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MOTOR FUEL

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This invention relates to fuels and more particularly to leaded gasolines for high compression, spark ignition engines.

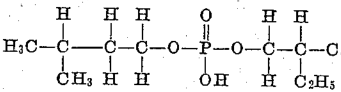
It has long been recognized that for greater economy with respect to fuel requirement and greater efficiency in the operation of a gasoline engine high compression ratios are desired. As a result, several automobile manufacturers have increased the compression ratios of their spark ignition engines to 8.5 to 1 and even as high as 9 to 1, the future trend of the automotive industry indicating that substantially all engines will be operating at such high compression ratios in the foreseeable future. In order to obtain smooth engine operation at these high compression ratios, it has been necessary to employ a fuel having a high octane number. To obtain a high octane number most fuels require the addition of an anti-knock agent such as tetraethyl lead. While the addition of tetraethyl lead to gasoline improves its octane number, the resulting fuel has certain disadvantages arising from the presence of the lead. One of the chief objections to the use of leaded gasolines arises from the tendency of the fuel upon being burned to form decomposition products of lead which products are deposited on the walls of the combustion chambers of the engine and on the electrodes and insulators of the spark plugs, thus reducing the efficiency of the engine and offsetting to some extent the increased efficiency obtained by the high compression ratios. The net effect of these deposits is that the octane number requirement of the engine gradually increases as the engine is operated until some equilibrium octane number requirement is reached. The equilibrium octane number requirement of some engines which have been in operation for 100 or more hours may be 10 to 15 numbers higher than the octane number requirement of the same engines at the start of their operation.

In an attempt to overcome the detrimental effect of the deposits of lead decomposition products in an engine, various "scavenging" agents have been added to the fuel to change the form of the lead decomposition products to those which are more volatile and thus less likely to be deposited within the engine. For example, various volatile alkyl halides such as ethylene dibromide and/or ethylene dichloride have been used with tetraethyl lead to produce the corresponding halides of lead which are more volatile than the oxides. The volatile alkyl halides, however, have not completely overcome the deposition of the decomposition products. The decomposition products comprise various salts including the oxides, sulfates, bromides and chlorides of lead. These decomposition salts deposited within the combustion chamber of the engine have been found to alter adversely the ignition characteristics. The adverse effect encountered as a result of the deposits of the decomposition salts is frequently evidenced by "engine knocking." The "knocking" thus encountered is that associated with preignition of the fuel in the combustion chamber of a spark ignition engine. This "knocking" associated with preignition

should not be confused with "knocking" due to explosive autoignition of the unburned portion of the fuel-air mixture to be traversed by the normal flame from the spark plug.

We have discovered that a motor fuel, and particularly a gasoline to which a mixture consisting of tetraethyl lead and an ethylene halide has been added in an amount sufficient to produce a leaded fuel having a research octane number of at least 90, can be improved with respect to its tendency to preignite in an engine by incorporating in said gasoline a small amount of the cyclohexylamine salt of 3-methylbutyl, 2-ethylhexyl acid orthophosphate.

The cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate is oil soluble and is a relatively stable compound under ordinary conditions of temperature and pressure. However, if the compound is heated to excessive temperatures, in the order of 260° F. or above, for long periods, it is converted into the corresponding amide compound, water being split off at such high temperatures. However, at temperatures below said conversion temperature, it is a relatively non-volatile material. At such elevated temperatures, it is an oily liquid, being rather viscous at room temperature. Upon prolonged standing at room temperature it becomes more or less crystalline, it being definitely crystalline at lower tempreatures. This salt is insoluble in water and aqueous liquids, and is resistant to hydrolysis. It can be readily prepared by reacting isoamyl octyl acid phosphate with cyclohexylamine in approximately equimolecular proportions, the reaction being so controlled as to produce substantially neutral reaction mixtures having a pH value within the range of 5.5 to 7.5. The isoamyl octyl acid phosphate employed is a di-ester of orthophosphoric acid having the following formula:



$$H_3C-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{H}{\overset{H}{C}}-\underset{C_2H_5}{\overset{H}{C}}-C_4H_9$$

This compound is also known as 3-methylbutyl,2-ethylhexyl acid orthophosphate.

The reaction between the cyclohexylamine and the isoamyl octyl acid phosphate is quite exothermic, thus requiring cooling means to maintain the reaction temperature within the desired limits. The temperature is advantageously maintained between 160° and 180° F.

The amount of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate which is incorporated in the fuel depends upon the amount of tetraethyl lead in the fuel. In general, the amount is based upon that amount theoretically required to convert the lead introduced into the fuel in the form of tetraethyl lead to lead orthophosphate. Good results are obtained by using at least 0.3 times the theoretical amount required. In general, it is not necessary to employ more than 1.5 times the amount theoretically required. Amounts greater than 1.5 times the theoretical amount can be employed, but for economic reasons, we prefer to use only the amount required to give the desired improvement. When less than 0.3 times the theoretical amount is used the preignition characteristic of the leaded gasoline in engines having compression ratios in the order of 9 to 1 is not substantially improved. The theoretical amount of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate required to convert the lead in tetraethyl lead to lead orthophosphate on a molecular proportion basis is two mols of the cyclohexylamine salt to three mols of tetraethyl lead.

In view of the fact that the amount of tetraethyl lead in the gasoline varies from one fuel to another, it is difficult to state on a weight basis the amount of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate based upon the weight of gasoline. However, once knowing the amount of tetraethyl lead present in the gasoline the amount of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate required can be readily calculated. Based upon fuels containing three cubic centimeters of tetraethyl lead per gallon of gasoline, we have determined that the amount of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate required in accordance with our invention is between 0.045 and 0.225 percent by weight based on the weight of a 60° API gravity gasoline. It will be understood of course that when commercially available products are used the optimum amount of product on a weight basis will vary depending upon the purity of the product. If, for instance, a commercially available anti-knock mixture comprising tetraethyl lead and ethylene halides is used, the percent by weight of the cyclohexylamine salt will be less than if substantially pure tetraethyl lead is used. For example, if three cubic centimeters of a tetraethyl lead mixture comprising 61.5 percent by weight of tetraethyl lead is used, the amount of the cyclohexylamine salt required in one gallon of a 60° API gravity gasoline to give between 0.3 and 1.5 theories is between about 0.027 and about 0.138 percent by weight. A cyclohexylamine material consisting of about 25 percent by weight of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate will be used in greater proportions than the pure product. In order to incorporate between 0.045 and 0.225 percent by weight of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate in gasoline when using the 25 percent concentrate, it would be necessary to employ between about 0.18 and about 0.9 percent by weight of the concentrate. Since the above weight percents are based upon three cubic centimeters of tetraethyl lead, the percents will vary directly with the lead content as more or less than three cubic centimeters of tetraethyl lead are employed. In any event, the amount of the cyclohexylamine salt of 3-methylbutyl,-2-ethylhexyl acid orthophosphate used is sufficient to inhibit or substantially prevent preignition of a gasoline containing tetraethyl lead and an ethylene halide in an amount normally tending to cause preignition of the gasoline in the combustion chamber of an engine.

The motor fuel to which the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate is added can comprise a mixture of hydrocarbons boiling in the gasoline boiling range. However, the problem of preignition is primarily present in heavily leaded gasolines having a research octane number of at least about 90. The gasoline to which the tetraethyl lead is added can be either a straight-run gasoline or a gasoline obtained from a conventional cracking process, or mixtures thereof. The gasoline to which the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate is added in accordance with our invention can also contain components obtained from processes other than cracking, such as alkylation, isomerization, hydrogenation, polymerization, hydrodesulfurization, hydroforming, "Platforming," or combinations of two or more of such processes, as well as synthetic gasoline obtained from the Fischer-Tropsch and related processes.

In addition to the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate, the leaded gasoline of our invention can contain other conventional additive agents including upper cylinder lubricants, oxidation inhibitors, anti-freeze agents, metal deactivators, dyes, and the like.

The cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate presents no particular problem with respect to its addition to gasoline. While the cyclohexylamine salt can be added directly to the gasoline, one convenient method of adding it to the fuel is to form a concentrate thereof with a liquid hydrocarbon solvent and thereafter adding the concentrate to the fuel. Any solvent which does not adversely affect the desirable properties of the fuel can be used. One concentrate which we have found suitable for the purpose of our invention consists of about 25 percent by weight of the cyclohexylamine salt of 3-methylbutyl, 2-ethylhexyl acid orthophosphate and 75 percent by weight of toluene. The concentrate can, of course, contain other conventional gasoline additives, if desired.

Thus, a gasoline-benefiting concentrate can be formed by admixing an organo-metallic anti-knock composition with the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate. In such instances, a mutual solvent may be desirable. When such gasoline-benefiting concentrates are prepared, they can, of course, contain other additive agents such as an oxidation inhibitor, an anti-freeze agent, a metal deactivator, an upper cylinder lubricant, a lead scavenging agent, a dye and the like. Since the amount of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate depends upon the amount of the tetraethyl lead present, this method of adding the cyclohexylamine salt to the gasoline serves as a convenient way of adding the correct amount of cyclohexylamine salt to unleaded gasolines. Thus, a gasoline-benefiting concentrate can be made by admixing tetraethyl lead with the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate. Such concentrates advantageously contain volatile alkyl halides. Thus, a gasoline-benefiting concentrate can be made by admixing tetraethyl lead and a halide of ethylene with the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate wherein the cyclohexylamine salt is present in an amount between 0.3 and 1.5 times the theoretical amount required to convert the lead to lead phosphate.

The proportions of the constituents in such a gasoline-benefiting concentrate may vary depending upon the characteristics of the base gasoline as well as the compression ratio of the engine in which the gasoline is to be used. Good results can be obtained, however, with a composition consisting of about 35 to about 55 percent by weight of tetraethyl lead, about 20 to about 35 percent by weight of a mixture of ethylene halides and about 10 to about 45 percent by weight of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate, the cyclohexylamine salt being present in at least 0.3 times the theoretical amount required to convert the lead in the tetraethyl lead to lead phosphate.

One convenient method of preparing a gasoline-benefiting concentrate is to start with a commercially available concentrate comprising tetraethyl lead and the halides of ethylene. One such commercially available product consists of about 61.5 percent by weight of tetraethyl lead, about 17.9 percent by weight of ethylene dibromide and about 18.8 percent by weight of ethylene dichloride. This commercially available concentrate has a specific gravity of 1.587 at 20° C. The amount of the gasoline-benefiting concentrate added to gasoline will vary depending upon the octane number of the gasoline desired. Ordinarily the concentrate is added in an amount sufficient to incorporate between about one and about three cubic centimeters of tetraethyl lead in a gallon of gasoline.

In order to illustrate the improved preignition characteristics obtained with a fuel of the invention, a test was employed in which the fuel was burned in a stationary Cadillac engine having a 9 to 1 compression ratio. In this test, the engine was operated on a cycling schedule consisting of three minutes at 1500 R. P. M., road load followed by a one-minute idle at 450 R. P. M. At the end of each twenty-four hours under this cycling schedule, preignition determinations were made at 1000 and 2000 R. P. M. After the preignition determinations were made the engine was then put back on the cycling schedule. The test was continued until violent preignition was encountered for two successive periods, regardless of whether such preignition occurred at 1000 or 2000 R. P. M. The engine conditions at the time of the preignition evaluation were as follows:

Speed	1000 and 2000 R. P. M.
Spark advance	10°
Air:fuel ratio	11.5:1 and 10.3:1 at 1000 and 2000 R. P. M., respectively.

In this test the load and throttle position are varied, dependent upon when preignition is encountered. At the start of the test the engine is under no load. The throttle is gradually increased until preignition is observed. If full throttle is reached without preignition, the engine is operated at full throttle for 30 seconds, or less if preignition occurs sooner. If preignition is not encountered after 120 hours (5 days), the test is usually discontinued. The data set forth in Table I was obtained when the Cadillac engine was operated under the above test procedure with a reference gasoline, normally tending to preignite, containing about 2.0 cubic centimeters (3.32 grams) of tetraethyl lead and about 1.98 grams of about a 50–50 mixture of ethylene dibromide and ethylene dichloride per gallon of gasoline. The comparative test was made with the same base gasoline containing 0.78 gram (0.3 times the theory) of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate per gallon of gasoline. This quantity of the cyclohexylamine salt was incorporated in the gasoline in the form of a concentrate consisting of 25 percent by weight of the cyclohexylamine salt and 75 percent by weight of toluene. The concentrate was added in an amount corresponding to 0.106 percent by weight based on the gasoline. The gasoline employed in this test had a CFR research method octane number of about 96.

Table I

Hours of Operation	Amount of preignition			
	With Reference Gasoline at—		With Reference Gasoline Containing 0.78 Gram (0.3 Times the Theory) of the Cyclohexylamine Salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate at—	
	1,000 R. P. M.	2,000 R. P. M.	1,000 R. P. M.	2,000 R. P. M.
0	none	none	none	none.
24	do	do	do	Do.
48	violent	violent	mild	Do.
72	do	do	none	Do.
96			do	Do.
120			mild	mild.

It will be noted from the data in Table I that the engine operating with the reference gasoline went into violent preignition within 48 hours. This preignition was sustained as determined after cycling was continued for another 24 hours. Since sustained violent preignition occurred within 72 hours, the engine was not operated past the 72-hour period. When the same engine was operated with the reference gasoline containing 0.3 times the theory of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate, there was no violent preignition even after 120 hours of operation. Thus, it can be seen that the normal tendency of the reference gasoline to preignite was overcome by the addition of 0.3 times the theory of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate.

While our invention is described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A motor fuel consisting essentially of a gasoline containing tetraethyl lead and an ethylene halide in an amount normally tending to cause preignition of said gasoline in the combustion chamber of a spark ignition engine and at least 0.3 times the theoretical amount required to convert the lead to lead phosphate of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate.

2. A motor fuel consisting essentially of a gasoline containing tetraethyl lead and an ethylene halide in an amount normally tending to cause preignition of said gasoline in the combustion chamber of a spark ignition engine, said fuel containing between 0.3 to 1.5 times the theoretical amount required to convert the lead to lead phosphate of the cyclohexylamine salt of 3-methylbutyl,-2-ethylhexyl acid orthophosphate.

3. A gasoline-benefiting concentrate consisting essentially of tetraethyl lead containing the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate in an amount between about 0.3 and 1.5 times the theoretical amount required to convert the lead to lead phosphate.

4. A gasoline-benefiting concentrate consisting of about 35 to about 55 percent by weight of tetraethyl lead, about 20 to about 35 percent by weight of a mixture of ethylene halides and about 10 to about 45 percent by weight of the cyclohexylamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate, the cyclohexylamine salt being present in at least 0.3 times the theoretical amount required to convert the lead in said tetraethyl lead to lead phosphate.

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