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FUEL

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This invention relates generally to fuels for high-compression, spark-ignition engines and more particularly to fuels in which there is less tendency to cause preignition when high compression internal combustion engines are operated thereon than is the case when present well-known fuels are used under similar operating conditions.

It has long been recognized that there are two distinguishable but related combustion phenomena that act as barriers to the utilization of higher compression ratios in internal combustion spark-ignition engines. By preventing the use of higher compression ratios or higher pressures attained by other means, these two barriers prevent the attainment of fuel economy and efficiency that would otherwise be possible.

These two barriers are: first, knock and second, preignition. Substantial progress has been made in the control of knock through the discovery of the antiknock effect of lead alkyls such as tetraethyl lead and through progress in the manufacture of hydrocarbon fuels having high antiknock value.

The present invention has as its principal object the control of the second barrier, namely, preignition in gasoline-carbureted spark-ignition engines. In accordance with this invention, this object is accomplished by the use of fuels containing addition agents which affect the ignition characteristics of the combustion chamber deposits.

In order to make clear the object of this invention it is necessary to distinguish between the phenomena of preignition and knock which are often confused. Preignition, as the name implies, is an ignition of the mixture in advance of the regular, timed spark ignition. When preignition occurs in its most objectionable form, the observer hears a loud "knock" similar to that which might be expected if the spark had been advanced far beyond its normal timing. During preignition the observer will often find that the electric spark ignition switch can be shut off and the preignition will continue unaffected. This is because preignition is caused by incandescent particles of combustion chamber deposit which are undergoing oxidation on the combustion chamber surface and cause ignition of the fresh fuel mixture during compression and in advance of the electric spark at the spark plug.

Knock is a phenomenon associated with the compression-ignition of an unburned mixture of fuel and air ahead of the normal flame front. The phenomena associated with knock can occur

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regardless of whether the initial source of ignition was an electric spark at the spark plug or an incandescent particle of engine deposit at some point in the combustion chamber.

The present invention has as its principal object the reduction or suppression of preignition in spark ignition engines. In accordance with the invention, this object is accomplished by the use of fuels or gasolines containing addition agents which affect the chemical composition and oxidation characteristics and to some extent the weight and other mechanical characteristics of the combustion chamber deposits.

Acting upon the aforesaid concept of the causes of preignition, namely, an uncontrolled ignition ahead of the spark ignition caused by incandescent particles of engine deposit—an investigation has been made of the oxidation characteristics of various combustion chamber deposits and of various mixtures of inorganic compounds with carbon. Of particular significance, it has been found that certain compounds of lead commonly found in combustion chamber deposits have an unusual and unexpected effect upon the ignition and burning characteristics of carbon.

Gasolines used today in automobile engines commonly contain a small amount of lead alkyl antiknock compound, tetraethyl lead being employed commercially. Common automotive fuels may contain up to about 3 cc. of tetraethyl lead per gallon of gasoline. Along with the tetraethyl lead various volatile alkyl halides are commonly employed, for exampe bromides and chlorides such as ethylene dibromide and ethylene dichloride. When a gasoline containing lead tetraethyl, and the bromide and/or chloride compounds are used as a fuel in internal combustion engines it is found that the deposits on the walls of the combustion chamber contain carbon and various lead compounds such as lead bromide, basic lead bromide, lead chloride, basic lead chloride, lead sulfate and basic lead sulfate. Lead compounds such as these and also engine deposits from leaded-gasolines exert a catalytic effect and not only lower the ignition temperature of carbon, but they impart to the mixture an ability to continue to burn after the primary source of heat is removed that is not had by carbon alone.

The effect of several lead compounds on ignition temperature is given in Table I below in which the ignition temperatures of mixtures containing 10 per cent of various substances and 90 per cent of carbon, in the form of carbon black, were determined under certain controlled conditions:

TABLE I

Material tested	Chemical formula	Ignition temperature, °F.
Pure carbon	C	Over 1200
Combustion chamber deposit from engine operated on gasoline containing Ethyl fluid		680–750
Individual lead compounds known to exist in combustion chamber deposits:		
Lead bromide	$PbBr_2$	[1] 720
Basic lead bromide	$PbO.PbBr_2$	[1] 727
Lead chloride	$PbCl_2$	[1] 727
Basic lead chloride	$PbO.PbCl_2$	[1] 727
Lead sulphate	$PbSO_4$	[1] 939
Basic lead sulphate	$PbO.PbSO_4$	[1] 950

[1] Results obtained by averaging results of four separate determinations.

As indicated in this table, the halogen compounds of lead are extremely active in promoting the oxidation of carbon. Accordingly, the presence of these compounds in combustion chamber deposits will tend to produce preignition when other conditions are favorable.

I have found that the activating effect of lead on ignition of carbon can be inhibited and even prevented altogether by the presence of phosphorus compounds. In accordance with the present invention, therefor, I propose a fuel for internal combustion, spark-ignition engines containing a small percentage, usually less than one per cent by volume, of a liquid phosphorus-containing compound in addition to the other ingredients which have normally been used in leaded-gasolines heretofore. The phosphorus-containing compound should be soluble in the gasoline and of sufficient volatility as to vaporize with the hydrocarbon constituents of the gasoline. For example, tributyl phosphite is illustrative of a readily available liquid, organic, compound of phosphorus of suitable volatility and solubility in gasoline which I have found to be effective in concentrations less than one-tenth of one per cent by volume. Tests indicate that the ignition temperatures of deposits from the combustion chambers of internal combustion engines which have been run on leaded-fuels containing relatively small amounts of tributyl phosphite are increased substantially as compared with deposits obtained from similar fuels containing none of the phosphorus compound. An analysis of the deposits indicates appreciably less lead, bromine, chlorine and sulphur in engine deposits obtained from engines run on leaded-fuels containing the organic phosphorus compound than where the organic phosphorus compound is absent. These results are indicated in Table II below which is based on combustion chamber deposits of a single-cylinder test engine.

TABLE II

EFFECTS OF THE USE OF TRIBUTYL PHOSPHITE IN THE FUEL ON THE COMPOSITION OF LEAD DEPOSITS IN THE COMBUSTION CHAMBER OF A SINGLE-CYLINDER TEST ENGINE

Analysis	Fuel used in producing engine deposit	
	White Crown Ethyl gasoline	3 cc. tributyl phosphite per gallon Ethyl gasoline
Bromine, per cent	8.2	2.4
Chlorine, do	9.0	0.5
Sulphur, do	2.4	0.5
Phosphorus, do		6.8
Lead, do	55.9	42.6
Ignition temperature, °F.	747	1,050

Engine conditions maintained while using the fuels:

Speed	2000 R. P. M.
Spark advance	20°
Air-fuel ratio	Ranged between 13 and 14 to 1
Compression ratio	8.5 to 1
M. E. P	90 lbs. per sq. in.

Table III given below shows data obtained from tests on late model test cars. During the first test, Car No. 1 was operated on ethyl gasoline and Car No. 2 on ethyl gasoline containing 1 cc. per gallon of tributyl phosphite; otherwise, the experimental conditions were substantially the same. In the second test, Car No. 2 ran on ethyl gasoline containing 2 cc. per gallon of tributyl phosphite, while Car No. 1 was running on ethyl gasoline alone. At the end of each test the engine deposits were removed, weighed and analyzed. The results of the tests are tabulated in Table III. These two tests demonstrate clearly the effect of the phosphorus additive on the weights and chemical compositions of the engine deposits, namely, a reduction in the lead, bromine, chlorine and sulphur in engine deposits from engines run on leaded-fuels.

TABLE III

EFFECT OF TRIBUTYL PHOSPHITE ON ENGINE DEPOSITS OF MULTICYLINDER ENGINES WHEN IT IS USED IN THE FUEL TO INHIBIT PREIGNITION

End of first 3,000-mile test

Properties of deposits	Car No. 1 Fuel—Ethyl gasoline		Car No. 2 Fuel—Ethyl gasoline+1.0 cc. per gal. tributyl phosphite	
	Heads	Pistons	Heads	Pistons
Weight, grams	54.7	30.5	48.8	19.9
Chemical analysis:				
Bromine, per cent	16.1	15.7	6.2	7.4
Chlorine, do	7.9	2.9	6.3	3.1
Sulphur, do	1.4	1.5	1.3	1.3
Phosphorus, do	0.5	0.2	3.2	2.5
Lead, do	55.0	51.0	52.1	48.2

End of second 3,000-mile test

Properties of deposits	Car No. 1 Fuel—Ethyl gasoline+2.0 cc. per gal. tributyl phosphite		Car No. 2 Fuel—Ethyl gasoline	
	Heads	Pistons	Heads	Pistons
Weight, grams	58.5	20.1	73.2	28.2
Chemical analysis:				
Bromine, per cent	9.8	7.2	16.8	9.1
Chlorine, do	4.4	2.8	8.5	8.7
Sulphur, do	1.1	1.2	0.9	1.0
Phosphorus, do	2.9	1.9	Trace	Trace
Lead, do	54.7	47.9	57.5	54.1

It is equally important to note in Table IV below the relative effects of these engine deposits on the preignition tendencies of the two test cars. There, the preignition tendency is expressed in terms of octane number of the fuel which is required to suppress preignition at a series of different speeds. At 15 miles per hour, for example, 1 cc. per gallon of tributyl phosphite in ethyl gasoline is equivalent to an increase of 4 octane numbers in the fuel rating and 2 cc. per gallon of tributyl phosphite in ethyl gasoline is equivalent to an increase of 13 octane numbers in the fuel rating. Similar differences may be observed at the other speeds listed in Table IV. Finally, it should be noted that, when the com-

bustion chambers were clean, no preignition could be observed in these cars even though they were run under severe knocking conditions on 40-octane-number gasoline.

TABLE IV

EFFECT OF TRIBUTYL PHOSPHITE ON THE PREIGNITION TENDENCIES OF TEST CARS AFTER 3,000 MILES OF AVERAGE OPERATION

End of first 3,000-mile test

Speed, miles per hour	Car No. 1 Octane number of fuel required to stop preignition, no additive	Car No. 2 Octane number of fuel required to stop preignition, 1.0 cc./gal. additive
10	77	71
15	83	79
20	83	79
25	83	77

End of second 3,000-mile test

Speed, miles per hour	2.0 cc. per gal. additive	No additive
10	Less than 65	89
15	74	87
20	74	83
25	74	----
30	74	----
35	71	79

NOTE.—Neither one of these cars would preignite on gasoline of 40 octane speeds below 40 miles per hour with clean combustion chambers.

Tributyl phosphite is readily available commercially and is illustrative of a phosphorus-containing compound that has proven effective in greatly reducing preignition in using leaded-gasolines as a fuel in spark-ignition internal combustion engines. Other phosphorus-containing compounds have been tested and found to be effective. It is contemplated that any phosphorus compound having sufficient solubility and being sufficiently volatile will accomplish the desired result. I believe that I am the first to have discovered the effect of phosphorus-containing compounds in leaded-gasolines in order to prevent or suppress preignition in spark ignition engines and it is desired to cover such discovery in broad terms.

The invention is useful, also, in combating preignition in gasolines which have not been treated with lead but which may preignite due to the presence of lead compounds in the combustion chamber acquired previous to the use of the non-leaded fuel.

I claim:

A leaded-gasoline for use in spark-ignition internal combustion engines containing a small amount of a tributyl phosphite, said small amount being not greater than about .1% of the fuel by volume.

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