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MOTOR FUEL

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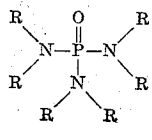
5 Claims. (Cl. 44—69)

This invention relates to fuels and more particularly to leaded-fuels 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. In order to obtain smooth operation at high compression ratios, it has generally 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-fuels arises from the tendency of the fuel upon being burned to form lead deposits on the walls of the combustion chamber of the engine and on the terminals of the spark plugs, thus reducing the efficiency of the engine. 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 requirement is reached. The equilibrium octane number requirement of some engines which have been in operation for 100 or more hours may be 50 to 60 percent 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 lead deposits in an engine, various "scavenging" agents have been added to the fuel to change the form of the lead deposit to one which is less detrimental. For example, various volatile alkyl halides such as ethylene dibromide and/or ethylene dichloride have been used with the result that the lead deposits have comprised the bromides and chlorides of lead. The bromides and chlorides of lead deposited within the combustion chamber of the engine, however, have been found to alter adversely the ignition characteristics. The adverse effect encountered as a result of the deposits of the chlorides and bromides of lead is frequently evidenced by "engine knocking." The "knocking" thus encountered is that resulting from the initiation of a flame front at any point in the fuel-air mixture prior to the regularly-timed spark ignition. This "knocking" 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 leaded-gasoline can be improved with respect to its tendency to preignite in an engine and that the octane number requirement of an engine in which it is used can be lowered by incorporating in the fuel a small amount of an organo-phosphoramide having the following structural formula:



where R is a substituent selected from the class consisting of an alkyl group and hydrogen. Specific examples of the alkyl radicals which we intend to include are methyl; ethyl; propyl; isopropyl; butyl; sec-butyl; amyl; hexyl; heptyl; octyl; nonyl; decyl; undecyl; dodecyl; tridecyl; tetradecyl; pentadecyl; hexadecyl; heptadecyl; octadecyl; and the like.

While all the compounds designated by the above structural formula can be used to produce a motor fuel having improved preignition characteristics, it will be understood, of course, that their effectiveness may vary.

The alkyl-phosphoramides are particularly advantageous for use in the motor fuels of our invention. While compounds wherein the R group is a long-chain alkyl radical such as octyl, nonyl, decyl, octadecyl, and the like can be employed, we prefer, for economic reasons, to use those alkyl-phosphoramides wherein the alkyl group contains from 1 to 4 carbon atoms. For example, we prefer to employ the methyl, ethyl, propyl and butyl phosphoramides. Hexamethylphosphoramide has been found to be particularly effective in reducing the preignition characteristics of a gasoline normally tending to preignite in the combustion chamber of a spark-ignition engine. Hexamethylphosphoramide has also been found to be effective in reducing the octane number requirement of an engine.

Specific examples of other compounds coming within the above structural formula and which can be used to produce an improved motor fuel are N,N',N''-trimethylphosphoramide; N,N',N''-triethylphosphoramide; N,N,N'-triisopropylphosphoramide; and N,N',N''-trimethyl-N,N',N''-tributylphosphoramide.

While any single organo-phosphoramide can be used in conjunction with a motor fuel to produce the improved fuels of our invention, it should be understood that mixtures of two or more organo-phosphoramides can be used. For example, a mixture of trimethylphosphoramide and hexamethylphosphoramide can be used instead of either one of these compounds alone. Therefore, when the term "organo-phosphoramide" is used herein and in the appended claims, it will be understood that one or more organo-phosphoramides is intended.

The amount of the organo-phosphoramide which is incorporated in the fuel depends to some extent upon the particular fuel employed, as well as the particular organo-phosphoramide selected. 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. While improved results can be obtained with very small amounts, amounts corresponding to at least about 0.1 times that theoretically required are preferred. Especially good results are obtained by the use of at least about 0.2 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. Therefore, we prefer to employ an amount equal to about 0.2 to about 1.5 times that theoretically required to convert the lead to lead orthophosphate. 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 organo-phosphoramide based upon the weight of gasoline. However, once knowing the amount of tetraethyl lead present in the gasoline, it is an easy matter to calculate the amount of the organo-phosphoramide required. Most gasolines on the market today contain up to about three cubic centimeters of tetraethyl lead per gallon of gasoline. Based upon fuels containing up to about three cubic centimeters of tetraethyl lead per gal-

lon of gasoline, we have determined that the amount of organo-phosphoramide required in accordance with our invention is between about 0.001 and about 4.0 percent by weight based on the weight of the gasoline. It will be understood, of course, that the optimum amount on a weight basis for one particular compound may not be the optimum amount for another compound. One reason for this is that the effectiveness of the compounds varies from one compound to another. Another reason is that the molecular weight of one compound may be twice the molecular weight of another compound, so that to get an equivalent amount of phosphorus when using the compound having the greater molecular weight, one is required to use twice the amount of compound on a weight basis. In any event, the amount of organo-phosphoramide used is sufficient to inhibit or substantially prevent preignition of a gasoline normally tending to preignite in the combustion chamber of an engine.

The motor fuel to which the organo-phosphoramide is added can comprise a mixture of hydrocarbons boiling in the gasoline boiling range. For instance, the gasoline employed can be either a straight-run gasoline or a gasoline obtained from a conventional cracking process, or mixtures thereof. The gasoline to which the organo-phosphoramide 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 organo-phosphoramide, the motor fuel can contain other "additive" agents including oxidation inhibitors, anti-rust, anti-knock and anti-freeze agents, metal deactivators, dyes, and the like. When the anti-knock agent is an organo-metallic composition such as tetraethyl lead, the motor fuel may also contain a lead scavenging agent such as a volatile alkyl halide or a mixture of volatile alkyl halides such as ethylene dichloride and/or ethylene dibromide. When these halides are used they are ordinarily present in an amount corresponding to about one or two cubic centimeters per gallon of gasoline. As the amount of tetraethyl lead used goes down, however, the lead scavenging agent required also decreases. In accordance with our invention, the organo-phosphoramide can replace in whole or in part the volatile alkyl halide lead scavenging agent. However, the organo-phosphoramide can be used in conjunction with the usual amount of volatile alkyl halide without deleteriously affecting the beneficial effects of the organo-phosphoramide.

The organo-phosphoramides present no particular problem when it comes to adding them to the gasoline. While the organo-phosphoramide can be added directly to the gasoline, one convenient method of adding it to the fuel is by forming a concentrate thereof, thereafter adding the concentrate to the fuel. Thus, a gasoline-benefiting concentrate can be formed by admixing an organo-metallic anti-knock composition with an organo-phosphoramide. In some instances, it may be desirable to employ a mutual solvent. Any solvent which does not adversely affect the desirable properties of the fuel can be used. The concentrate can, of course, contain other additive agents such as an oxidation inhibitor, an anti-rust agent, an anti-knock agent, an anti-freeze agent, a metal deactivator, a scavenging agent and a dye. When the anti-knock agent is an organo-metallic composition, such as tetraethyl lead, the scavenging agent can comprise a mixture of ethylene dibromide and ethylene dichloride. Since the amount of organo-phosphoramide required depends to some extent upon the amount of the organo-metallic anti-knock composition, this method of adding the organo-phosphoramide to the gasoline serves as a convenient way of adding the correct amount. Thus, a gasoline-benefiting concentrate can be made by admixing tetraethyl lead with an alkyl-phosphoramide wherein the alkyl-phosphoramide is present in an amount between about 0.1 and 1.5 times the theoretical amount required to convert the lead to lead phosphate.

In order to illustrate the decrease in octane number requirement for an engine when operating with an improved gasoline in accordance with this invention, octane rating tests were made in a single-cylinder engine. The engine installation used was a modification of the standard ASTM assembly as described in the laboratory knock-rating test procedure CRC designation F–1–545 and CRC designation F–2–545. These tests are described in the CRC Handbook, 1946 edition, compiled by the Coordinating Research Council, Incorporated. The engine assembly was modified to the extent that the Waukesha CFR engine was equipped with an L-head cylinder instead of an overhead valve.

The engine was operated on a cycling schedule alternating between the following conditions:

Duration, seconds	50	150.
Speed, R. P. M.	600	900.
Load	None	Full.
Air:Fuel Ratio	13:1	11:1.
Ignition Timing	TDC [1]	TDC.[1]
Coolant Temperature, °F	148±3	148±3.
Oil Temperature, °F	160±5	160±5.
Carburetor, Intake Air, °F	110±5	110±5.
Humidity Control	Ice Tower	Ice Tower.

[1] TDC=Top Dead Center.

In carrying out these tests, octane number requirements were recorded at the beginning of each test when the engine was clean and then periodically until the octane requirement had reached an equilibrium point. Table I sets forth the data obtained when the engine was operated with a reference gasoline containing about three cubic centimeters of tetraethyl lead per gallon of gasoline and the same leaded-gasoline containing 1.5 grams of hexamethylphosphoramide per gallon of gasoline. The amount of hexamethylphosphoramide employed corresponded to about 0.73 times that theoretically required to react with all of the lead present to form lead phosphate. In each case, the gasoline also contained a small amount of an antioxidant, a metal deactivator, a lead scavenging agent, and a dye.

Table I

Hours of Operation	Engine Octane Requirement [1]	
	Reference Gasoline	Reference Gasoline Containing 1.5 Grams of Hexamethylphosphoramide Per Gallon of Gasoline
0	55	53
12	74	52
24	82	50
48	85	51
72	88	51
100	88	63
120	88	68
140	88	68

[1] Research method.

The above data show that the equilibrium octane requirement of a single cylinder CFR engine employed in the test was about 88 when operating with the reference gasoline and about 68 when operating with the reference gasoline containing 1.5 grams of hexamethylphosphoramide per gallon of gasoline. Thus, the equilibrium octane requirement of the engine operating with the improved gasoline was about 20 numbers below the requirement of the same engine operating with unimproved gasoline. Table II gives the inspection data on the gasolines used in the engine octane number requirement test.

Table II

Inspection	Reference Gasoline	Reference Gasoline Containing 1.5 Grams of Hexamethylphosphoramide Per Gallon of Gasoline
Gravity, °API	60.8	60.3
Distillation, Gasoline:		
Over Point, °F	101	101
End Point, °F	411	416
50 percent Evaporation, °F	224	228
Recovery, percent	98.7	98.8
Residue, percent	1.2	1.2
Octane Rating:		
Motor Method	82.7	81.6
Research Method	92.9	92.8

In order to illustrate the improved results with respect to preignition, a test was employed in which the fuel was burned in a stationary Cadillac engine having a 9:1 compression ratio. The engine conditions at the time of the preignition evaluation were as follows:

Speed ..... 1,000 and 2,000 R. P. M.
Spark advance ..... 10°.
Air:Fuel ratio ..... 11.5:1 and 10.3:1 at 1,000 and 2,000 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 III was obtained when the Cadillac engine was operated under the above test procedure with a reference gasoline normally tending to preignite containing about 1.5 cubic centimeters of tetraethyl lead per gallon of gasoline and the same leaded-gasoline containing 1.0 (1.1 times the theory) gram of hexamethylphosphoramide per gallon of gasoline. In each instance, the gasoline also contained a small amount of an antioxidant, a metal deactivator, and a lead scavenging agent.

Table III

Hours of Operation	Tests for Preignition	
	Reference Gasoline	Reference Gasoline Containing 1.0 Gram of Hexamethylphosphoramide Per Gallon of Gasoline
0	No preignition	No preignition.
48	Mild preignition	Do.
72	Violent preignition	Do.
100	do	Do.
120	do	Mild preignition.

It will be noted from the data in Table III that the engine operating on the reference gasoline showed mild preignition within 48 hours and that violent preignition occurred within 72 hours. When the same engine was operated with the improved gasoline of the invention, there was no preignition even after 100 hours of operation. After 120 hours of operation with the improved fuel, only mild preignition was observed.

Table IV gives the inspection data on the gasolines employed in the preignition test.

Upon examination of the engine after operation with the reference gasoline and the reference gasoline containing hexamethylphosphoramide, it was observed that the engine deposits were dissimilar in many respects.

Table IV

Inspection	Reference Gasoline	Reference Gasoline Containing 1.0 Gram of Hexamethylphosphoramide Per Gallon of Gasoline
Gravity, °API	59.6	60.8
Distillation, Gasoline:		
Over Point, °F	98	103
End Point, °F	402	401
50% Evaporation, °F	218	208
Recovery, percent	98.0	98.0
Residue, percent	1.0	1.2
Octane Rating:		
Motor Method	84.0	83.2
Research	96.0	95.7

The engine deposits resulting from using the reference gasoline were brownish-black in color, had a tendency to adhere to metal surfaces and, when scraped from metal surfaces, were inclined to peel off in the form of flakes. The engine deposits resulting from using the reference gasoline containing hexamethylphosphoramide, however, were light-colored, powdery, and were removed from the metal surfaces upon which they had been deposited with little difficulty.

In each of the preignition tests described above, when using the reference gasoline and the same gasoline containing hexamethylphosphoramide, the combustion chambers and spark plugs of the Cadillac engine at the start of the test were substantially free from deposits giving rise to preignition. In order to illustrate the effect of the improved motor fuel of the invention on an engine in which preignition has already commenced, the above test was repeated with the exception that when deposit-induced preignition was encountered when using the reference gasoline, the fuel was changed to the gasoline containing hexamethylphosphoramide without shutting down the engine. Thus, when violent preignition was encountered with the reference gasoline at 72 hours, the fuel supply was switched to the same gasoline containing 1.0 gram of hexamethylphosphoramide. While the violent preignition did not subside immediately, probably because of the deleterious deposits laid down by the reference gasoline, there was a gradual improvement. For instance, at the end of 16 hours of operation with the fuel containing hexamethylphosphoramide, the engine was still violently preigniting. However, at the end of 39 hours only mild preignition was encountered and at the end of 77 hours no preignition was encountered. Even after 101 hours of operation no preignition was evidenced. However, when the engine was switched back to the reference gasoline, mild preignition was encountered within 22 hours and violent preignition occurred within 46 hours. Table V gives the data just reported in tabular form.

Table V

Hours of Operation			Tests for Preignition
Reference Gasoline	Reference Gasoline Containing 1.0 Gram of Hexamethylphosphoramide Per Gallon of Gasoline	Total Hours	
0	----------	0	No preignition.
48	----------	48	Mild preignition.
72	----------	72	Violent preignition.
---------	16	88	Violent preignition.
---------	39	111	Mild preignition.
---------	63	135	Do.
---------	77	149	No preignition.
---------	101	173	Do.
22	----------	195	Mild preignition.
46	----------	219	Violent preignition.

The improved results obtained wtih a motor fuel of the invention are thus quite striking even when starting with an engine in which preignition has already been encountered.

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 having improved preignition qualities comprising a major amount of gasoline containing about 1 to about 3 cubic centimeters of tetraethyl lead per gallon of gasoline, a lead scavenging amount of a halo-hydrocarbon and between about 0.1 and 1.5 times the theoretical amount of an alkyl-phosphoramide required to convert the lead to lead phosphate, wherein the alkyl group in said alkyl-phosphoramide contains from 1 to 4 carbon atoms.

2. A motor fuel having improved preignition qualities comprising a major amount of gasoline containing about 1 to about 3 cubic centimeters of tetraethyl lead per gallon of gasoline, a lead scavenging amount of a halo-hydrocarbon and between about 0.001 and about 4.0 percent by weight based on the gasoline of hexamethylphosphoramide.

3. A motor fuel having improved preignition qualities comprising a major amount of gasoline containing about 1 to about 3 cubic centimeters of tetraethyl lead per gallon of gasoline, a lead scavenging amount of a halohydrocarbon and between about 0.1 and 1.5 times the theoretical amount of hexamethylphosphoramide required to convert the lead to lead phosphate.

4. A gasoline preignition improving additive comprising a major amount of tetraethyl lead containing a lead scavenging amount of a halohydrocarbon and an alkyl-phosphoramide in an amount between about 0.1 and 1.5 times the theoretical amount required to convert the lead to lead phosphate, wherein the alkyl group in said alkyl-phosphoramide contains from 1 to 4 carbon atoms.

5. A gasoline preignition improving additive comprising a major amount of tetraethyl lead containing a lead scavenging amount of a halohydrocarbon and hexamethylphosphoramide in an amount between about 0.1 and 1.5 times the theoretical amount required to convert the lead to lead phosphate.

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