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LEADED MOTOR FUELS

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1 Claim. (Cl. 44—69)

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This invention relates to improved motor fuels containing tetraethyl lead. More particularly this invention relates to leaded fuels containing scavenging agents.

When fuels containing only tetraethyl lead are burned in an internal combustion engine, a deposit of lead compounds tends to accumulate to various parts of the combustion chamber, for example, on the spark plugs, valve stems, etc. This deposit of lead may cause severe deterioration of the effective parts, resulting in failure of spark plugs, sticking of the valves, etc. It is known to use scavenging agents for tetraethyl lead such as certain halogen compounds; for example, alkyl mono- or dichlorides or bromides, particularly ethylene dibromide or mixtures of ethylene dibromide and ethylene dichloride are always used in leaded fuels to overcome the above disadvantages. These scavenging agents reduce lead deposits by releasing halogens during combustion which react with the lead to form volatile lead halides which are removed from the combustion chamber with the products of combustion during the exhaust stroke.

The above scavenging agents have several disadvantages when used in a motor fuel, especially in multi-cylinder engines. In the first place, these halogen compounds are more volatile than tetraethyl lead and as a consequence they vaporize more readily than tetraethyl lead itself which has a boiling point of about 200° C. thus leading to a greater excess of halogen in some of the engine cylinders with a deficiency of halogen in other cylinders. In a multi-cylinder automotive or aircraft engine, the lean cylinders receive predominantly vaporized fuel which has an excess of halogen compound for its tetraethyl lead content. Conversely, the rich cylinders may receive only a small amount of vaporized fuel and an excess of liquid fuel which has an extremely high tetraethyl lead content and a very low concentration of ethylene bromide in the case of aviation fuels, or a mixture of ethylene chloride and ethylene bromide in the case of motor fuels. Accordingly, in carbureted multi-cylinder engines where mixture distribution is almost certain to be non-uniform, valve and cylinder barrel corrosion as well as other difficulties may be expected in the lean cylinders because of the excess halide and spark plug fouling will occur in the richest cylinders

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because of the lack of halide lead scavenging agent coupled with a disproportionate share of tetraethyl lead.

In addition to being more volatile, these halogen compounds tend to react with metals to form products harmful to the fuel. This reaction is believed to be accelerated by the presence of water. For example, the halide may react with the zinc of a galvanized container in the presence of water.

In addition to the harmful effects the maldistribution of the halides and tetraethyl lead may have on the engine itself, the excess halide present in fuel going to the lean cylinders may lower the antiknock quality of that portion of the fuel as shown by the work of Holloway and Bonnell (Industrial and Engineering Chemistry, volume 37, 1089 (1945)). Since the lean cylinders usually limit the knock-free power output of the engine, the segregation of halide may also reduce maximum knock-free power of the engine.

It is therefore an object of this invention to produce motor fuel mixtures in which the boiling temperature of the halogen compound is so nearly the same as that of the knock agent that the constituents of the fuel are more uniformly vaporized and distributed.

It is another object of this invention to prepare fuel mixtures which do not contain any compounds which will react with a metal of storage containers to form injurious products.

It is a still further object of this invention to prepare fuel mixtures which contain halogen scavenging agents which will be more equally distributed among the various cylinders of a multi-cylinder engine.

An additional object of this invention is to produce fuel mixtures having less tendency to corrode or cause the formation of deposits on parts of internal combustion engines especially in multi-cylinder engines than leaded gasolines heretofore available.

These and other objects of this invention may be accomplished by adding to any motor fuel containing lead a small amount of the compound generally known in the commercial trade as hexachlorbutadiene which is specifically 1,1-dichloro-2.3-chloro-4,4-dichloro butadiene-1,3.

Hexachlorbutadiene may be prepared by any known method. One suitable method is to react

polychlorbutanes, preferably having a specific gravity of 1.65 to 1.67 with a slight excess of chlorine at atmospheric pressure and a temperature of 475° C. for about four seconds. The polychlorobutanes can be prepared by the photochemical chlorination of butane or chlorobutanes.

Hexachlorbutadiene does not present the disadvantages with respect to the other and more usual types of halogen compounds. For example, the maldistribution of halide and tetraethyl lead is avoided by the practice of this invention since hexachlorbutadiene has approximately the same vapor pressure as tetraethyl lead under intake manifold conditions. The following data illustrate the marked advantages in vapor pressure when using hexachlorbutadiene in the place of ethylene chloride and ethylene bromide.

Temp., °F. Material	Vapor Pressure, mm. Hg Abs.				
	80	100	120	140	160
Tetraethyl lead	0.5	1.0	2.0	4.0	6.3
Hexachlorbutadiene	0.7	1.3	2.3	3.9	6.3
Ethylene chloride	94	150	240	355	505
Ethylene bromide	13.5	24	42	65	105

It is evident from the above tabulation that the vapor pressure of hexachlorbutadiene closely approximates that of tetraethyl lead whereas ethylene chloride and ethylene bromide are much more volatile than tetraethyl lead.

These indications have been confirmed by flash distillations carried out on samples of a commercial motor gasoline containing 2.0 ml. tetraethyl lead per gallon. One sample contained tetraethyl lead added as commercial fluid (62 mix) and the other sample contained tetraethyl lead added as the pure compound and 1.0 theory of halogen as hexachlorbutadiene. A theory of halogen is defined as the amount required to form PbX_2 from the lead present in the fuel where "X" represents a halogen atom. The commercial fluid (62 mix) contains 1.0 theory of ethylene dibromide and 0.5 theory of ethylene dichloride. The fuels were flash distilled to 70 volume per cent overhead and blends having (1) 70 parts of overhead and 15 parts of bottoms and (2) 70 parts of overhead and 45 parts of bottoms were prepared. The halogen and tetraethyl lead analyses on these fractions are summarized in the following tabulation.

Test Sample	Per Cent Overhead	TEL, ml./gal.	Per Cent Theoretical Halogen	
			By Analysis	By Composition
Motor gasoline+2.0 ml. TEL/gal. as "62 mix"	70	0.38	790	
	[1] 85	1.27	185	
	100	1.97	130	150
	[2] 115	2.36	95	
Motor gasoline+2.0 ml. pure TEL/gal.+1.0 theory halogen as hexachlorbutadiene	70	0.42	90	
	[1] 85	1.24	[3] 60	
	100	1.95	100	100
	[2] 115	2.10	95	

[1] 70 parts overhead and 15 parts bottoms by volume.
[2] 70 parts overhead and 45 parts bottoms by volume.
[3] Result appears to be low.

These results demonstrate that the distribution of the hexachlorbutadiene follows that of the tetraethyl lead much more closely than does that of the halides in the commercial tetraethyl lead fluid. It follows, therefore, that the difficulties encountered in practice, caused by the partial segragation in multicylinder engines of the tetraethyl lead and the currently used halide scavenging agents, would not occur if hexachlorbutadiene were used.

The following example illustrates that the more uniform distribution of halide scavenging agent and tetraethyl lead effected by using hexachlorbutadiene rather than materials previously used may result in an increase in antiknock quality of the fuel when the octane number is determined with multicylinder engines. Road octane numbers were determined by the Uniontown method on two base fuels containing 2.0 ml. tetraethyl lead per gallon. One portion of each fuel contained tetraethyl lead added as commercial fluid (62 mix) and the other contained pure tetraethyl lead and 1.0 theory of halogen as hexachlorbutadiene. The following tabulation shows the road octane numbers that were obtained together with laboratory octane numbers.

Composition of Base Fuel	Experimental Paraffinic Blend		
2.0 ml. TEL Added as	62 Mix	Pure TEL+1.0 Theory Cl as C_4Cl_6	
Octane Number:			
ASTM-Motor O. N.	80.3	79.6	
CFR-Research O. N.	79.9	79.0	ΔO. N.
Road O. N.[1]	72.8	75.3	+2.5

Composition of Base Fuel	Commercial Gasoline		
2.0 ml. TEL/gallon Added as	62 Mix	Pure TEL+1.0 Theory Cl as C_4Cl_6	
Octane Number:			
ASTM-Motor O. N.	80.8	80.8	
CFR-Research O. N.	87.5	87.7	ΔO. N.
Road O. N.[1]	82.5	81.8	−0.7

[1] Average of ratings on 4 cars.

On the basis of these data it appears that for the paraffinic fuel, the lean cylinders were knock-limiting. Since the predominantly vaporized fuel reaching these cylinders contained an excess of knock-promoting halide in the case where the commercial fluid was used, an increase in antiknock performance (2.5 octane numbers) is effected by the use of hexachlorbutadiene. However, the antiknock-volatility characteristics of the commercial motor gasoline was such that the leanest cylinders were not knock-limiting and therefore no difference was observed in the performance of the two samples containing different scavenging agents.

Furthermore, hydrochlorbutadiene is much more stable to hydrolysis than other halogenated compounds. The rates of hydrolysis of several different halides were determined at 104° F. by

placing 2 ml. of the halide in a 100 ml. volumetric flask, adding 1¾" by ⅝" zinc strip and adding water to bring the total volume to the mark. The flask was brought to 104° F. in a constant temperature bath and stirred at a constant rate. Periodically, the aqueous layer was analyzed for halide by Volhard silver nitrate-thiocyanate method. The rate of hydrolysis was taken as the per cent of the halide reacting between 200 and 300 minutes elapsed time to compensate for the possible effects of small amounts of impurities. The results obtained are shown in the following table along with the vapor pressures of the halides and tetraethyl lead at 120° F.

Material	Vapor Pressure mm. Hg Abs. at 120° F.	Hydrolysis Rate
Tetraethyl lead	2.0	
Hexachlorbutadiene	2.3	0.00
Ethylene chloride	240	0.00
Ethylene bromide	42	0.50
1,2,2-Trichlorpropane	56	0.05
1,2,3-Trichlorpropane	15	0.05
2,2,3-Trichlorpropane	26	0.07
2-Chlor-2, 3-dibrombutane	4.6	0.09

From the above results the superior physical and chemical properties of hexachlorbutadiene is apparent.

The amount of hexachlorbutadiene which operates satisfactorily to supply the necessary scavenging to keep the engine clean is between 75 and 100% of the theoretical amount of chlorine necessary to react with the lead present in the fuel. However, slightly greater amounts may be used if found necessary under severe engine conditions.

This invention is further illustrated by the following example. A sample of commercial motor gasoline was divided into four portions and to each portion was added 4.0 ml. tetraethyl lead per gallon in the following forms:

(a) Pure tetraethyl lead.

(b) Pure tetraethyl lead plus 1.0 theory of halogen as hexachlorbutadiene.

(c) Pure tetraethyl lead plus 1.0 theory halogen as ethylene dibromide.

(d) Commercial fluid (62 mix).

Each of these blends was run in a single cylinder Lauson engine for 40 hours. At the end of each run, the combustion chamber was inspected and the deposits were collected and analyzed. The condition of the combustion chamber also was rated by means of a demerit system in which a part was given a rating of 0 to 10 depending on its condition. A condition of no deposit or corrosion would be rated as 0 and an extremely heavy deposit or corrosion would be rated as 10. The results of these tests are shown in the following table:

Composition of Fuel 4.0 ml. TEL/gallon	Spark Plug Condition	
	Demerit	Description
No scavenging agent	6	Heavy yellow-white deposit on electrodes. Porcelain completely covered with heavy deposit.
1.0 theory hexachlorbutadiene	3	Light grayish-white deposit on electrodes. Porcelain only partially covered by a very light deposit.
1.0 theory ethylene dibromide	3	Light dark-gray deposit on electrodes. Porcelain almost completely covered by a light dark-gray deposit.
Commercial fluid (62 mix; 1.5 theory halogen).	5	Medium heavy dark-gray deposit on electrodes. Porcelain completely covered by light deposits.

The above data show that the spark plug condition of a single-cylinder engine using leaded fuel and containing hexachlorbutadiene as a scavenging agent is equal or superior to that resulting from the use of commercial leaded gasolines. Furthermore, the condition of a multicylinder engine using leaded gasoline containing hexachlorbutadiene would be markedly superior to that resulting from the use of leaded gasolines containing scavenging heretofore available because of the similar volatility characteristics of tetraethyl lead and hexachlorbutadiene.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

A composition of matter comprising a hydrocarbon fuel boiling in the gasoline boiling range, lead tetraethyl, and 1,1-dichloro-2,3-chloro-4,4-dichloro butadiene-1,3, in which the amount of the said 1,1-dichloro-2,3-chloro-4,4-dichloro butadiene-1,3, is equivalent to 75% to 100% of the chlorine necessary to react with the lead in the fuel.

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