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TREATMENT OF HYDROCARBONS

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This invention relates to a process for reducing the sulfur content and improving other properties of hydrocarbon oils and distillates. More specifically, it relates to a process for improving antiknock properties, particularly the susceptibility of straight-run, natural, and cracked gasolines to octane number improvement upon the addition of antiknock agents such as tetraethyl lead.

In one specific embodiment the present invention relates to a process which comprises treating hydrocarbon distillates with chalk at a temperature within the range of from about 500° F. to about 1200° F. under non-cracking conditions and recovering the treated gasoline.

Chalk is a calcareous mineral found in the Cretaceous age in many parts of the world and is a relatively soft substance formed from the calcareous remains of microscopic organisms. It is usually soft, compact, fine grained, and is derived from the remains of foraminifera, echinoderms, coccoliths, and other marine organisms which develop calcareous structures exceedingly minute in size and which are believed to have been deposited in shallow waters. The resulting deposit, when examined under a microscope, reveals fragments of the shells of which chalk is composed. The chalk is usually soft, porous, white or grey and sometimes buff in color, and is massive in appearance. This is in contrast to the usual appearance and structure of crystalline limestones which may be deposited from calcareous waters due to chemical action, supersaturation, or evaporation of the waters.

The composition of chalk varies considerably but is essentially calcium carbonate, some chalks being composed of as much as 95% calcium carbonate, while others contain substantial quantities of materials such as, for example, compounds of silica, aluminum, iron, magnesium, sulfur, alkali metals etc.

In the United States the true chalks of Cretaceous age are more or less limited to the Central and Southern States. Niobrara chalk outcrops are found in Wyoming, Nebraska, Western Kansas and the Black Hills in South Dakota. Some outcroppings are found in Central Arkansas, Oklahoma, and Texas. Chalk is also found in Tennessee, Mississippi, Alabama, Louisiana, Florida, and South Carolina. These chalks are not all of the same origin but do belong to the Cretaceous age; for example, the chalk found in Alabama is known as Selma chalk. Chalk is usually found in relatively thick deposits, for example, 20-1000 feet or more. In some cases chalk

deposits are inter-bedded with clays and shales while in others there may be inclusions of foreign substances. In still others the chalk is of substantially pure form and quite uniform in its appearance and physical properties. Because of the size and type of fossils making up the major portion of chalk it differs from crystalline limestone deposits and from deposits such as coquina which is a limestone composed of loosely aggregated shells and shell fragments which are considerably larger and less uniform than chalk. Chalk differs from travertine which is deposited as a rule from calcareous springs and is sometimes called calcareous tufa or calcareous sinter. Travertine, another type of limestone, is precipitated by virtue of a chemical action from waters containing lime.

In other words, while chalk may be included within the term "limestone" as used in its broadest sense, the term chalk refers to certain more or less specific forms of calcareous deposits made up largely of the shells of microscopic animals indigenous to shallow waters and has physical characteristics of porosity, density, and fossil make-up peculiar only to itself, and occurring only in Cretaceous time. It is with minerals of this type that my invention is concerned.

The invention is carried out by subjecting hydrocarbon oil, particularly distillates, which can be vaporized without substantial decomposition, at a temperature within the range of about 500-1200° F. and preferably about 650-950° F., to the action of chalk. Normally atmospheric or slightly superatmospheric pressures of the order of 100 pounds per square inch are used. The contact time is so regulated as to prevent or minimize cracking which might result in loss of oil and the deposition of undesirable carbonaceous deposits on the chalk. The length of time for which the chalk may be employed is dependent upon the degree of desulfurization desired and is largely related to the type and origin of the hydrocarbon undergoing treatment. Usually larger quantities of straight-run or natural gasoline can be treated than of cracked per unit weight of chalk. However, this depends, to a certain extent, upon the amount of sulfur and other impurities in the oils.

The chalk may be used in the form of granules or lumps or may be formed into pellets, spheres, or other convenient forms of packing material by well-known methods. It is also within the scope of the invention to use powdered chalk which may be contacted with the oil in any convenient manner.

It should be borne in mind that not all deposits of chalk are equivalent in their action and some are of greater activity than others. The hydrocarbon oil undergoing treatment may have some influence on the relative activities of any particular chalk.

The following examples are given to illustrate the usefulness of the process and should not be construed as limiting the invention to the exact conditions given:

Example I

A West Texas straight-run gasoline of approximately 400° F. end-point was contacted with granular chalk obtained near Bartley, Nebraska, the chalk being of Upper Cretaceous age and Niobrara formation. Treatment was carried out in substantially vapor phase at 825° F. at a tower pressure of approximately 22 pounds per square inch. The mercaptan content was reduced from 0.085% in the original to 0.001% in the treated gasoline, which amounts to 98.9% reduction in mercaptan sulfur. The total sulfur was reduced from 0.28% in the original gasoline to 0.04%, or a reduction of 84% of the total sulfur content. The octane number of this gasoline was 56.5, both before and after treatment, but upon the addition of 3 cc. of tetraethyl lead per gallon the original gasoline went to 68 octane number while the treated gasoline had an octane number of 72.

Example II

The gasoline treated was a cracked West Texas gasoline having a mercaptan content of 0.1, a total sulfur content of 0.53, an octane number of 65.7 clear and 72.5 with 3 cc. of tetraethyl lead per gallon. The gasoline was treated with Niobrara chalk at a temperature of 820° C. and 18 pounds per square inch pressure. The mercaptan content was reduced to 0.0008 which is more than 99% reduction in mercaptan sulfur and the total sulfur was reduced to 0.34% which is a reduction of approximately 36%. The octane number was not increased but upon the addition of 3 cc. of tetraethyl lead an octane number of 73.5 was obtained.

Both of the above runs were carried out under conditions such that substantially no cracking of the gasoline occurred. The operations took place in a packed tower of conventional design

which was preceded by a heating coil to bring the temperature to the desired point.

I claim as my invention:

1. A process for refining a hydrocarbon oil to desulfurize it which comprises treating said oil with a contact agent comprising essentially chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur.
2. A process for refining a hydrocarbon oil to desulfurize it which comprises treating said oil with a contact agent comprising essentially chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur and under a pressure of from approximately atmospheric to about 100 pounds per square inch.
3. A process for treating gasoline which comprises contacting said gasoline with a contact agent comprising essentially chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur.
4. A process for refining a gasoline which comprises treating said gasoline with a contact agent comprising essentially chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur and under pressure of approximately atmospheric to about 100 pounds per square inch.
5. A process for refining a gasoline to desulfurize it which comprises treating said gasoline with chalk at a temperature of from about 650° F. to about 950° F., said treatment being under conditions such that substantial cracking does not occur, and recovering the treated gasoline.
6. A process for refining a gasoline to desulfurize it which comprises treating said gasoline with Niobrara chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur.
7. A process for refining a hydrocarbon oil to desulfurize it which comprises treating said oil with chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur.
8. A process for refining a gasoline to desulfurize it which comprises treating said gasoline with chalk at a temperature in excess of about 500° F. but under conditions such that substantial cracking does not occur.

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