For example, it is known to remove objectionable sulfur compounds from petroleum oils, particularly from petroleum oils boiling in the motor fuel boiling range, by contacting the same with bauxite at elevated temperatures which vary over a relatively wide temperature range. In these operations it has been found that, providing the temperature of the bauxite-treating operation be controlled within a relatively narrow critical temperature range, not only will the petroleum oils be desulfurized in an efficient and economical manner, but the treated feed stock will have unexpected, desirable properties which could not be foreseen from disclosures in the prior art. These improvements apparently are secured by a chemical rearrangement of the molecules, such as isomerization, dehydrogenation, and perhaps scission of the same. However, due to the fact that the reaction when desulfurizing oils of this character is exothermic, it has been extremely difficult to maintain the temperature in the reaction zone within the critical temperature range desired. In order to control the temperature within the desired operating range, various proposals have been made. It has been proposed that the feed stock be introduced into the bauxite-treating zone somewhat below the pre-

ferred temperature. When operating in this manner, a portion of the exothermic heat is taken up by the feed stock and undesirable degradation of the feed stock is prevented. It has also been proposed to utilize various cooling means, such as cooling coils and the like, throughout the reaction zone. This, however, has not been entirely satisfactory due to the fact that in order adequately and positively to control the temperature of the reaction, the feed zone must have a relatively small diameter. I have, however, now discovered a process by which it is possible to positively control the temperature of the reaction throughout the reaction zone within the desired narrow critical temperature range. In accordance with my process, the temperature within the treating zone is maintained substantially constant by taking out the exothermic heat of reaction by the use of a cooling liquid which is preferably introduced at a plurality of stages.

The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same. For purposes of illustration, it is assumed that the feed oil comprises a cracked petroleum distillate boiling in the motor fuel boiling range. The feed oil is introduced into heating coil or equivalent means 1 by means of feed line 2. In heating coil 1 the feed oil is raised to the desired temperature, preferably in the range of about 700° F. to 850° F. The feed oil is withdrawn by means of line 3, introduced into bauxite treating zone 5, and passed downwardly through reaction zone 5, and withdrawn by means of line 9. The reaction being exothermic, the temperature tends to rise. In accordance with my process, small quantities of a liquid are introduced at a plurality of points into reaction zone 5 by means of lines 4, 6, 7 and 8, respectively. The treated oil withdrawn from reaction zone 5 by means of line 9 may be further handled or refined in any manner desirable. It is to be understood that bauxite contacting zone 5 may comprise any suitable number and arrangement of contacting units.

The process of the present invention may be widely varied. The invention essentially comprises desulfurizing a petroleum oil by passing the same through a bauxite-treating zone and removing the exothermic heat of reaction by introducing a cooling fluid at a plurality of stages in the bauxite-treating zone. The process may be adapted for the treatment of any mineral oil with bauxite or with other metallic catalysts, in which the reaction is exothermic, and in which

it is desired to control the temperature within a narrow critical temperature range. The invention is particularly applicable in bauxite desulfurization of cracked petroleum feed oils boiling in the motor fuel boiling range.

In these operations, it is desirable that the temperature in the reaction zone be controlled in the range from about 600° F. to 900° F., preferably in the range from about 750° F. to 820° F. The operation, in general, is conducted under substantially non-cracking conditions. Thus, when treating high refractory stocks, the desulfurization operation may be conducted at temperatures as high as 900° F. without securing any substantial cracking of the feed oil.

The cooling fluid added at a plurality of stages may be varied widely. The cooling fluid, however, preferably comprises water in the liquid or vaporous state. A particularly desirable cooling fluid comprises wet steam. In general, we have found that it is preferred to introduce the water at at least three stages, and to introduce approximately 0.1% of water by weight, or 0.5% of steam by weight, based upon the feed oil. Particularly desirable results are secured by utilizing a plurality of thermostats or equivalent means in the path of flowing vapors immediately preceding the respective points of introduction of the cooling fluid, in a manner adapted to regulate and control the flow of the cooling fluid introduced at the particular point.

The bauxite preferably comprises a native aluminum hydroxide containing from 50% to 70% of Al_2O_3 and from 25% to 30% of water. In general, it is preferred that the bauxite be activated by burning the same at a temperature in the range from about 500° F. to 1100° F., preferably at a temperature in the range from about 600° F. to 900° F. The feed rates may vary considerably depending upon the general operating conditions, the character of the feed oil being treated, as well as upon the type of bauxite employed. In general, the feed rates are in the range from about 1 volume to 10 volumes of oil per volume of bauxite per hour. The preferred rates are from about 2 to 4 volumes of oil per volume of bauxite per hour. The bauxite also may be any desired particle size. I have found that granular bauxite is desirable.

In order to illustrate the invention further, the following example is given which should not be construed as limiting the same in any manner whatsoever:

Example

Various operations were conducted in which cracked feed oils, having a gravity of 60° A. P. I. and which boiled in the motor fuel boiling range, were desulfurized utilizing bauxite. The results of these operations were as follows:

	Operation		
	I	II	III
Feed rate (vol. per cent feed oil per volume of catalyst per hour).....	2	10	10
Length of cycle—Hours.....	6	6	6
Reactor inlet temp.—deg. F.....	800	800	800
Reactor outlet temp.—deg. F.....	950	950	950
Pressure—#1 sq. in. Ga.....	0	0	0

Amount of water or steam injected at a plurality of stages into the reactor to give an average catalyst temperature of 800° F.

Injected	Boiler feed water at 230° F.	Fresh water at 60° F.	Exhaust steam at 15# pressure and approximately 267° F.
(a) Pounds necessary to inject per 100 gallons of feed oil.....	4.0	3.0	18.3
(b) Per cent by weight based on feed oil.....	0.11	0.08	0.5

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

1. Process for removing objectionable sulfur compounds from petroleum oils, which comprises passing the petroleum oil in the vaporous state through a bed of bauxite, and removing the heat of reaction by the introduction of a cooling fluid comprising water at a plurality of stages, the total amount of water introduced being not greater than about 0.5% based upon the quantity of oil being treated per unit of time.
2. Process as defined by claim 1, in which said petroleum oil is a cracked petroleum naphtha boiling in the motor fuel boiling range, and in which said petroleum oil is contacted with the bauxite at a temperature in the range from about 600° F. to 900° F.
3. Process for removing objectionable sulfur compounds from petroleum oils, which comprises passing the petroleum oil in the vaporous state through a bed of bauxite, and removing the heat of reaction by the introduction of wet steam at a plurality of points, the total amount of water introduced being not greater than about 0.5% based upon the quantity of oil being treated per unit of time.
4. Process as defined by claim 3, in which petroleum oil comprises a cracked naphtha boiling in the motor fuel boiling range.
5. Method of controlling the temperature of a treating process, in which a mineral oil is treated by passing the same through a bed of bauxite catalyst and exothermic heat is thereby evolved, which comprises introducing water as a cooling fluid into the catalyst at a plurality of points, the total amount of water introduced being not greater than about 0.5% based upon the quantity of oil being treated per unit of time.
6. Method as defined by claim 5, in which the treating process comprises a desulfurization reaction.
7. Method as defined by claim 5, in which about 0.1% of liquid water is introduced into the catalyst.
8. Method as defined by claim 5, in which about 0.5% of steam is introduced into the catalyst.
9. The process as defined by claim 1, in which the water is introduced in at least three stages and in which the amount of water introduced into each stage is thermostatically controlled so that the temperature within the catalyst bed is maintained at about 600° to about 900° F.

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