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[54] **FUELS FOR AUTOMOTIVE ENGINES**

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[57] **ABSTRACT**

Exhaust valve seat wear of automotive engines operated on unleaded gasoline can be catastrophic under severe operating conditions. This results in severe loss of engine power, marked reduction in fuel economy and sharp increases in exhaust emissions to intolerable levels. This problem may be ameliorated by utilizing high octane gasolines containing suitable quantities of phosphorus esters. Methods of preparing and dispensing the fuels are also described.

28 Claims, No Drawings

FUELS FOR AUTOMOTIVE ENGINES

This invention relates to fuel compositions for spark ignition internal combustion engines. More particularly, this invention is concerned with providing new and useful gasoline fuels to ameliorate certain catastrophic engine failures which might otherwise be encountered in actual service.

BACKGROUND

Proposals have been made to require the elimination of alkyllead antiknock agents from gasoline. Implementation of such proposals would, however, create new problems of a serious nature, such as more rapid depletion of natural resources, increased costs to the refiner and the motoring public, and the like.

This invention is concerned with one such problem which, if not eliminated or at least ameliorated, could prove disastrous.

THE INVENTION

It has been discovered that exhaust valve seat wear with unleaded gasoline can be catastrophic under severe operating conditions. For example, using normal passenger car cycling schedules, engine dynamometer tests have shown that such valve seat wear is 25 to 50 times as great as that occurring with normally leaded gasolines. Among the consequences of excessive exhaust valve seat wear are severe loss of engine power, marked reduction in fuel economy and, perhaps of paramount concern, sharp increases in exhaust emissions to intolerable levels.

This invention provides the means of ameliorating the severity of the foregoing disastrous consequences.

In accordance with this invention, there is provided an unleaded automotive gasoline fuel of sufficiently high octane quality to satisfy the octane requirements of automotive engines but having the tendency of causing an excessive rate of exhaust valve seat wear containing a gasoline soluble, engine inductible, fully esterified ester of an oxy-acid of phosphorus (e.g., a phosphate ester, a phosphite ester, etc.) in an amount sufficient to decrease the rate of such wear. The foregoing compositions will normally require gasoline fuels having a Research Octane Number of at least about 90, and preferably, of at least about 95. In addition, it is preferable to formulate the gasoline fuel such that it has a content of aromatic gasoline hydrocarbons ranging from about 10 to about 60 volume percent, a content of olefinic gasoline hydrocarbons ranging from 0 to about 30 volume percent and a content of saturated gasoline hydrocarbons ranging from about 40 to about 80 volume percent, these percentages being based on the whole fuel.

The amounts of the phosphorus esters used in the base fuel will be dependent both on the precise makeup of the gasoline fuel itself and the identity and character of the ester being utilized. As a general rule, however, it will be found that the minimum quantity will be in the order of at least about 0.02 gram of phosphorus per gallon and thus for general purposes it will generally be sufficient to employ the ester in an amount equivalent to from about 0.02 to about 1.0 gram of phosphorus per gallon although even greater quantities of the additives may be found entirely acceptable. Preferred concentrations fall in the range of from about 0.05 to about 0.5 gram phosphorus per gallon.

Among the preferred embodiments of this invention is an unleaded automotive gasoline fuel having a Research Octane Number of at least about 100 and having a content of aromatic gasoline hydrocarbons of at least about 25 volume percent based on the whole fuel and having the tendency of causing an excessive rate of exhaust valve seat wear containing from about 0.05 to about 0.5 gram of phosphorus per gallon of a gasoline soluble, engine inductible, fully esterified ester of an oxy-acid phosphorus having a boiling point at (or extrapolated to) atmospheric pressure of not more than about 425°C., the quantity being sufficient to decrease the rate of such wear substantially uniformly from cylinder to cylinder.

This invention also provides a method of ameliorating exhaust valve seat wear of automotive vehicular engines operating on an unleaded gasoline which comprises dispensing to such vehicles an unleaded gasoline fuel of sufficiently high octane quality to satisfy the octane requirements of the engines, said fuel containing from about 0.02 to about 1.0 gram of phosphorus per gallon of a gasoline soluble, engine inductible, fully esterified ester of an oxy-acid of phosphorus.

Still another embodiment of this invention involves an improvement in the manufacture of finished gasolines for use in automotive fuels, this improvement comprising formulating unleaded gasoline having a Research Octane Number of at least about 90 and preferably from about 90 to about 104, a content of aromatic gasoline hydrocarbons ranging from about 10 to about 60 volume percent, a content of olefinic gasoline hydrocarbons ranging from 0 to about 30 volume percent and a content of saturated gasoline hydrocarbons ranging from about 40 to about 80 volume percent, said percentages being based on the whole fuel; and incorporating in the finished gasoline from about 0.02 to about 1.0 gram of phosphorus per gallon of a gasoline soluble, engine inductible, fully esterified ester of an oxy-acid of phosphorus so that said finished fuel does not have the tendency of causing an excessive rate of exhaust valve seat wear in the engines of the vehicles in which it is used.

The above and other embodiments, features, advantages, and characteristics of this invention will become still further apparent from the ensuing description and appended claims.

ADDITIONAL CONSIDERATIONS RELATIVE TO THE BASE FUEL

In formulating the fuels of this invention the requisite octane quality (e.g., a Research Octane Number of at least about 90) is best achieved by selecting appropriate blending stocks and blending them in suitable proportions. In accordance with present refinery technology the achievement of these high octane levels is most readily accomplished by employing aromatics (e.g., BTX, catalytic reformate or the like) or alkylate (e.g., C_6–C_9 saturates prepared by reacting C_4 olefin with isobutane using an acid catalyst such as HF or H_2SO_4) or blends of both of these hydrocarbon types. The balance of the whole fuel may be made up of other components such as other saturates, olefins, or the like. The olefins are generally formed by using such procedures as thermal cracking, catalytic cracking and polymerization. Dehydrogenation of paraffins to olefins can supple-

ment the gaseous olefins occurring in the refinery to produce feed material for either polymerization or alkylation processes. The saturated gasoline components comprise paraffins and naphthenes. These saturates are obtained from (1) virgin gasoline by distillation (straight run gasoline), (2) alkylation processes (alkylates) and (3) isomerization procedures (conversion of normal paraffins to branched chain paraffins of greater octane quality). Saturated gasoline components also occur in so-called natural gasoline. In addition to the foregoing, thermally cracked stocks, catalytically cracked stocks and catalytic reformates contain saturated components.

The classification of gasoline components into aromatics, olefins and saturates is well recognized in the art. Procedures for analyzing gasolines and gasoline components for hydrocarbon composition have long been known and used. Commonly used today is the FIA analytical method involving fluorescent indicator adsorption techniques. These are based on selective adsorption of gasoline components on an activated silica gel column, the components being concentrated by hydrocarbon type in different parts of the column. Special fluorescent dyes are added to the test sample and are also selectively separated with the sample fractions to make the boundaries of the aromatics, olefins and saturates clearly visible under ultraviolet light. Further details concerning this method can be found in "1969 Book of ASTM Standards," Jan. 1969 Edition, under ASTM Test Designation D 1319–66T.

The motor gasolines used in formulating the improved fuels of this invention generally have initial boiling points ranging from about 80° to about 105°F. and final boiling points ranging from about 380° to about 430°F. as measured by the standard ASTM distillation procedure (ASTM D–86). Intermediate gasoline fractions boil away at temperatures within these extremes.

From the standpoint of minimizing atmospheric pollution to the greatest extent possible, it is best to keep the olefin content of the fuel as low as can be economically achieved as olefins reportedly give rise to smog-forming emissions, especially from improperly adjusted vehicular engines. Accordingly, in the preferred base stocks of this invention the olefin content will not exceed about 10 volume percent and the most particularly preferred fuels will not contain more than about 5 percent olefins. Table I illustrates the hydrocarbon type makeup of a number of particularly preferred fuels for use in this invention.

TABLE I

Hydrocarbon Blends of Particularly Preferred Base Fuels

Fuel	Volume Percentage Aromatics	Olefins	Saturates
A	35.0	2.0	63.0
B	40.0	1.5	58.5
C	40.0	2.0	58.0
D	33.5	1.0	65.5
E	36.5	2.5	61.0
F	43.5	1.5	55.0
G	49.5	2.5	48.0

It is also desirable to utilize base fuels having a low sulfur content as the oxides of sulfur tend to contribute an irritating and choking character to smog and other forms of atmospheric pollution. Therefore to the extent it is economically feasible the fuel will contain not more than about 0.1 weight percent of sulfur in the form of conventional sulfur-containing impurities. Fuels in which the sulfur content is no more than about 0.02 weight percent are especially preferred for use in this invention.

Utilization of non-hydrocarbon blending stocks or components in formulating the fuels of this invention is feasible and in some instances may actually be desirable. Thus, use may be made of methanol, tertiary butanol and other inexpensive, abundant and non-deleterious oxygen-containing fuel components.

It will of course be understood that the hydrocarbon fuels used in the practice of this invention will be resistant to oxidative degradation on exposure to air. Through improvements and advances made in refining techniques there is no longer a necessity for relying heavily upon use of catalytically cracked or thermally cracked stocks which tend to be the most oxidatively unstable fuel components. Greater utilization of the more stable components (aromatics and saturates) is now possible and customary. Nevertheless, in any instance where the base fuel has insufficient storage stability in the presence of air, use will be made of an appropriate quantity of an antioxidant. This provides a gasoline of suitable stability for storage, transportation, and use.

ADDITIONAL CONSIDERATIONS RELATIVE TO THE PHOSPHORUS ESTER

In choosing the phosphorus additives to be employed in the practice of this invention the essential requirements to be observed are, as already indicated, that they be soluble in the gasoline and that they be engine inductible. As a general rule the greater the gasoline solubility of the phosphorus ester, the greater the likelihood it will have sufficient engine inductibility. For this reason one should choose phosphorus esters which are either infinitely soluble or at least very highly soluble in the gasoline base stock being used. A vast amount of information is already available on the suitability of numerous phosphorus esters for use in preparing gasoline-type fuels by virtue of the fact that such phosphorus additives have long been known to have the properties of cooperating effectively with alkyllead antiknock agents in order to alleviate such problems as spark plug fouling, surface ignition, and rumble. Thus, phosphorus esters of the type described for such usage will generally be found satisfactory. See for example the disclosures of U.S. Pat. Nos. 2,405,560; 2,427,173; 2,765,220; 2,860,958; 2,870,186; 2,889,212; 2,897,071; 2,911,431; 2,948,599; 2,948,600; 3,000,709; 3,004,838; and 3,038,791, all disclosures of which are incorporated herein as if fully set forth in this specification.

From the cost effectiveness standpoint the use of tertiary phosphite esters, especially trihydrocarbyl phosphites, is preferred, although the most preferred phosphorus additives for use in this invention are the tertiary phosphate esters, especially trihydrocarbyl phosphates, as these are inexpensive and have the optimum physical characteristics for use in commercial service. Exemplary of such particularly preferred compounds are tricresyl phosphate (e.g., tri-o-cresyl phosphate, tri-p-cresyl phosphate, tri-m-cresyl phosphate and tricresyl phosphate involving mixed isomers); cresyl diphenyl phosphate; mixed methyl-phenyl phosphates

(see U.S. Pat. No. 3,038,791); and trimethyl phosphate.

Other parameters which should be considered in choosing the phosphorus ester for use in this invention include its stability, its water solubility and its volatility. Stability of the phosphorus additive is of course important as it must not rapidly deteriorate into sludge or other insoluble precipitates. As a general proposition, the vast majority of the phosphorus oxy-acid esters referred to in the above patents will be found to satisfy this stability parameter. Water solubility may assume significance in the event of prolonged storage or shipment of finished fuels in contact with water. Obviously if the additive is preferentially dissolved in the water it will no longer remain present in the fuel in order to exert the exhaust valve seat wear inhibiting characteristics for which it is intended pursuant to this invention. Here again, the vast majority of the phosphorus oxy-acid esters referred to in the above patents fulfill the requirement of being at most no more than slightly soluble in water.

The volatility of the phosphorus additive used in this invention bears a direct relationship with its engine inductibility. That is to say, the higher its volatility the more inductible the phosphorus ester. To achieve the best results possible from this invention one should utilize a normally liquid, gasoline soluble, engine inductible, fully esterified ester of an oxy-acid of phosphorus which has a volatility essentially equal to, or greater than, that of tricresyl phosphate. Thus the use of esters having a boiling point at, or extrapolated to, atmospheric pressure of not more than about 425°C. is especially recommended. Besides insuring that the additive is well inducted into the engine and thus does not contribute to excessive induction system deposits, this volatility is especially advantageous in assuring sufficient uniformity of distribution of the additive among the different cylinders of the engine. Self-evidently, if the additive does not reach all cylinders of an operating engine in sufficient quantity to inhibit exhaust valve seat wear in each valve train a failure may be rapidly encountered. Just as a chain is only as strong as its weakest link, the proper performance of the engine is only as efficient as its least efficient exhaust valve system. In short, if one exhaust valve seat is excessively worn the vehicle may emit intolerable quantities of atmospheric pollutants even though the remaining exhaust valve mechanisms are working up to designed efficiency. It will be seen therefore that it is especially desirable to use suitably volatile phosphorus esters in the practice of this invention—clearly phosphorus-containing salts or other non-volatile forms of phosphorus are unsuitable as they have insufficient engine inductibility and are incapable of adequate distribution among the cylinders of the engine.

The following examples illustrate the gravity of the problem and the extent to which it may be ameliorated by means of this invention.

EXAMPLE I

A brand new 1970 model four-door sedan made by a well known U.S. automobile manufacturer with a six-cylinder, 230 cubic inch engine and an automatic transmission was chosen to represent an inexpensive family car. After making sure all adjustments in the engine were set to manufacturer's specifications and a 500 mile break-in run completed, the car was loaded with sufficient weight to equal that of a family of two adults and three children. Turnpike operation was chosen to simulate a vacation trip. The car was equipped with a car top carrier and some weight was added to the trunk. Prior to the start of the program, the following measurements were made:

1. Exhaust valve stem tip height.
2. Exhaust emissions using the hot cycle portion of the Federal Cycle (see Federal Register, Volume 33, Number 108, Tuesday, June 4, 1968).
3. Maximum rear wheel power at 50 miles per hour.
4. Constant speed fuel consumption at 50 miles per hour, road load (beam reading of 8 horsepower).

Each day during the test, measurements were made of Items 1–4 above.

Each day the vehicle was driven an average of 883 miles in turnpike operation at an average speed of about 66 miles per hour. After each four hours of driving the car was refueled with the same gasoline from the same storage tank.

The factory fill oil was drained at the prescribed mileage and a popular 10W–30 motor oil was used during the remainder of the test run.

The gasoline used had an RON (Research Octane Number) of 101, contained no phosphorus, and was composed of 31.5 volume percent aromatics, 2.0 volume percent olefins and 66.0 volume percent saturates.

Exhaust valve seat recession began immediately after the test was started and continued for 10,500 miles at which point hydrocarbon exhaust emissions were almost 15 times that found at the beginning of the test. Carbon monoxide emissions had increased about 520 percent and oxides of nitrogen had been reduced about 1.8 percent. Due to the nature of the test schedule, all emission measurements were made using only the hot cycle portion of the Federal Cycle. At the end of the test power had dropped 36.2 percent and fuel economy had been reduced by about 25 percent. Inspection of the cylinder head revealed that exhaust valve seat recession in Cylinder No. 6 had reached 0.077 inch and had caused excessive valve seat run-out which resulted in excessively high exhaust emissions, poor fuel economy and loss in power. Compression pressures were found to be zero in Cylinder 6, and down 23 psi and 25 psi in Cylinders 3 and 5.

The results obtained are further summarized in the following Table.

TABLE II

Results of Highway Operation on Unleaded, Phosphorus-Free Gasoline

Test Miles	Exhaust Emissions, ppm Federal Cycle Hot Cycle Only HC	CO	NOx	Maximum Rear Wheel Power At 50 mph HP	Fuel Consumption At 50 mph Road Load MPG	Exhaust Valve Stem Tip-Height Change, Inches Avg.	Max.
536	83	.23	988	47.0	25.1	—	—
1378	79	.21	986	48.0	24.6	.003	.005
2256	85	.23	990	48.0	22.4	.006	.009
3190	141	.32	1144	48.0	25.0	.009	.018
4095	154	.26	1127	49.0	25.4	.012	.022
5055	98	.24	1132	48.5	25.8	.021	.037

TABLE II – Continued

Test Miles	Exhaust Emissions, ppm Federal Cycle Hot Cycle Only HC	CO	NOx	Maximum Rear Wheel Power At 50 mph HP	Fuel Consumption At 50 mph Road Load MPG	Exhaust Valve Stem Tip-Height Change, Inches Avg.	Max.
	Results of Highway Operation on Unleaded, Phosphorus-Free Gasoline						
5985	120	.26	1143	48.5	27.0	.031	.054
6858	119	.31	1149	47.5	24.9	.036	.062
7714	94	.39	1161	48.0	24.8	.039	.065
8507	94	.40	1168	48.0	25.4	.043	.071
9739	229	.51	1056	46.0	25.3	.050	.077
10526	1201	1.24	970	30.0	18.9	.056	.078

After replacement of the excessively worn engine parts the test was repeated using a different batch of the same 101 RON fuel which analyzed 46.5, 4.0, and 49.5 volume percent aromatics, olefins and saturates, respectively. This fuel, however, was blended so that it contained 0.11 gram of phosphorus as mixed methyl-phenyl phosphates (marketed by Ethyl Corporation as "Ethyl" Ignition Control Compound 3). With this phosphorus-containing fuel the test was conducted for 10,498 miles under the same conditions as described above. Valve seat wear averaged 0.009 inches with a maximum of 0.015 inch. Emissions increased more regularly than on the unleaded fuel without phosphorus, from 75 ppm hydrocarbons to 126 ppm. A fuller summary of the data from this test is presented in Table III.

TABLE III

Test Miles	Exhaust Emissions, ppm Federal Cycle Hot Cycle Only HC	CO	NOx	Maximum Rear Wheel Power At 50 mph HP	Fuel Consumption At 50 mph Road Load MPG	Exhaust Valve Stem Tip-Height Change, Inches Avg.	Max.
	Results of Highway Operation on Unleaded, Phosphorus-Containing Gasoline						
0	75	.52	922	47.5	23.7	—	—
2228	—	—	—	—	—	.004	.008
3073	99	.38	1075	50.5	30.6	.005	.007
5279	121	.34	1275	50.0	28.2	.006	.011
8397	111	.44	1201	—	—	.007	.011
10498	126	.38	1042	48.0	27.3	.009	.015

speeds from 3,100–3,400 rpm.

In each test of this series a non-leaded fuel blend of 75 volume percent aviation alkylate plus 25 volume percent toluene was employed. This fuel blend had a Research Octane Number of approximately 100. In one test the engine was operated on the above cycling schedule on this base fuel blend which did not contain any phosphorus additive. In the other two tests a phosphorus additive was incorporated in the same base fuel blend so that the effect of the additive on exhaust valve seat wear could be directly ascertained. In each of these tests the same crank case lubricating oil (a well known brand) was employed. The results of these tests are summarized in the following Table.

It can be seen from the above results that the use of

TABLE IV

Test	Fuel Composition	Test Duration, Hours	Inches per 100 Hours Exhaust Valve Seat Wear, Max. Cyl.	Avg. Cyl.
	Results of Operation under a Passenger Car Cycling Schedule			
1	Base Fuel - No P	107	0.106	0.082
2	Base Fuel plus 0.095 g. P/gal.[1]	200	0.015	0.008
3	Base Fuel plus 0.189 g. P/gal.[2]	200	0.014	0.009

[1]Mixed methyl-phenyl phosphates. [2]Trimethyl phosphate.

EXAMPLE II

A series of tests was conducted using a 1964 model of a popular make of a six-cylinder U.S. automobile engine having a 230 cubic inch displacement. In these tests the engine was operated on a dynamometer under a passenger car cycling schedule of city-suburban operation. This consisted of a 12-hour cycle divided into first an 8-hour period of city-suburban operation, followed by a 4-hour period of turnpike operation. The first 8-hour period was conducted at a basic speed of 2200 rpm (50 miles per hour road load) with 40-second engine idle operation interspersed every three minutes. The four hours of simulated turnpike operation involved one hour at constant speed of 3,200 rpm (75 miles per hour road load), one hour of cycling at speeds from 3,100–3,400 rpm, one hour at constant speed of 3,200 rpm, and finally one hour of cycling at

phosphorus additives pursuant to this invention does reduce the rate of exhaust valve seat wear and thereby extends the period before which a catastrophic failure may be encountered. Thus, the tendency of the unleaded fuels of causing an excessive rate of exhaust valve seat wear and consequent emission of excessive quantities of air pollutants via the engine exhaust is decreased although in point of fact, the reduced rates achieved by this invention are still significantly greater than experienced when using conventional leaded gasolines under the same service conditions.

Inasmuch as the phosphorus esters used in the practice of this invention are consumed in the engine combustion process so that their function is properly attributable to the elemental phosphorus content of the additive, the remainder of the phosphorus molecule is of significance only insofar as it contributes to the proper physical properties needed for an efficient and effec-

tive gasoline additive. Thus, as pointed out above, use may be made of a very large variety of fully esterified esters of oxy-acids of phosphorus so long as they are capable of being introduced in each cylinder of the engine in sufficient quantities so that on combustion the exhaust valve seat wear inhibiting action of the phosphorus will be manifested. Some exemplary phosphorus additives suitable for use in accordance with this invention are triethyl phosphate, dimethylpropyl phosphate, methyldipropyl phosphate, tripropyl phosphate, triisopropyl phosphate, diethylbutyl phosphate, tributyl phosphate, triisobutyl phosphate, triamyl phosphate, triisoamyl phosphate, triphenyl phosphate, ethyldiphenyl phosphate, phenyldibutyl phosphate, phenyldiethyl phosphate, xylyl diphenyl phosphate, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, triisopropyl phosphite, tributyl phosphite, triisobutyl phosphite, triisoamyl phosphite, diphenylpropyl phosphite, diphenylbutyl phosphite, triphenyl phosphite, tricresyl phosphite, dimethyl methane phosphonate, triethyl methane phosphonate, di-m-tolyl methane phosphonate, di-p-tolyl methane phosphonate, diethyl ethane phosphonate, dibutyl ethane phosphonate, diethylpropane phosphonate, dipropylpropane phosphonate, diethylbutane phosphonate, dibutylbutane phosphonate, diethyl-n-hexane phosphonate, dibutyl-n-octane phosphonate, diethyl-n-decane phosphonate, dibutyl-n-dodecane phosphonate, diethyl-n-tetradecane phosphonate, diethylphenylmethane phosphonate, dimethylbenzene phosphonate, diethylbenzene phosphonate, dibutylbenzene phosphonate and di-p-tolyl-p-tolune phosphonate. Other suitable phosphorus additives are described in the patents referred to hereinabove. Those skilled in the art should now have no difficulty in identifying other types of suitable additives for use in the practice of this invention. As pointed out above, particularly preferred additives because of their cost effectiveness, good physical properties and long history of successful commercial service in leaded gasoline are tricresyl phosphate, cresyldiphenyl phosphate, trimethyl phosphate, and mixed methyl-phenyl phosphates. It is worth noting that unlike the situation existing in leaded gasolines the utilization of phosphorus additives in an unleaded fuel would not involve some of the problems encountered in finding suitable phosphorus additives for use in leaded fuel. When employing a phosphorus additive in leaded gasoline it was essential to avoid excessive destruction of the antiknock effectiveness contributed by the alkyllead antiknock compound. In the present situation such a problem would not be encountered as there would be no interaction between lead and its deposits, and the phosphorus additive.

Antioxidants can be effectively used in the compositions of this invention. Particularly useful materials for this purpose are N,N′-di-sec-butyl-p-phenylene diamine, p-N-butylaminophenol, 4-methyl-2,6-di-tert-butyl phenol; 2,6-di-tert-butyl phenol and 2,4-dimethyl-6-tert-butyl phenol. Good results are achieved when these antioxidants are present in the fuels of this invention in concentrations ranging from about 0.5 to about 25 pounds per 1000 barrels.

Metal deactivators can also be used to advantage in the compositions of this invention. One very suitable material is N,N′-disalcylidene-1,2-diaminopropane. Generally speaking, concentrations ranging from about 0.1 to about 3 pounds per 1,000 barrels are satisfactory.

Additives imparting anti-icing and anti-stalling characteristics can also be used in the fuels of this invention. Preferred for this purpose are such materials as methanol, isopropanol, or mixtures thereof (concentrations ranging from about 0.5 to about 2 percent by volume are satisfactory); substantially neutral salts formed from primary alkyl amines and alkyl acid orthophosphates (concentrations corresponding to about 2.5 to about 25 pounds per 1,000 barrels are satisfactory); and the β-hydroxyethyl ethylenediamine amides of oleic acid (satisfactory concentrations range from about 50 to about 200 parts per million based on the fuel). Some of these additives also confer detergency properties upon the fuels.

Among the other additives which may be employed in the fuels of this invention are lead-free antiknock agents, dyes, induction system cleanliness agents, top-cylinder lubricants, corrosion inhibitors, inert solvents, and the like.

We claim:

1. An unleaded automotive gasoline fuel having a Research Octane Number of at least about 90 to satisfy the octane requirements of automotive engines but having the tendency of causing an excessive rate of exhaust valve seat wear containing a gasoline soluble, engine inductible, fully esterified organic ester of an oxy-acid of phosphorus in an amount sufficient to decrease the rate of such wear.

2. The composition of claim **1** wherein the ester is a phosphate ester.

3. The composition of claim **1** wherein the ester is a phosphite ester.

4. The composition of claim **1** wherein the ester is tricresyl phosphate.

5. The composition of claim **1** wherein the ester is cresyl diphenyl phosphate.

6. The composition of claim **1** wherein the ester is trimethyl phosphate.

7. The composition of claim **1** wherein the ester is mixed methyl-phenyl phosphates.

8. The composition of claim **1** wherein said ester is present in an amount equivalent to from about 0.02 to about 1.0 gram of phosphorus per gallon.

9. The composition of claim **1** wherein said ester is present in an amount equivalent to from about 0.05 to about 0.5 gram of phosphorus per gallon.

10. The composition of claim **1** wherein said ester is present in an amount equivalent to about 0.1 gram of phosphorus per gallon.

11. The composition of claim **1** wherein said gasoline fuel has a content of aromatic gasoline hydrocarbons ranging from about 10 to about 60 volume percent, a content of olefinic gasoline hydrocarbons ranging from 0 to about 30 volume percent and a content of saturated gasoline hydrocarbons ranging from about 40 to about 80 volume percent, these percentages being based on the whole fuel, and wherein said ester is a phosphate ester.

12. The composition of claim **1** wherein said gasoline fuel has a Research Octane Number of at least about 95.

13. The composition of claim **1** wherein said gasoline fuel has a Research Octane Number of about 100.

14. The composition of claim **1** wherein said gasoline fuel has a content of aromatic gasoline hydrocarbons

ranging from about 10 to about 60 volume percent, a content of olefinic gasoline hydrocarbons ranging from 0 to about 30 volume percent and a content of saturated gasoline hydrocarbons ranging from about 40 to about 80 volume percent, these percentages being based on the whole fuel.

15. An unleaded automotive gasoline fuel having a Research Octane Number of at least about 100 and having a content of aromatic gasoline hydrocarbons of at least about 25 volume percent based on the whole fuel and having the tendency of causing an excessive rate of exhaust valve seat wear containing from about 0.05 to about 0.5 gram of phosphorus per gallon as a gasoline soluble, engine inductible, fully esterified organic ester of an oxy-acid of phosphorus having a boiling point at, or extrapolated to, atmospheric pressure of not more than about 425°C., the quantity being sufficient to decrease the rate of such wear substantially uniformly from cylinder to cylinder.

16. The composition of claim **15** wherein said ester is a phosphate ester.

17. The composition of claim **15** wherein said ester is a phosphite ester.

18. The composition of claim **15** wherein said ester is tricresyl phosphate.

19. The composition of claim **15** wherein said ester is cresyl diphenyl phosphate.

20. The composition of claim **15** wherein said ester is trimethyl phosphate.

21. The composition of claim **15** wherein said ester is mixed methyl-phenyl phosphates.

22. The composition of claim **15** wherein said fuel has a content of aromatic gasoline hydrocarbons ranging from about 30 to about 60 volume percent based on the whole fuel.

23. A method of ameliorating exhaust valve seat wear of automotive vehicular engines operating on an unleaded gasoline which comprises dispensing to such vehicles an unleaded gasoline fuel of sufficiently high octane quality to satisfy the octane requirements of the engines, said fuel containing from about 0.02 to about 1.0 gram of phosphorus per gallon as a gasoline soluble, engine inductible, fully esterified organic ester of an oxy-acid of phosphorus.

24. The method of claim **23** wherein the fuel dispensed has a Research Octane Number in the range of from about 90 to about 104.

25. The method of claim **23** wherein said ester is tricresyl phosphate.

26. The method of claim **23** wherein said ester is cresyl diphenyl phosphate.

27. The method of claim **23** wherein said ester is trimethyl phosphate.

28. The method of claim **23** wherein said ester is mixed methyl-phenyl phosphates.

* * * * *

PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,807,974 Dated April 30, 1974

Inventor(s) Robert V. Kerley and Arthur E. Felt

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 3 of TABLE IV, the heading "Inches per 100 Hours" should appear directly under "Exhaust Valve Seat Wear,".

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents