Patented Dec. 19, 1950 2,534,309

UNITED STATES PATENT OFFICE

2,534,309

COMPOSITION FOR INTERNAL-COMBUSTION ENGINES

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No Drawing. Application November 6, 1947, Serial No. 784,519

9 Claims. (Cl. 44—57)

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This invention relates to an improvement in the ignition and combustion characteristics of gasoline as a fuel for internal combustion engines, and to the prevention and the removal of carbon and gum deposits from the combustion chambers of internal combustion engines.

Many materials, such as alcohols, ketones, nitroalkanes and organometallic compounds have been proposed for addition to gasoline to improve the ignition and combustion properties of this fuel. Various methods and reagents also have been suggested for purging the internal parts of an internal combustion engine of accumulated contaminants incident to both the current and past operation of the engine, most of these reagents having been organic liquids having a solvent action on the gummy deposits which retain a good share of the carbon. Exemplary of such liquid organic solvents are ethyl alcohol, furfuryl alcohol, kerosene, coal oil, carbon tetrachloride, chloroform, benzene, toluene, xylene, the various liquid terpene hydrocarbons, and organic esters, ethers, ketones, amines and amides. Numerous mixtures of such solvents also have been proposed. Many of these reagents have exerted a limited beneficial effect on the operation of internal combustion engines, but they have generally been unsatisfactory due to incomplete removal of carbon and gum deposits and in not effecting the desired result; namely, a significant increase in compression.

Now in accordance with this invention it has been found that a composition comprising an α,α-dialkylarylmethyl hydroperoxide and gasoline not only will act as an improved fuel but also will be of utility in removing deposits of carbon and gum efficiently and economically. When used as fuels, the compositions of this invention give added power to internal combustion engines, effect a cleaner combustion in that carbon formation is decreased, and facilitate gradual removal of carbon deposits already present. When utilized as purging agents, the compositions remove carbon and gum deposits from the combustion chambers of the engines and, barring mechanical faults in the engines, restore the compression of the engines to a normal level.

As an illustration of the present invention, carbon and gum deposits may be removed from an internal combustion engine by the process of admitting a gasoline solution of an α,α-dialkylarylmethyl hydroperoxide, such as α,α-dimethylbenzyl hydroperoxide, to the combustion chambers of the engine through the usual fuel system, including the carburetor, while the engine is

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running under normal operating conditions. The solution also may be formed, then added to the engine by introducing the hydroperoxide through the air intake of the carburetor while the engine is running at idling speed. In this instance the solution of the hydroperoxide in gasoline is formed within the carburetor. Upon completion of the addition of the gasoline solution of the hydroperoxide the engine speed may be accelerated to effect removal of the loosened deposits through the exhaust.

The following examples constitute specific embodiments of the invention.

EXAMPLE 1

The α,α-dialkylarylmethyl hydroperoxide used in this example was α,α-dimethylbenzyl hydroperoxide, obtained by the air oxidation of cumene in the liquid phase in the presence of aqueous sodium hydroxide. The α,α-dimethylbenzyl hydroperoxide was used in the form of the reaction product obtained by the air oxidation. This reaction product contained 46.3% by weight of the hydroperoxide, the balance of product being primarily α,α-dimethylbenzyl alcohol and cumene, but also containing a small amount of acetophenone.

The cylinder head was removed from a six-cylinder International motor, and it was found that the motor contained a moderate carbon deposit and a considerable deposit of gummy material. Upon replacement of the cylinder head the motor was warmed up to normal running temperature and the compression in each cylinder determined. The motor then was run at a moderate speed while 250 ml. of the α,α-dimethylbenzyl hydroperoxide-containing reaction product was added rapidly directly into the carburetor air intake, the rate being such that the motor did not quite choke down. Following addition of the hydroperoxide, the motor was run at a moderate speed for 10 minutes, then the compression of each cylinder was again determined. It was observed that the spark plugs had been cleaned as a result of the hydroperoxide addition. The motor then was run at a moderate speed on 0.9 gallon of gasoline in which was dissolved 31 ml. of the hydroperoxide-containing reaction product per gallon, the gasoline solution being added through the fuel line leading into the carburetor. Again the compression of each cylinder was determined. Removal of the cylinder head showed that the carbon and gum deposits had been effectively removed from the head and the valves, although a small amount of gummy matter re-

mained on the pistons. The results of each compression test are given in Table I.

Table I

Cylinder Number	Compression (lbs./sq. in)					
	1	2	3	4	5	6
Initial	93	89	88	72	84	75
After First Hydroperoxide Addition	102	105	96	110	105	95
After Hydroperoxide-Gasoline Feed	112	107	105	112	110	110

EXAMPLE 2

A six-cylinder Continental motor was warmed up to normal running temperature and the compression in each cylinder determined. The motor then was run at a moderate speed while 250 ml. of the α,α-dimethylbenzyl hydroperoxide-containing reaction product used in Example 1 was rapidly introduced through the carburetor air intake. The motor was run at a moderate speed for 10 minutes following addition of the hydroperoxide, then the compression of each cylinder again was determined. The results of each compression test are given in Table II.

Table II

Cylinder Number	Compression (lbs./sq. in.)					
	1	2	3	4	5	6
Initial	95	97	85	103	105	120
After Hydroperoxide Addition	145	127	125	115	140	143

EXAMPLE 3

The procedure of Example 2 was followed on a six-cylinder Chevrolet motor. The compression data are given in Table III.

Table III

Cylinder Number	Compression (lbs./sq. in.)					
	1	2	3	4	5	6
Initial	100	103	111	105	115	142
After Hydroperoxide Addition	129	125	130	128	125	142

EXAMPLE 4

A six-cylinder Mack motor was warmed up to normal running temperature and the compression in each cylinder determined. The motor then was run on 1.0 gallon of gasoline containing, per gallon, 273 ml. of the α,α-dimethylbenzyl hydroperoxide-containing reaction product utilized in Example 1, the gasoline solution being added through the fuel line leading into the carburetor. The compression of each cylinder again was determined. The results are given in Table IV.

Table IV

Cylinder Number	Compression (lbs./sq. in.)					
	1	2	3	4	5	6
Initial	104	65	75	81	91	114
After Hydroperoxide-Gasoline Feed	118	100	97	110	114	125

EXAMPLE 5

The α,α-dimethylbenzyl hydroperoxide used in this example was a product which contained 72.8% of the hydroperoxide and which was obtained by the air oxidation of cumene in the liquid phase in the presence of aqueous sodium hydroxide to give a reaction product containing 33% of the hydroperoxide, this reaction product then being steam stripped of unreacted cumene to give the 72.8% product.

An eight-cylinder Buick engine was tested for compression, and all cylinders were found to be 140 lbs./sq. in., indicating that the engine was in excellent condition. However, a considerable carbon deposit was noticed on all spark plugs, consequently 107.7 ml. of the 72.8% hydroperoxide product was added through the carburetor air intake while the engine was running at idling speed. The engine speed then was accelerated to 2000 R. P. M. for 2 minutes. The spark plugs were removed and found to be completely free of carbon.

EXAMPLE 6

Using the 72.8% α,α-dimethylbenzyl hydroperoxide product of Example 5, a six-cylinder Plymouth engine was subjected to a purging operation. The initial compression of each cylinder was determined, then 107.7 ml. of the 72.8% hydroperoxide product was added through the carburetor air intake while the engine was running at idling speed. The engine then was operated at 2000 R. P. M. on 0.5 gallon of gasoline containing 26.9 ml. of the hydroperoxide product per gallon, the gasoline solution being added through the fuel line leading into the carburetor. The 107.7 ml. hydroperoxide addition and the hydroperoxide-gasoline feed steps then were repeated, after which the compression of each cylinder again was determined. The compression data are shown in Table V.

Table V

Cylinder Number	Compression (lbs./sq. in.)					
	1	2	3	4	5	6
Initial	95	90	90	80	90	50
After Hydroperoxide Additions	100	110	105	105	95	30

The cylinder head was removed before and after the above treatment. Cylinder number 6 was not firing prior to the treatment and the comparatively low initial compression of this cylinder was due to mechanical wear. The further loss of compression incurred by the treatment was due to removal of gummy material which had helped to seal some of the leakage induced by mechanical wear. Both carbon and gum deposits were partially removed from the valves and cylinder head by the purging treatment.

EXAMPLE 7

The α,α-dimethylbenzyl hydroperoxide used in this example was a product which contained 78.4% of the hydroperoxide and which was obtained by the air oxidation of cumene in the liquid phase in the presence of aqueous sodium hydroxide to give a reaction product containing 33% of the hydroperoxide, this reaction product then being steam stripped of unreacted cumene over aqueous sodium hydroxide to give the 78.4% product.

An eight-cylinder V-type Ford engine was warmed up to normal operating temperature and the compression in each cylinder determined. The engine was operated at a fixed throttle setting until the speed became constant, then the

engine was run successively on 0.5 gallon of gasoline containing about 26.9 ml. of the 78.4% hydroperoxide product per gallon, 0.5 gallon of gasoline containing about 53.8 ml. of the 78.4% hydroperoxide product per gallon, and finally on straight gasoline, all additions being made through the fuel line leading into the carburetor. The R. P. M. values were observed during each phase of the test, and upon completion of the test the compression of each cylinder again was determined. It was noticed upon completion of the test that the spark plugs were considerably cleaner. The test data are given in Tables VI and VII.

Table VI

	Compression (lbs./sq. in.)							
	Right bank				Left bank			
Cylinder Number	1	2	3	4	1	2	3	4
Initial	101	115	122	120	116	110	114	116
After hydroperoxide additions	110	120	127	126	121	122	118	121

Table VII

Fuel	Engine R. P. M.
Straight gasoline (initial)	1,210
Gasoline containing 26.9 ml. hydroperoxide/gal. (0.5 gal.)	1,320
Gasoline containing 53.8 ml. hydroperoxide/gal. (0.5 gal.)	1,330
Straight gasoline (final)	1,360

EXAMPLE 8

The α,α-dialkylarylmethyl hydroperoxide used in this example was α,α-dimethyl-p-methylbenzyl hydroperoxide obtained by the oxidation of p-cymene in the liquid phase in the presence of aqueous sodium hydroxide using molecular oxygen. The α,α-dimethyl-p-methylbenzyl hydroperoxide was used in the form of the reaction product obtained by the oxidation. This reaction product contained 36.9% by weight of the hydroperoxide.

A six-cylinder Chevrolet engine was warmed up to normal running temperature and the compression in each cylinder determined. The engine then was operated at idling speed on 0.5 gallon of gasoline containing 29.9 ml. of the hydroperoxide product per gallon. Upon completion of this operation the engine was operated using 0.5 gallon of gasoline containing 59.7 ml. of the hydroperoxide per gallon, after which the compression of each cylinder again was determined. Both hydroperoxide-gasoline solutions were added through the fuel line leading into the carburetor. The compression data are shown in Table VIII.

Table VIII

	Compression (lbs./sq. in.)					
Cylinder Number	1	2	3	4	5	6
Initial	148	140	155	145	138	138
After hydroperoxide-gasoline feed	151	150	155	155	150	155

EXAMPLE 9

The α,α-dimethylbenzyl hydroperoxide used in this example was a product which contained 52% of the hydroperoxide and which was obtained by the air oxidation of cumene in the liquid phase in the presence of aqueous sodium hydroxide.

An Oldsmobile automobile containing an eight-cylinder engine was operated under actual driving conditions using six gallons of gasoline in which was dissolved 37.7 ml. of the hydroperoxide per gallon of gasoline. The automobile then was operated on straight gasoline for an additional 250 miles. The compression of each cylinder of the engine was measured both before and after the test while the engine was running at normal operating temperature. The results of each compression test are given in Table IX.

Table IX

	Compression (lbs./sq. in.)							
Cylinder Number	1	2	3	4	5	6	7	8
Initial	105	110	110	100	110	95	80	100
After hydroperoxide-gasoline and straight gasoline feeds	108	113	113	113	110	113	106	105

EXAMPLE 10

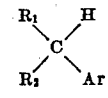
The α,α-dimethylbenzyl hydroperoxide used in this example was a product which contained 43.5% of the hydroperoxide and which was obtained by the air oxidation of cumene in the liquid phase in the presence of aqueous sodium hydroxide.

A Dodge truck and a Chevrolet truck, both containing six-cylinder engines, were operated under actual driving conditions using gasoline in which was dissolved a specified amount of the hydroperoxide per gallon of gasoline. The compression of the cylinders in each engine was measured both before and after the test while the engine was running at normal operating temperature. The results of the tests are given in Table X.

Table X

Vehicle	Dodge	Chevrolet
Amount hydroperoxide (ml.) per gallon of gasoline	3.3	32.8
Gallons of fuel used	90	45
Average initial compression	110	115
Average final compression	119	127

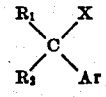
The compositions used in accordance with this invention have been shown by the examples as involving the use of the hydroperoxides obtained from the oxidation of cumene and p-cymene, but other α,α-dialkylarylmethyl hydroperoxides also are operable. Such hydroperoxides may be prepared by the oxidation of alkyl-substituted aromatic organic compounds having the structural formula



in which R_1 and R_2 represent alkyl groups and Ar represents a substituent selected from the group consisting of aryl and alkaryl groups. The oxidation may be carried out in the liquid phase utilizing air or molecular oxygen as the oxidizing agents. A preferred method of preparing these hydroperoxides involves the liquid phase oxidation of the alkyl-substituted aromatic organic compounds having the above structural formula by passing an oxygen-containing gas through the compounds at a temperature between about 25° C. and about 95° C.

in the presence of an aqueous alkali. The concentration of the aqueous alkali may be between about 1% and about 35% although it is preferable to use concentrations of about 2% to about 8%. Vigorous agitation is desirable during the oxidation reaction.

The α,α-dialkylarylmethyl hydroperoxides used in accordance with this invention have the following structural formula



in which R_1 and R_2 represent alkyl groups, Ar represents a substituent selected from the group consisting of aryl and alkaryl groups and X represents the hydroperoxy (—OOH) group. As illustrative of the alkyl-substituted aromatic organic compounds which may be oxidized, p-cymene, cumene, and diisopropylbenzene may be mentioned. These compounds lead to α,α-dimethyl-p-methylbenzyl, α,α-dimethylbenzyl, and α,α-dimethyl-p-isopropylbenzyl hydroperoxides, respectively. Also in the case of diisopropylbenzene there may be obtained α,α,α',α'-tetramethyl-p-xylylene dihydroperoxide. These compounds also may be named as aryl(dialkyl)methyl hydroperoxides; for example, α,α-dimethylbenzyl hydroperoxide may be designated as phenyl(dimethyl)methyl hydroperoxide. The aryl and alkaryl groups need not be derived from benzene, as is the case in the afore-mentioned compounds, for compounds containing aromatic nuclei derived from naphthalene, anthracene, phenanthrene, and the like also are operable when dissolved in a suitable solvent during the oxidation. The aryl group may be substituted with alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, and the like, to give alkaryl substituents, the same alkyl groups also being representative of R_1 and R_2 in the structural formula. R_1 and R_2 may be either the same or different.

In carrying out this invention the compositions comprising an α,α-dialkylarylmethyl hydroperoxide and gasoline may be prepared using several different modifications of the hydroperoxide material. The hydroperoxide may be used, for example, either in the form of the pure hydroperoxide, or in the form of a crude reaction mixture containing the hydroperoxide and obtained by the oxidation with air or oxygen of an alkyl-substituted aromatic organic compound having the structural formula shown previously. When the hydroperoxide is obtained by such an oxidation, the oxidation usually is interrupted before all of the hydrocarbon has reacted in order to avoid or limit side reactions. In this manner the α,α-dialkylarylmethyl hydroperoxide is obtained in mixture with smaller or larger amounts of the original hydrocarbon, which is an α,α-dialkylarylmethane, and the mixture also may contain secondary reaction products such as the corresponding alcohols, which are α,α-dialkylarylmethyl alcohols. The oxidation of cumene, for example, leads to a reaction product containing α,α-dimethylbenzyl hydroperoxide, α,α-dimethylbenzyl alcohol, a small amount of acetophenone, and unchanged cumene. Such a reaction product may be used per se in forming the gasoline-hydroperoxide compositions of this invention. In case it is desirable, however, to obtain the hydroperoxide in a more concentrated form, the hydroperoxide may be separated from the other constituents of the crude reaction mixture. The hydroperoxides may be separated from the reaction mixtures by, for example, fractional distillation at very low pressures, of the order of 0.01 to 1.0 mm./sq. cm., the hydroperoxides having higher boiling points than the related hydrocarbon, alcohol and ketone. In some instances the hydroperoxides also may be separated from the oxidation reaction mixtures by crystallization, which may be facilitated by first distilling off at least part of the hydrocarbon. Steam distillation usually is sufficient to remove the hydrocarbon.

The concentration of the gasoline and the α,α-dialkylarylmethyl hydroperoxide in the composition comprising the hydroperoxide and gasoline will depend somewhat upon the particular use to which the composition is to be placed. In general, the concentration of gasoline preferably will be at least 10% by weight, based on the total composition, and the remainder of the composition may be the hydroperoxide. The concentration of the hydroperoxide may be varied, however, from about 0.05% to 90% by weight, based on the total composition. Except in the extreme instance in which the composition is composed of 10% gasoline and 90% hydroperoxide by weight, other components may be present in the composition. When the composition is to be used as a fuel, the concentration of the hydroperoxide may be from about 0.05% to about 10% by weight, based on the total composition, and desirably is from about 0.05% to about 2%. A preferable range on this basis is from about 0.05% to about 1%. When the composition is to be used as a purging agent, the concentration of the hydroperoxide may be from about 10% to 90% by weight, based on the total composition. Preferably the concentration is from about 30% to about 80%, and a particularly applicable range is from about 40% to about 70%. The amount of gasoline in the composition therefore may range generally from 10% to about 99.95% by weight, based on the total composition. When the composition is to be used as a fuel, it is desirable that the amount of gasoline be at least about 75% by weight, based on the total composition, preferably at least about 90% by weight. Thus, in this use of the composition the concentration of gasoline desirably is from about 75% to about 99.95%, and preferably from about 90% to about 99.95%.

In carrying out a purging operation the simplest procedure involves utilization of the air intake of the carburetor. Through the intake there may be added a solution of the hydroperoxide in gasoline, or, for example, a crude oxidation reaction mixture containing the hydroperoxide. There also may be added a more concentrated solution of the hydroperoxide formed by removing unreacted hydrocarbon from a crude oxidation reaction mixture, and there even may be added those pure hydroperoxides which when pure exist as liquids. In the case of the pure hydroperoxides, however, whether liquid or solid, it is preferable to dissolve them in gasoline or other suitable solvent prior to addition to the carburetor. Other solvents, such as ethanol, benzene, toluene, xylene, diisopropylbenzene, cumene, cymene, petroleum ether, heptane, and, in general, the nonpolar, volatile hydrocarbons of the paraffinic, naphthenic and aromatic series may be used, in other words, to take the hydroperoxide into solution prior to the carburetor addition. Lubricating oils also are advantageous

as solvents for the hydroperoxide, and the hydroperoxide may be either in a pure or concentrated form, or in the form of a crude oxidation reaction product. In any of these instances, however, the composition entering the combustion chambers of the internal combustion engine comprises the hydroperoxide and gasoline. This is due to the fact that gasoline, as well as the hydroperoxide, enters the carburetor and a mixing of the two components takes place, resulting in the formation of the hydroperoxide-gasoline composition. The final concentration of the hydroperoxide in the composition in this instance will depend to a great extent on the original concentration of the hydroperoxide in the material added to the carburetor, since the amount of gasoline being fed through the carburetor at any one time may be relatively low in comparison to the amount of hydroperoxide.

When used as fuels the compositions in accordance with this invention are easily prepared merely by dissolving the hydroperoxide, in the form of any of the modifications previously discussed, in the gasoline. This may be done, for example, either at the refinery, thereby incorporating the hydroperoxide as one of the original constituents of the fuel as it is to be sold to the consumer, or by adding a certain amount of the hydroperoxide to the engine's fuel tank containing a prescribed amount of gasoline.

As shown by the examples, the compositions may be used primarily as fuels or primarily as purging agents depending upon the type of treatment most required by the engine, but, as also shown by the examples, the two types of treatment may be combined with beneficial results. The engine may, for example, first be given a purging treatment with a relatively high hydroperoxide-content composition, then be operated on a fuel composition containing a relatively small amount of hydroperoxide. No matter what the treatment, the most beneficial results are obtained when the engine is being operated at a normal running temperature. With most engines such a temperature is on the order of at least 140° F. and generally is within the range of 140° F. to 180° F. During a purging operation the addition of the hydroperoxide may be as rapid as possible without causing the engine to choke, and upon completion of the addition the speed of the engine may be accelerated in order to expel the loosened carbon and gum deposits out the exhaust.

By practicing this invention the engine knock present when the motor has excess carbon deposits will be gone and, in general, the performance of the engine will be noticeably improved. The condition of sticky valves caused by gum deposits on the valve stems is remedied and spark plugs are cleaned, improving slow speed performance and idling. The compositions of this invention are superior to other materials suggested by the art in that the hydroperoxide compositions effect a more complete removal of carbon and gum deposits and result in a significant increase in compression.

What I claim and desire to protect by Letters Patent is:

1. A gasoline fuel containing an α,α-dialkylarylmethyl hydroperoxide.

2. A gasoline fuel containing from about 0.05% to about 90% by weight, based on the total composition, of an α,α-dialkylarylmethyl hydroperoxide.

3. A gasoline fuel containing from about 0.05% to about 10% by weight, based on the total composition, of an α,α-dialkylarylmethyl hydroperoxide.

4. A gasoline fuel containing from about 10% to about 90% by weight, based on the total composition, of an α,α-dialkylarylmethyl hydroperoxide.

5. A gasoline fuel containing an α,α-dialkylarylmethyl hydroperoxide and an α,α-dialkylarylmethyl alcohol.

6. A gasoline fuel containing an α,α-dialkylarylmethyl hydroperoxide, an α,α-dialkylarylmethyl alcohol and an α,α-dialkylarylmethane.

7. A gasoline fuel containing α,α-dimethylbenzyl hydroperoxide.

8. A gasoline fuel containing α,α-dimethyl-p-methylbenzyl hydroperoxide.

9. A gasoline fuel containing α,α-dimethyl-p-isopropylbenzyl hydroperoxide.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
929,503	Selden	July 27, 1909
1,766,501	Buerk	June 24, 1930
2,403,772	Vaughan et al.	July 9, 1946