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HIGH OCTANE MOTOR FUEL AND METHOD OF PRODUCING SAME

Richmond T. Bell, Deerfield, Ill., assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

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This invention relates to a method for inhibiting knocking of motor fuels in internal combustion engines of the spark ignition type, and to high antiknock motor fuel. The invention also relates to a method for simultaneously converting "doctor" sour sulfur compounds in hydrocarbon motor fuels into "doctor" sweet compounds and for raising the octane rating of the fuel.

It is common practice in the petroleum industry to either remove the "doctor" sour sulfur compounds, particularly mercaptans, from hydrocarbon oil containing them or to convert the mercaptans to disulfides which are sweet to the "doctor" test. The removal of the mercaptans has the advantage of removing the sulfur from the oil but in order to obtain a "doctor" sweet oil by removal of mercaptans a costly and time-consuming operation is involved. On the other hand, "doctor" sweetening is a simple operation which can be accomplished by means of the so-called "doctor" solution but has the disadvantage of leaving the sulfur in the motor fuel with its resulting deleterious effect on the octane rating and lead susceptibility of the motor fuel.

One of the objects of this invention is to provide a method for raising the octane rating of motor fuel and to inhibit the knocking tendency thereof when used in ignition type internal combustion engines.

Another object of my invention is to provide a method for converting "doctor" sour sulfur compounds contained in hydrocarbon oils into "doctor" sweet compounds.

A still further object of the invention is to provide a method for simultaneously converting "doctor" sour to "doctor" sweet sulfur compounds and to raise the octane number of motor fuel.

A further object of this invention is to provide a motor fuel which has a high antiknock rating when used in ignition type internal combustion engines.

Other objects of my invention will be revealed by the following detailed description of my invention.

I have discovered that the tricarbonyl mercaptides of iron and cobalt both have the property of being soluble in gasoline and of inhibiting knocking tendencies thereof when the gasoline is used in ignition type internal combustion engines. Moreover, the compounds are stable and do not decompose under ordinary conditions to which motor fuel is subjected and they are sweet to the "doctor" test. The stability of the tricarbonyl mercaptides is evidenced by the fact that they are unaffected by the reagents used in the determination of mercaptan sulfur by the standard silver nitrate method. The stability of the tricarbonyl mercaptides is an outstanding advantage which these compounds possess over iron pentacarbonyl and iron tetracarbonyl which have previously been suggested as antiknock addition agents for motor fuel.

The tricarbonyl mercaptides may be added as such to the motor fuel or may be made in situ either by adding iron or cobalt tetracarbonyl to mercaptan-containing motor fuel, or by adding both mercaptans and the metal tetracarbonyl to the gasoline. Where the tricarbonyl mercaptide is made in situ, it is advantageous to heat the motor fuel in the presence of the reacting agents to a temperature of approximately 90–100° C. either under pressure or under reflux for a period of from approximately one to two hours with exclusion of air and oxygen. Lower temperatures may be used to bring about the reaction of the metal tetracarbonyl and the mercaptans, but the reaction requires a longer period of time. Care should be exercised not to heat the reaction mixture to temperatures at which decomposition products form in the reacting mixture.

The invention is particularly useful in connection with motor fuels which contain "doctor" sour sulfur compounds, since it is possible in accordance with my invention to convert part or all of the "doctor" sour sulfur compounds into "doctor" sweet compounds at the same time that the octane rating of the motor fuel is increased. Thus, where the gasoline or other motor fuel contains mercaptans, it is advantageous to form the metal tricarbonyl mercaptide in situ. After determining the amount of sulfur present in the motor fuel as mercaptan, a sufficient amount of iron or cobalt tetracarbonyl can be added to react with that amount of mercaptan which it is desired to convert. Obviously, the higher the mercaptan content of the motor fuel, the more of the tetracarbonyl which will be required to sweeten the motor fuel, but at the same time the quantity of tricarbonyl mercaptide formed is greater and the octane number of the gasoline is consequently higher.

Where the quantity of mercaptans present in the motor fuel is below that amount which is necessary to react with the quantity of tetracarbonyl which it is desired to add, in order to get a desired octane rating, additional mercaptans may be added to the motor fuel to supply the deficiency.

The reaction which occurs when the iron or cobalt tetracarbonyl reacts with the mercaptan may be represented by the following equation:

$$2Fe(CO)_4+2RSH=2Fe(CO)_3SR+H_2+2CO$$

in which R represents either an aryl or alkyl radical.

Where the gasoline is "doctor" sweet and it is desired to increase the antiknock rating of the gasoline, the amount of the tricarbonyl mercaptide added may range from approximately .02 to 1% by weight based on the motor fuel. Where the motor fuel to be treated contains mercaptans in insufficient quantities to produce the quantity of tricarbonyl mercaptide necessary to obtain a desired octane number, sufficient tetracarbonyl may be added to react with the mercaptans and a sufficient amount of tricarbonyl mercaptide added to bring the octane number up to the required point. It will, of course, be understood that where the tricarbonyl mercaptide is added as such to the gasoline, it is merely necessary to intimately mix the mercaptide with the motor fuel in order to prepare a motor fuel of the required octane rating.

In order to illustrate the results obtained in accordance with my invention, the following examples are given:

Example I.—To one pint of "doctor" sweet reference fuel blend having an A. S. T. M. octane number of 50, was added 0.4 gram of dark red crystals of phenyl mercapto iron tricarbonyl ($Fe(CO)_3SC_6H_5$). The crystals dissolved in the gasoline and colored it a deep orange color. The resulting had an A. S. T. M. octane number of 53.2.

Example II.—Cracked gasoline prepared by high pressure thermal cracking of petroleum oil containing .0282% of sulfur as mercaptans and having an A. S. T. M. octane number of 61.9 was treated by adding thereto various amounts of iron tetracarbonyl and refluxing the mixture at 90–100° C. for a period of from one to two hours under an atmosphere of nitrogen in order to prevent oxidation. The following results were obtained:

Iron tetracarbonyl added, gms. per gal.	"Doctor" test	Percent sulfur as mercaptans in treated gasoline	A. S. T. M. octane number of treated gasoline
1.2	Sour	0.0150	63.6
2.8	do	0.0092	65.7
5.6	Slightly sour	0.0018	66.7
7.2	Sweet	0.0000	68.2

The treated gasoline ranged in color from dark orange to dark red, depending on the amount of iron tetracarbonyl which had been added.

The foregoing examples clearly show that the objects of my invention are achieved by adding the tricarbonyl mercaptide directly to the gasoline. An increase in octane number is obtained which is proportional to the amount of mercaptide added. By adding a metal tetracarbonyl to the sour gasoline, the octane number of the gasoline is raised in direct proportion to the amount of tetracarbonyl added and the proportion of the mercaptans converted to "doctor" sweet tricarbonyl mercaptide is likewise directly proportional to the amount of the tetracarbonyl compound added. The examples further show that a "doctor" sweet product can be prepared from a "doctor" sour gasoline and in so doing the octane rating of the gasoline can be considerably increased.

I claim:

1. The method for simultaneously converting "doctor" sour to "doctor" sweet sulfur compounds present in hydrocarbon motor fuel and increasing the octane rating thereof, which comprises adding to the motor fuel a small amount of tetracarbonyl of metal selected from the class consisting of iron and cobalt, reacting the metal tetracarbonyl with the mercaptans in said fuel at a temperature of approximately 90–100° C. and allowing the metal-containing reaction products to remain in solution in the motor fuel.

2. Method in accordance with claim 1 in which the metal is iron.

3. Method in accordance with claim 1 in which the amount of tetracarbonyl added is substantially equal to that amount necessary to convert all the "doctor" sour to "doctor" sweet sulfur compounds.

4. The method of improving sour motor fuel which comprises treating the sour motor fuel with sufficient tetracarbonyl of metal selected from the class consisting of iron and cobalt to react with the sour compounds whereby to produce a treated sweet motor fuel of increased octane number.

5. Method in accordance with claim 4 in which the treatment is effected at temperatures not substantially in excess of 100° C.

6. Method in accordance with claim 4 in which the sour compounds consist substantially entirely of mercaptans.

RICHMOND T. BELL.