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## IMPROVED GASOLINE FUEL COMPONENTS

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The present invention concerns the treatment of naphtha fractions that are ordinarily not suitable as components of gasolines for modern automotive engines to render them acceptable for that use. The invention is particularly directed to a process for improving the engine cleanliness characteristics of such naphtha fractions when they are used in motor gasolines as well as to the improved naphtha fractions themselves.

In order to provide motor fuels that will perform satisfactorily in modern automotive engines, it is necessary to employ anti-knock agents. The agent ordinarily used is tetra ethyl lead. Related tetra alkyl lead compounds have also been suggested such as tetra methyl lead. It is well recognized in the art, however, that although organic lead compounds of the nature of tetra methyl lead and tetra ethyl lead are valuable gasoline constituents in that they reduce engine knocking that is attributable to compression ignition phenomena, they are at the same time detrimental in that they cause the formation of engine deposits which in the long run will increase the octane level requirements and give unsatisfactory engine operation. These deposits become incandescent during engine operation and ignite the mixture of fuel and air prematurely by a phenomenon commonly referred to as surface ignition. The deposits also build up on the points and insulators of spark plugs and thus cause spark plug misfiring. Such deposit build-ups are customarily avoided or minimized by employing scavenger agents. The most commonly used agents are ethylene dichloride and ethylene dibromide which, during combustion, furnish halogen acids that combine with the lead and convert it to a relatively volatile lead halide which is removed with the gasoline engine exhaust gases. These scavenger agents are not entirely satisfactory, however, and deposit formation and the resulting difficulties occur in modern high compression engines in spite of the use of these scavenger agents.

It has been found more recently that organic compounds of phosphorus are desirable additives for inclusion in leaded gasolines in that they are effective for overcoming the difficulties that are associated with the use of conventional lead scavenging agents. It is one function of the present invention to introduce minor proportions of phosphorus compounds into the motor fuel for the purpose stated. It is another function of this invention to convert cracked naphtha fractions that are normally unsuitable as gasoline components into fractions that can be used to advantage in gasoline compositions.

In accordance with the present invention petroleum cracked naphthas, particularly the higher boiling fractions of heavy thermal reformates, are treated with the reaction products of phosphorus sulfides and olefin polymers, thereby removing from those fractions the impurities that normally cause engine fouling when gasolines containing the cracked naphthas are used in an internal combustion engine. At the same time the treat-

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ment of the cracked naphtha fractions in this manner introduces into those fractions organic phosphorus compounds that are useful in assisting in the scavenging of lead from leaded gasolines burned in the engines.

The reaction products employed in the present invention for treating the cracked naphtha fractions are obtained by reaction of a sulfide of phosphorus, preferably  $P_2S_5$ , with a  $C_2$  to  $C_4$  olefin polymer, i.e., of ethylene, propylene, butylene or isobutylene, of from about 250 to about 10,000 molecular weight, and preferably about 1,000 to 5,000 molecular weight. Isobutylene polymers are preferred. The reaction product is readily obtained by a reaction of the phosphorus sulfide with the olefin polymer at a temperature of about  $200^\circ$  to  $600^\circ$  F. and preferably from about  $300^\circ$  to about  $500^\circ$  F. Preferably, from about 2 to about 5 molecular proportions of the olefin polymer are employed for each molecular proportion of the phosphorus sulfide in the reaction. It is ordinarily desirable to employ an amount of the phosphorus sulfide that will react completely with the olefin polymer. The reaction is continued until substantially all of the phosphorus sulfide has been reacted.

The phosphorus sulfide-olefin polymer reaction product is then employed to treat a cracked naphtha fraction. The amount of phosphorus sulfide reaction product used will be in the range of from about  $\frac{1}{50}$  of the weight of the naphtha fraction treated to about an equal weight based on the naphtha fraction and preferably about  $\frac{1}{10}$  to  $\frac{1}{2}$  of the weight of the latter. Treating temperatures will range from about  $150^\circ$  to about  $350^\circ$  F. and preferably from about  $180^\circ$  to about  $250^\circ$  F. The reaction is continued for a period of from  $\frac{1}{2}$  to 10 hours and the reaction product is then distilled to recover the treated naphtha as the distillation product. Although almost any normally undesirable cracked gasoline fraction may be treated by the process of the present invention, it is particularly adaptable to the treatment of heavy reformat fractions, from the well known petroleum refining processes of reforming and hydroforming, and especially to the treatment of what are known as heavy thermal reformat fractions, i.e., the fractions boiling above  $200^\circ$  F. and below  $550^\circ$  F., e.g., between  $250^\circ$  F. and  $450^\circ$  F.

The following examples are illustrative of the invention.

## EXAMPLE 1

A quantity of isobutylene polymer of 1100 Staudinger molecular weight was heated with 10 percent by weight of  $P_2S_5$  at about  $425^\circ$  F. for about four hours. The material was then diluted with a quantity of a light hydrocarbon oil to about 60 percent concentration for ease in filtration and further handling. The filtered concentrate analyzed 2.63 percent sulfur and 1.42 percent phosphorus.

## EXAMPLE 2

The  $P_2S_5$  treated polyisobutylene of Example 1 was used for treating a total heavy thermal reformat that had a boiling range of  $200^\circ$  to  $450^\circ$  F. and was made by thermal reforming a virgin petroleum naphtha at a temperature of about  $950^\circ$  F. Equal weights of the reformat and of the reaction product of Example 1 were mixed and heated at a temperature of  $190^\circ$  to  $200^\circ$  F. for 9 hrs. The product was then subjected to a vacuum stripping operation in which it was distilled to an overhead temperature of  $292^\circ$  F. at 150 mm. Hg and then to  $270^\circ$  F. at 10 mm. Hg pressure. The treated reformat was recovered as the distillate. The optical density of the recovered product was measured as an indication of the improvement obtained by the treatment. The results are given in Table I for the materials, untreated or

"raw," and washed with a 20% aqueous solution of caustic soda, i.e., "NaOH Washed."

Table I

	Optical Density	
	Raw	NaOH Washed
Regular Thermal Reformate	0.692	0.652
Thermal Reformate Treated With P <sub>2</sub> S <sub>5</sub> /Polyisobutylene Reaction Product	0.112	0.103

Optical density is measured in terms of the logarithm of (100/percent light transmitted). It is well known in the art that the engine cleanliness characteristics of cracked or reformed petroleum naphthas can be evaluated by a comparison of the optical densities of the naphthas after treatment with suitable reagents such as fluoboric acid, sulfuric acid etc. The values of optical density in Table I above and Table III below were obtained by measuring light transmission in a Lumetron colorimeter after the samples of naphtha had been treated as follows: Treat 1 cc. of sample with 10 cc. of reagent consisting of 10 parts of dilute sulfuric acid and 90 parts of acetic acid; then dilute to 100 cc. with acetic acid, and measure optical density.

By actual tests of various gasolines in a Chevrolet engine, it was established that the optical density measured the relative quantities of deposits in the engine as shown in Table II wherein the sludge rating of 100 was obtained on a commercial motor gasoline of regular grade and average cleanliness quality.

Table II

CORRELATION BETWEEN SULFURIC ACID TEST AND ENGINE TEST

Sulfuric Acid Test Rating (Optical density) × 100	Engine Test Sludge Rating—Relative Quantity of Deposit in Chevrolet Engine
0	27
3	34
5	48
9	56
12	69
15	72
18	83
24	100
36	107
45	121

<sup>1</sup> Test procedure ER-4-45 described by D. T. Rogers, W. W. Rice and F. L. Jonach before meeting of Society of Automotive Engineers, November 10, 1955. Test consumes 6 hours in 3 cycles of about 2 hours each at 40 B.H.P. output. First cycle 500 r.p.m., water jacket and oil temperatures 115° F.; second cycle 2000 r.p.m., water jacket temperature 160° F., oil temperature 175° F.; third cycle 2000 r.p.m., water jacket temperature 160° F., oil temperature 225° F. Total test duration, 110 hrs.

## EXAMPLE 3

In the same manner as in Example 2, various fractions of the thermal reformat were individually treated with the reaction product of Example 1. The optical density measurements of the treated products and the optical densities of the corresponding untreated cuts are given in Table III. The data in Tables I and III indicate that the various thermal reformat cuts were considerably improved by the process of the present invention.

Table III

	(Optical Density) × 100	
	Untreated	Treated
Thermal Reformate Cut <sup>1</sup>	66.8	1.4
Thermal Reformate Cut <sup>2</sup>	92.1	2.8
Thermal Reformate Cut <sup>3</sup>	188.6	6.9

<sup>1</sup> Boiling range 400-416° F.

<sup>2</sup> Boiling range 416-427° F.

<sup>3</sup> Boiling range 427° F. +

Each of the treated fractions was found on analysis to contain phosphorus as shown in Table IV.

Table IV

Boiling Range of Reformate Fraction (° F.)	Phosphorus Content (Wt. Percent)
400-416	0.0005
416-427	0.0003
427+	0.0005

For lead scavenging purposes, the phosphorus content of gasoline is controlled between 0.05 and 1.0 theory, or stoichiometric proportion, of the lead. If 3 cc. of tetraethyl lead, i.e., 5 grams, is added to one gallon of gasoline, which weighs 3000 grams, the lead content of the gasoline will be about 0.1 percent, since the lead content of tetraethyl lead is 64 percent. One theory of phosphorus is equal to about 10 percent of the weight of lead. One theory of phosphorus in a gasoline containing 0.1 percent lead would amount to about 0.01% by weight of the gasoline. Thus, the treated reformat analyzing 0.0005% phosphorus contained 0.05 theory of phosphorus when the reformat was leaded with 3 cc. of tetraethyl lead per gallon.

This invention is not to be limited to the specific examples herein presented for the purpose of illustrating the invention as modifications thereof within the skill of the art are contemplated. The scope of the invention is limited only by the claims appended hereto.

What is claimed is:

1. An improved cracked naphtha component for a gasoline composition to which an alkyl lead antiknock agent is to be added, which improved naphtha component is obtained by treating a cracked naphtha fraction, containing materials that normally tend to cause engine fouling when employed as a component of an internal combustion engine fuel, at from 150 to 350° F. for from ½ to 10 hours with from ½ its weight to an equal weight of the reaction product of a sulfide of phosphorus with a C<sub>2</sub> to C<sub>4</sub> olefin polymer of from 250 to 10,000 molecular weight; distilling the naphtha material thus obtained; and recovering the treated improved naphtha fraction as the naphtha distillate.

2. A naphtha component as defined by claim 1 wherein said olefin polymer comprises polyisobutylene of from 1000 to 5000 molecular weight.

3. A naphtha component as defined by claim 1 wherein said cracked naphtha fraction comprises a thermal reformat fraction boiling in the range of 200 to 550° F.

4. A naphtha component as defined by claim 1 wherein said reaction with said sulfide of phosphorus is conducted at temperatures in the range of about 200 to 600° F.

5. The method of improving a cracked naphtha fraction containing materials that normally tend to cause engine fouling when said cracked naphtha fraction is employed as a component of an internal combustion engine fuel, which method comprises treating said naphtha fraction at from 150 to 350° F. for from ½ to 10 hours with from ½ its weight to an equal weight of the reaction product of a sulfide of phosphorus with a C<sub>2</sub> to C<sub>4</sub> olefin polymer of from 250 to 10,000 molecular weight, distilling the naphtha material thus obtained and recovering the treated naphtha fraction as a distillate.

6. A method as defined in claim 5 wherein said reaction of said sulfide of phosphorus with said olefin poly-

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mer is conducted at temperatures in the range of about 200 to 600° F.

7. The method as defined by claim 5 wherein said olefin polymer comprises polyisobutylene of from 1,000 to 5,000 molecular weight.

8. The method as defined by claim 5 wherein said cracked naphtha fraction comprises a thermal reformat fraction boiling in the range of 200° to 550° F.

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