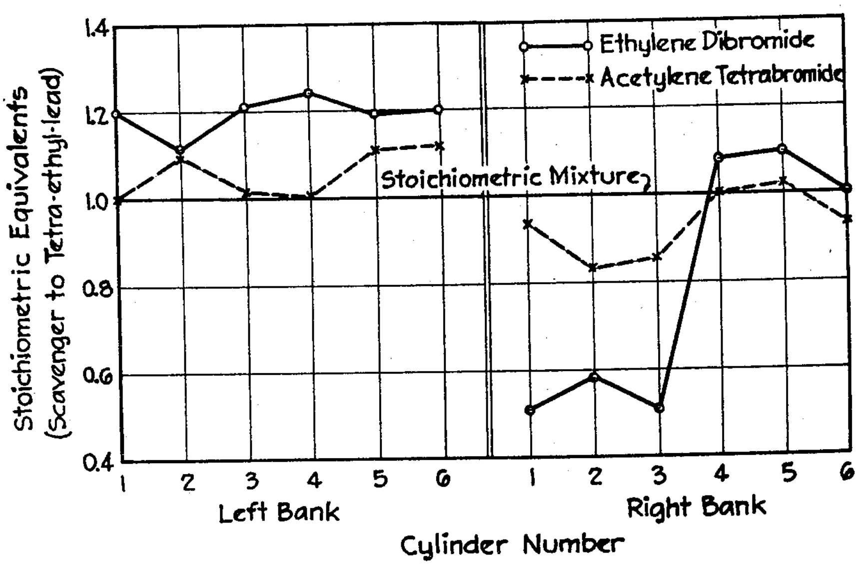
Dec. 6, 1949 C. G. WILLIAMS ET AL 2,490,606

FUEL COMPOSITIONS

Filed May 20, 1948



Inventors: Charles G. Williams
George H. N. Chamberlain

By their Attorney: [signature]

Patented Dec. 6, 1949

2,490,606

UNITED STATES PATENT OFFICE

2,490,606

FUEL COMPOSITIONS

Charles Garrett Williams, Chester, and George Humfrey Neville Chamberlain, Cambridge, England, assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application May 20, 1948, Serial No. 28,236

6 Claims. (Cl. 44—69)

1

This invention relates to improved motor fuels for use in internal combustion engines, and more particularly to improved motor fuels containing tetra-ethyl-lead (T. E. L.).

The use of tetra-ethyl-lead in motor fuels to improve the antidetonation characteristics thereof has been widely accepted. However, when fuels containing only tetra-ethyl-lead compounds are burned in an internal combustion engine, deposits of lead compounds tend to accumulate on the various parts of the combustion chamber, e. g., the spark plugs, valve stems, etc. Such deposits may cause serious deterioration of the affected parts, resulting in failure of the spark plugs, sticking of the valves, etc. Scavenger fluids for tetra-ethyl-lead, such as halogenated compounds, e. g., alkyl mono- or dichlorides or bromides, particularly ethylene dichloride and ethylene dibromide, and especially the latter, or mixtures thereof, are always incorporated in leaded fuels. These scavengers reduce lead deposits by releasing halogens during combustion which react with the lead or lead compounds to form lead halides. These halides are volatile under the conditions of engine operation, so that they are expelled from the combustion chamber during the exhaust stroke.

Motor fuels are chiefly mixtures of hydrocarbons of widely varying boiling range, usually from about 100° F. to about 400° F. Therefore, in multicylinder engines, especially where the various cylinders are of unequal distance from the fuel intake of the manifold, the fuel constituents, including the tetra-ethyl-lead and scavengers therefor, are not equally distributed among the cylinders, so that one or more cylinders may receive a fuel composition containing an excess of scavenger, while other cylinders receive an excess of tetra-ethyl-lead and a paucity of scavenger. Selective distribution of fuel constituents to certain cylinders may be observed. These phenomena are especially serious during cold weather operation, on starting, and during slow engine operation, since, under such conditions, vaporization of the fuel in the intake manifold may be incomplete. Some cylinders, therefore, receive a fuel composition containing an excess of tetra-ethyl-lead, whereas other cylinders receive an excess of the scavenging agent. Deposits of lead compounds cause serious deleterious effects, as above-described, in those cylinders which receive an excess of tetra-ethyl-lead. On the other hand, in those cylinders which receive an excess of the scavenger, the excess halogen formed during combustion causes marked

2

corrosion to the metal parts it contacts, such as spark plugs, electrodes, valve seats, valve stems, cylinder walls, and the like.

In view of the present trend toward high octane fuels, obtainable at least in part by using relatively large amounts of tetra-ethyl-lead, the above-mentioned difficulties are becoming increasingly serious.

Accordingly, an object of the present invention is to provide fuel compositions of uniform scavenging properties. A further object is to provide new fuel compositions for use in multicylinder engines. Another object is to provide fuel compositions of properties such that uniform scavenging is achieved in each cylinder of a multicylinder engine. Other objects will become apparent hereinafter.

It has now been found that the use of acetylene tetrabromide as the scavenging agent in fuel compositions containing tetra-ethyl-lead results in substantially uniform scavenging in each cylinder of a multicylinder engine. Such fuel compositions exhibit excellent stability characteristics, and the octane rating is not adversely affected by the scavenger.

Acetylene tetrabromide is also known as 1,1,2,2,-tetrabromoethane, has a melting point of about 0.1° C., decomposes at about 200° C., has a density (20°/4°) of 2.9638 and a refractive index (n_D^{20}) of 1.63795.

In accordance with the present invention, the use of acetylene tetrabromide in place of heretofore known scavenging agents for tetra-ethyl-lead, such as ethylene dibromide (1,2-dibromoethane), results in a surprising decrease in the quantity of deposition of lead compounds on the various portions of the combustion chambers, and a marked decrease in corrosion caused by excess halogen.

In the accompanying drawing is shown in graphic form the relative effectiveness of acetylene tetrabromide and ethylene dibromide in supplying fuel containing stoichiometric quantities of tetra-ethyl-lead and the respective scavenger to the various cylinders of a 12 cylinder engine. These data were obtained by operating an Allison V1710 engine on 100 octane fuels containing 6.0 cc. of tetra-ethyl-lead per gallon, and containing a stoichiometric amount of either ethylene dibromide or acetylene tetrabromide.

In the graphical presentation of these data the engine cylinders are shown on the abscissas, and the deviations from stoichiometric quantities of the tetra-ethyl-lead and scavenger fed into the various cylinders are shown on the ordinate; 1.0

represents stoichiometric quantities thereof, 0.5 represents a mixture containing only one-half the theoretical quantity of scavenger to react with the tetra-ethyl-lead, while 1.5 represents a mixture containing one-half excess of the theoretical quantity of scavenger. The wide deviation from stoichiometric amounts of tetra-ethyl-lead and ethylene dibromide supplied to the various cylinders of the 12 cylinder engine, as compared to close adherence to stoichiometric quantities when acetylene tetrabromide is employed, is clearly evident from this diagram.

By the terms "stoichiometric amounts," "equivalent quantities," and terms of similar import, as used herein, is meant the amount of scavenger which contains an amount of halogen required to combine with the lead according to the equation:

$$2Hal. + Pb \rightarrow Pb(Hal)_2$$

In order to demonstrate the efficacy of acety-tetrabromide as a scavenger for tetra-ethyl-lead, tests were carried out in a Merlin single cylinder unit using aviation gasoline containing 4.6 cc. of tetra-ethyl-lead per gallon and either ethylene dibromide or acetylene tetrabromide as the scavenger therefore. The tests comprised two 50-hour runs, one with the fuel containing ethylene dibromide, and the other with the fuel containing acetylene tetrabromide. Each test was carried out in periods of 8 hours 20 minutes duration preceded by a 30 minute warming-up period to establish normal operating temperatures. Engine operating conditions were as follows:

Speed	R. P. M.	1,800
Manifold air pressure	in. Hg abs.	29.6
Intake air temperature	°C.	50
Air/fuel ratio		15:1
Coolant out temperature	°C.	80
Oil inlet temperature	°C.	70

Piston, inlet and exhaust valve, and spark plug deposits were determined by weighing these components before and after the test. Data obtained are shown in Table I.

Table I

Deposit formed on—	Weight of Deposits from use of Fuel containing—		Per Cent Difference
	Ethylene dibromide	Acetylene tetrabromide	
	Grams	*Grams*	
Exhaust plug	0.35	0.32	−8.6
Inlet plug	0.38	0.43	+13.2
Exhaust valve (front)	10.6	0.73	−93.
Exhaust valve (rear)	10.5	0.76	−93.
Inlet valve (front)	1.40	0.73	−48.
Inlet valve (rear)	1.65	2.05	+24.2
Piston	7.2	7.6	+5.6
Total deposit weight	32.08	12.62	−60.6

These data show a reduction of about 93% of the deposition on parts which accumulate a major portion of the deposits, with an overall decrease in deposition of 60.6%, and they demonstrate the value of the compositions of the present invention when used in single cylinder engines. Visual examination of the inlet valve head deposits showed the deposit from the fuel containing acetylene tetrabromide to be of lower melting characteristics than the deposit from the fuel containing ethylene dibromide, which was indicated by the fused appearance of the latter. Chemical analysis of the various deposits proved that the ratio of the more volatile lead bromide to the less volatile lead oxide was substantially increased when acetylene tetrabromide was used. These data are shown in Table II.

Table II

Fuel	Deposit location	Ratio lead bromide to lead oxide
E. D. B.[1]	Combustion chamber	1.75
A. T. B.[2]	do	3.03
E. D. B	Piston crown	2.65
A. T. B	do	3.87
E. D. B	Inlet valve	0.94
A. T. B	do	1.55
E. D. B	Exhaust valve	0.023
A. T. B	do	0.009
E. D. B	Inlet plug	3.18
A. T. B	do	5.12

[1] Ethylene dibromide as scavenger.
[2] Acetylene tetrabromide as scavenger.

The consistent increase in the lead bromide to lead oxide ratio when running on fuel containing acetylene tetrabromide is evident, which demonstrates that acetylene tetrabromide converts a greater portion of lead oxide to the more volatile lead bromide than does ethylene dibromide. It is further evident that even occasional hotter running will result in more efficient expelling of the lead bromide, while the lead oxide tends to remain. In practice, where long periods of low power cruising are interposed by high power bursts, such as for an airplane take off, the higher lead bromide to lead oxide ratio of deposits formed when using fuel containing acetylene tetrabromide will render them more easily detachable, while the total amount of the deposits, as has already been shown, will be less.

From the accompanying graphic drawing it is apparent that some cylinders of a multicylinder engine receive fuel compositions wherein the quantities of tetra-ethyl-lead and ethylene dibromide are far from stoichiometric. For example, cylinder 1 of the right bank received about one-half of the ethylene dibromide required for scavenging the lead present, while it received about 95% of the required acetylene tetrabromide. Hence, in order to show further the surprising advantages of acetylene tetrabromide as the scavenger for tetra-ethyl-lead, a series of experiments were performed using a Merlin single cylinder unit operated on a fuel consisting of aviation gasoline, various quantities of tetra-ethyl-lead, one-half the stoichiometric quantity of ethylene dibromide, and, for comparison, the same fuels with a stoichiometric quantity of acetylene tetrabromide. Each experiment was for 20 hours with engine operation under cruising conditions. The data obtained are shown in Table III.

Table III

Tetra-ethyl-lead content (cc./gal.)	Scavenger	Exhaust spark plug deposit (grams)
8.33	E. D. B.	0.35
8.33	A. T. B.	0.24
12.0	E. D. B.	0.70
12.0	A. T. B.	0.27

These data show that in those cylinders which receive a paucity of the scavenging agent, ethylene dibromide, which is commonly employed with tetra-ethyl-lead, there is an increase in deposition of over 100%, as compared to the deposition observed using acetylene tetrabromide.

The presence of acetylene tetrabromide in gasoline hydrocarbons does not adversely affect the octane number of the fuel. This was demonstrated by determining the octane number, according to the C. R. C. F-4 method (A. S. T. M. designation D909-47), of fuels consisting of a gasoline hydrocarbon fraction, various quantities of tetra-ethyl-lead, and stoichiometric quantities of ethylene dibromide and acetylene tetrabromide, respectively. The following data of Table IV show that, within the limits of experimental error, knock ratings are equal for the fuels containing ethylene dibromide and acetylene tetrabromide.

Table IV

T. E. L.[1] content, cc./gal.	Octane Number of Fuel Containing—	
	Ethylene dibromide	Acetylene tetrabromide
0	73.1	73.1
1.67	84.0	83.0
3.34	99.8	101.7
4.58	109.3	109.1

[1] Tetra-ethyl-lead.

Storage tests, including accelerated storage tests, on fuels containing acetylene tetrabromide have demonstrated that such blends are at least the equal of, or are superior to, fuels containing ethylene dibromide. Thus, fuels containing 6.0 ml. of tetra-ethyl-lead per gallon and an equivalent quantity of acetylene tetrabromide were unchanged after 10 weeks barrel storage, and the same fuel containing a large excess of acetylene tetrabromide, namely, a total of 2% by volume, was visibly unchanged after about 9 months storage. However, a concentrated mixture of tetra-ethyl-lead and acetylene tetrabromide may be unstable, but may be stabilized by dilution with gasoline, kerosene, and/or by the action of a stabilizing agent, such as 2,4-dimethyl-6-tertiary-butylphenol.

For example, a composition containing the following constituents (numerical values are in per cent by weight):

Tetra-ethyl-lead	63.2
Acetylene tetrabromide	33.9
Kerosene	2.8
2,4-dimethyl-6-tertiary-butylphenol	0.1

was subjected to accelerated storage tests at 120° F. The composition remained unchanged over a period of 2 weeks, while a corresponding composition containing ethylene dibromide instead of the acetylene tetrabromide gave a heavy deposit in this time.

The quantity of acetylene tetrabromide present in the present fuel compositions will, of course, vary according to the quantity of tetra-ethyl-lead present. Generally, because of the efficient scavenging action of the acetylene tetrabromide, as herein described, it is unnecessary to employ more than a stoichiometric quantity, and usually an approximately stoichiometric quantity will be used, though more or less may be employed when desired. Generally, the amount of tetra-ethyl-lead employed will be from about 0.5 to about 15 cc. per gallon, and an approximately stoichiometric quantity, say from about 75% to about 110%, and preferably from about 90% to about 100%, of acetylene tetrabromide should be present in order to fully realize the advantages of the present invention.

The invention claimed is:

1. A fuel composition for internal combustion engines comprising a gasoline hydrocarbon fraction, tetra-ethyl-lead, and an effective scavenging amount of acetylene tetrabromide.

2. A fuel composition for internal combustion engines comprising a gasoline hydrocarbon fraction, tetra-ethyl-lead, and an approximately stoichiometric quantity of acetylene tetrabromide.

3. A fuel composition for internal combustion engines comprising gasoline, from about 0.5 to about 15 cc. per gallon of tetra-ethyl-lead, and an approximately stoichiometric quantity of acetylene tetrabromide.

4. A gasoline hydrocarbon fraction containing tetra-ethyl-lead and containing acetylene tetrabromide as an essential scavenger therefor, wherein the amount of acetylene tetrabromide is about stoichiometric of the amount of tetra-ethyl-lead present in said gasoline.

5. A gasoline hydrocarbon fraction containing from about 0.5 to 15 cc. of tetra-ethyl-lead per gallon, and from about 90% to 100% of the stoichiometric amount of acetylene tetrabromide required to scavenge the tetra-ethyl-lead.

6. A gasoline hydrocarbon fraction containing from about 0.5 to 15 cc. of tetra-ethyl-lead per gallon, and from about 75% to 110% of the stoichiometric amount of acetylene tetrabromide required to scavenge the tetra-ethyl-lead.

CHARLES GARRETT WILLIAMS.
GEORGE HUMFREY NEVILLE CHAMBERLAIN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,364,921	Shokal	Dec. 12, 1944