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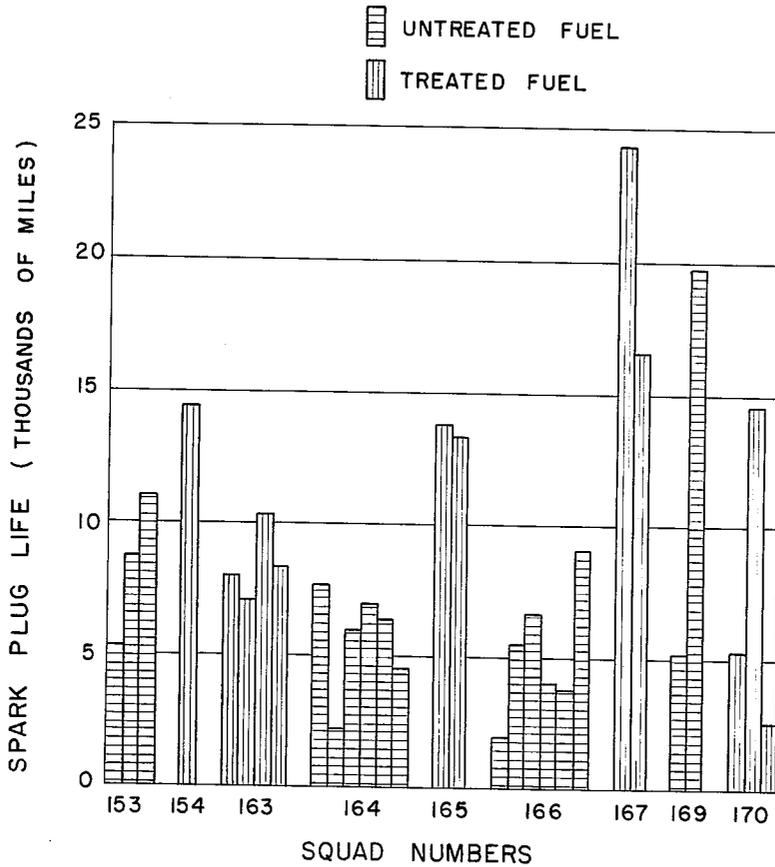
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ANTIWEAR GASOLINE COMPOSITION AND ADDITIVES THEREFOR

Filed Nov. 17, 1961

SPARK PLUG SET MILEAGE TO REPLACEMENT



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ANTIWEAR GASOLINE COMPOSITION AND ADDITIVES THEREFOR

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This invention relates to antiwear gasoline compositions containing a deposit-modifying agent, and a multipurpose additive serving as a detergent, de-icer, and surfactant. More particularly, this invention relates to leaded gasoline compositions containing dibutyl phthalate, mixed alkyl aryl phosphate esters, and a surfactant carburetor detergent, which meet the requirements for the operation of a modern, high-compression, internal-combustion engine as to performance rating, anti-knock qualities, fuel economy, spark-plug cleanliness, absence of induction-system deposits, and general increase in the power output of the engine. A particular feature of this invention is the finding that low concentrations of dibutyl phthalate, regardless of the presence of other additives, produce gasoline compositions which greatly reduce the wear of the parts of an internal combustion engine, particularly abrasive wear.

The dimensional changes of critical parts, such as bearings, cam lobes, cylinders, pistons, and piston rings, limit the useful life of an internal-combustion engine. Engine life has been extended by improved metallurgy, new metal alloys, improved lubricating-oil compositions, thermostatic temperature control, crankcase ventilation, and more recently, fuel additives. With the advent of high-compression, high-r.p.m., high-torque engines, the dimensional clearances of the parts were greatly reduced, and the influence of dimensional changes on engine performance and engine life have been amplified, particularly wear caused by the abrasive action of dust particles in the engine.

Little is known regarding the influence of dust-particle sizes on wear, the effects of concentration of the dust particles, or the physical properties of the abrasive portions of the dust in relation to wear or wear rates. Early tests, wherein large quantities of a composite dust with a wide range of particle size were introduced into the induction system of a spark-fired engine for relatively long periods of time, showed the effect of the size of abrasive particles on piston ring and cylinder wear. In these tests, the dust comprised silica particles of about 50 to 20 microns in size, containing 5% of particles of 20-10 microns, 2.0% of particles of 10-5 microns, and 2.5% of particles of 5-0 microns. Using a standard 4-cycle engine, it has been reported that the presence of an air filter reduced piston top-land wear by 75%, piston-ring wear by upwards of 80%, cylinder-bore wear by over 75%, valve-stem wear by about 50%, valve-guide wear by about 77%, main-bearing wear by about 80%, and crankshaft-journal wear by 30%, all of these values being approximations.

The use of both an air filter and an oil filter on an engine at the same time, according to previous investigations, further reduced the wear of these parts with the exception of the valve guides. The feed rate of the dust in these tests was high, being 0.236 g. per hundred cubic feet of air.

Corresponding tests with a single-cylinder diesel engine, using dust feed-rates of 0.033 g. per thousand cubic feet of air, well within normal operating conditions, also produced wear reductions, though not as pronounced, which were comparable to those from the internal-combustion engine tests.

C. E. Watson et al., in their more recent study entitled "Abrasive Wear of Piston Rings," presented at the January 1955, annual SAE meeting, found that the amount of wear depends on the size and properties of the abrasive and the method by which the abrasive enters into the engine. These investigators further found that some abrasives cause only limited wear while others continue to cause wear as long as they are in the engine. This prolonged wear characteristic is related to the physical properties of the abrasive.

There is evidence that during the operation of an internal-combustion engine, the piston rings are separated from the cylinder walls by finite distances and this area of separation is apparently maintained by a hydrodynamic oil film. Certain of the dust particles appear to be carried by this oil film and thus are present to produce prolonged wear. One method of reducing this type of abrasive wear is to increase the efficiency and prolong the effectiveness of the air filter itself. Another method is to provide special formulations for the crankcase oil. Both of these methods result in improved piston-ring life.

A feature of this invention is the provision of a gasoline composition which, when used in conjunction with adequate air-cleaner facilities and adequately compounded crankcase oils, results in reduction of engine wear, particularly wear due to the abrasive action of dust particles taken into the intake system of the engine.

The use of upper-cylinder lubricants in gasolines is well known. C. A. Bouman, Properties of Lubricating Oil and Engine Deposits, McMillan and Company, Limited, St. Martin's St., London, England, defines an upper-cylinder lubricant as an oil added to gasoline at concentrations from 0.25 to 0.5%. When an engine is stopped, the gasoline evaporates leaving an oil film which protects the wearing surfaces when the engine is next started. He points out the possible beneficial effect immediately after starting the engine, but also says that this effect is minor. He further points out that such materials, particularly at the higher concentrations, can lead to excessive engine deposits.

The additive treatment of gasolines described in this invention is distinct from conventional upper-cylinder lubricants in several respects, as follows.

(1) It is effective in concentrations considerably below the lower limit reported necessary for upper-cylinder lubricants.

(2) The antiwear effectiveness varies inversely with dibutyl phthalate concentration in the range from 12.5 lbs./1000 bbl. (0.005% wt.) to 75 lbs./1000 bbl. (0.03% wt.)

(3) The additive treatment of this invention exhibits carry-over properties, i.e., reduced wear can be observed for some time after a change from treated to untreated gasoline.

(4) The instant additive treatment has a beneficial effect on engine deposits rather than the observed deleterious effects associated with upper-cylinder lubricants.

Accordingly, it becomes a primary object of this invention to provide a novel gasoline composition which reduces engine wear, particularly that occurring when an engine is subjected to abrasive dust.

Another object of this invention is to provide a novel gasoline composition which, in addition to reducing engine wear, meets all of the requirements necessary for a modern, high-compression, high-speed, internal-combustion engine.

An object of this invention is to provide treated gasoline compositions for modern internal-combustion engines which increase the economy and performance of the engine, prolong spark-plug life, reduce carburetor and induction system deposits, and reduce piston ring and cylinder wear to a minimum.

Another object of this invention is to provide a gasoline composition containing small amounts of dibutyl phthalate, which composition may include deposit modifiers, such as mixed alkyl aryl phosphate esters, and a surfactant carburetor detergent, such as alkylphenoxypolyethoxy alkanols.

These and other objects of the invention will be described or become apparent as the description thereof proceeds.

The drawing is a bar graph showing spark-plug mileage to replacement in 25,000-mile fleet tests using modern cars under stop-and-go service.

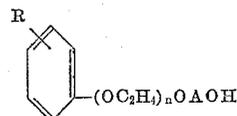
The gasoline compositions of this invention contain as the hydrocarbon portion thereof any of the known gasoline hydrocarbons boiling in the range of about 90° to 425° F., and preferably boiling in the range of about 90° to 400° F. The hydrocarbon portion of the gasoline may contain normal, branched-chain, and cyclic hydrocarbons having from 4 to 12 carbon atoms. The hydrocarbon portion of the gasoline also may contain products prepared in the chemical conversion of hydrocarbons to produce gasoline. Such conversion products include the products prepared by isomerization, alkylation, polymerization, cracking, disproportionation, hydrogenation, dehydrogenation, and combinations of such processes. A preferred gasoline composition contains a major proportion of the gasoline hydrocarbons prepared by fluid catalytic cracking and a minor proportion of an alkylate prepared from isobutane and C₃ and/or C₄ olefins. More specifically, the base fuel may comprise about 80% of gasoline from the fluid catalytic-cracking process, and about 20% of the aforementioned alkylate, with or without the addition of about 2 to 4 ml. TEL/gal. Other metal compounds and other lead alkyls, or combinations thereof, may be used in the compositions of this invention.

Based on a series of wear tests, we have determined that, quite unexpectedly, dibutyl phthalate is a most effective antiwear agent, regardless of and without effect on the functions of other additives present, and it is particularly effective at low concentrations on the order of 6 to 25 lbs. per 1000 bbls. of gasoline in overcoming abrasive wear at the top of the cylinder bore and on the piston rings of the engine. It has also been found that dibutyl phthalate, when used at 5 lbs. per 1000 bbls., is practically ineffective for this purpose, and the use of more than 25 lbs./1000 bbls. does not further enhance the wear inhibition. On a weight percent basis the concentration of dibutyl phthalate should be within the range of about 0.0024 to 0.01 wt. percent, and the most effective concentration is about 0.005 wt. percent, based on the hydrocarbon portion of the composition.

The alkyl aryl phosphate esters are from the group consisting of dimethyl phenyl phosphate, methyl diphenyl phosphate, and triphenyl phosphate. A preferred product comprises a mixture of dimethyl phenyl phosphate (45%), methyl diphenyl phosphate (15%), and triphenyl phosphate (40%), diluted with toluene to a phosphorus content of 11%.

About 0.2 to 0.45 and preferably about 0.3 theory of the alkyl aryl phosphate ester is used in the gasoline compositions of this invention.

The detergent portion of the gasoline composition of this invention, present in an amount ranging from about 0.001 to 0.01 weight percent based on the total composition, may be alkylphenoxypolyethoxy alkanols of the formula:



wherein R is an alkyl group of 8 or 9 carbon atoms, A is an alkylene group of 2 to 4 carbon atoms, and n is 4 to 16, but other surfactants which are sufficiently (to about 0.001% wt.) soluble in gasoline also may be used, e.g., aliphatic amine salts of carboxylic acids, such as the oleic acid salt of N-oleyl trimethylenediamine (Duomeen 0 Dioleate), and long-chain (16-22 carbon atoms) fatty acid salts of polyamines (RD 3134P); and long-chain aliphatic amides such as N-oleyl-N'-β-hydroxyethyl-ethylenediamine (MPA), one of a series of fatty amidomonamines.

The surfactant may be handled as a solution, e.g., 52% wt. MPA, 31% wt. isopropanol, 7% wt. xylene, and 10% wt. water, but all concentration figures given herein for dibutyl phthalate are in terms of 100% active ingredient.

EXAMPLE I

The effectiveness of various compounds as antiwear gasoline additives under abrasive wear conditions was studied using a single-cylinder COT engine. The compounds in this series of tests were selected because of some similarity to, or departure from, the physical or chemical characteristics of dibutyl phthalate, or of upper-cylinder lubricants of the prior art. The test results reported in the following table are separated into two categories, the "effective" category being those which caused a reduction in wear relative to the base fuel, and the "no effect" category being those which had no effect or caused an increase in wear relative to the base fuel. Each run included a test of the base fuel to provide a direct basis of comparison.

Table I.—Abrasive-wear test results

[COT screening tests]

Run No.	Wear rate, mg./hr.				
	Effective			No effect ¹	
	Base fuel	Additive fuel	Percent reduction	Base fuel	Additive fuel
1. Dibutyl phthalate.....	.93	.49	47		
2. Triaryl phosphate.....	1.16	.87	25		
3. Triaryl phosphate.....	.70	.56	20		
4. Diphenyl phthalate.....				.95	.92
5. Diphenyl phthalate.....				.72	.75
6. Polybutene.....				.76	.91
7. Dibutyl carbitol.....	.92	.70	23		
8. Dibutyl carbitol.....	1.04	.82	21		
9. Di-2-ethylhexyl azelate.....				1.17	1.11
10. Di-2-ethylhexyl azelate.....				.92	1.63
11. Castor oil #1 (a carboxylic ester).....				.97	1.59
12. Dibutyl phthalate.....	1.79	.99	45		
13. Polyalkylene glycol.....				1.27	1.48
14. Polyalkylene glycol.....				1.52	1.33
15. Methylphenylpolysiloxane.....				1.84	1.53
16. Methylphenylpolysiloxane.....				1.73	1.92
17. Dibutyl phthalate ²	2.19	1.77	19		
18. Dibutyl phthalate ²	2.21	1.54	30		
19. t-Butyl acetate.....	2.66	1.92	28		
20. t-Butyl acetate.....	2.16	1.44	33		

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Table I.—Abrasive-wear test results (Continued)
[COT screening tests]

Run No.	Wear rate, mg./hr.				
	Effective			No effect ¹	
	Base fuel	Additive fuel	Percent reduction	Base fuel	Additive fuel
21. Dibutyl terephthalate.....				1.83	1.00
22. Dibutyl terephthalate.....				1.84	1.58
23. Extract #36 from High VI Bright Stock.....	4.00	2.27	43		
24. Extract #36 from High VI Bright Stock.....	2.57	1.80	30		
25. Extract #36 from High VI Bright Stock.....	3.29	2.31	30		
26. Extract #44 from Int. VI Neutral.....				2.05	2.05
27. Extract #35 from Int. VI Bright Stock.....	1.54	1.15	25		
28. Extract #35 from Int. VI Bright Stock.....	2.32	1.78	23		
29. Int. VI Bright Stock.....	3.43	2.26	34		
30. Int. VI Bright Stock.....	2.87	2.24	22		
31. Dibutyl phthalate.....	3.40	1.89	44		

¹Additives showing zero, negative, or slightly positive antiwear effects.

²The rings were replaced after Run 17. Run 18 is the first test after the new rings had been broken in.

Base fuel: 80% FCC, 20% alkylate, plus 3 ml. TEL/gal. Additive dosage: 50 lb./1000 bbl. (as received, not necessarily 100% active ingredient).

As seen from the foregoing tests, piston-ring and top-cylinder wear were reduced by certain additives, and aggravated by others, and dibutyl phthalate was the most effective antiwear agent.

EXAMPLE II

The following description will demonstrate that dibutyl phthalate used in gasolines at concentrations from 12.5 to 25 lbs./1000 bbl. performs a unique antiwear function in modern engines in a manner not related to conventional upper-cylinder lubricants.

The unique effectiveness of this additive was demonstrated by laboratory engine tests in a single-cylinder Cooperative Oil Test Engine (COT engine), and a 1958 Cadillac passenger-car engine. Two sets of test conditions were used for this work:

(1) Abrasive-wear tests in which the engine was operated under conditions of constant speed, load, and temperature with 1-gram charges of dust introduced intermittently via the inlet manifold.

(2) Cyclic temperature tests in which the engine coolant temperature was cycled between 60° F. and 210° F. every 30 minutes.

This work, summarized below, shows the effectiveness of the subject additive treatment under these test conditions.

The cyclic temperature conditions force the ring and cylinder surfaces to continually re-orient themselves in response to the temperature changes, which in these tests occurred every half hour.

The laboratory wear tests were run by a matching technique in which each test involved a direct comparison between a base fuel and the base fuel treated with the additive being tested. The test was started with the engine running on the base fuel. When the base-fuel wear rate was established, usually 3-6 hours after starting the engine, the fuel supply was switched to the treated fuel without interrupting the engine run. The engine was then run for an equal period on the treated fuel. Test results were expressed as the percent reduction in wear for the

Table II.—Abrasive-wear tests

Engine	Lbs. DBP/1,000 bbl.	Average percent wear reduction
Cadillac.....	50	36
COT.....	75	10
COT.....	50	50
COT.....	25	44

additive fuel compared with the base fuel. This direct comparison eliminated variables due to restarting the engine and day-to-day variations in basic engine conditions.

Table III.—Cyclic-temperature tests

Engine	Lbs. DBP/1,000 bbl.	Average percent wear reduction
Cadillac.....	50	36
COT ¹	25	17.4
COT ¹	12.5	26
COT ²	12.5	28
COT.....	5	0

¹Includes .3 theory mixed alkaryl phosphate esters and 26 lb. alkylphenoxypolyethoxy alkanols/1,000 bbl.

²Includes .3 theory mixed alkaryl phosphate esters and 12 lb. alkylphenoxypolyethoxy alkanols/1,000 bbl.

Road tests were also carried out to evaluate the additive. A 1957 Oldsmobile equipped with a 12:1 compression ratio engine and equipment for radioactive ring-wear detection was used for this work. The car was driven over a 68-mile test course consisting of alternate sections of gravel and hard-surfaced roads. The data tabulated below represent the average of a number of repeated tests run over this course. The engine was equipped with a normally maintained oil-bath air cleaner. Base-fuel and additive-fuel were alternated to provide a direct comparison of wear rates.

Abrasive-wear road tests

Lbs. DBP/1000 bbl. ¹	Percent wear reduction
25	45
12.5	60

¹Both additive fuels also included .3 theory mixed alkaryl phosphate esters and 26 lb. alkylphenoxypolyethoxy alkanols/1000 bbl.

It can be concluded that if DBP were acting as a simple upper-cylinder lubricant, its effectiveness would be expected to increase as the concentration was increased. In every case the opposite was true. As concentration was increased from 12.5 lbs./1000 bbl., the effectiveness was reduced. At less than 12.5 lbs./1000 bbl., there was not enough material to produce any effect, as indicated by the single test at 5 lbs./1000 bbl.

EXAMPLE III

It was also observed that after an engine had been run on a treated fuel, wear was low for a considerable period of time before the base-fuel high wear rate was restored. We do not believe that a simple upper-cylinder lubricant would produce this effect. This carry-over effect is illustrated by the following data.

Extended tests equivalent to approximately 2500 miles of road operation were run in the COT engine under cyclic temperature conditions. Two tests were run on a gasoline without DBP. Two other tests were then run, alternating fuels, so that the equivalent of 200 miles of

each 1000 miles of operation were on the base fuel plus an additive package which included 12.5 lbs. DBP/1000 bbl. The remaining 800 miles of each 1000 mile period were run on the base fuel alone. The total ring-wear data for these 2500-mile tests were average to give the wear rates shown below:

Fuel:	Wear rate, mg./100 miles
Base -----	7.5
Base -----	5.9
200 miles treated fuel/800 miles base fuel -----	4.5
200 miles treated fuel/800 miles base fuel -----	5.3

The reduced average wear for the runs in which the treated fuel was used occurred during both the 200-mile period on treated fuel and the 800-mile periods on untreated fuel. Other examples of this carry-over effect have been observed in the engine test work.

EXAMPLE IV

The final evaluation, however, came from the overall evaluation of fuels from all standpoints. A series of fleet tests was conducted to evaluate the gasoline compositions of this invention to compare miles per gallon, spark-plug performance, antiwear benefits, and carburetor-detergency benefits obtained thereby. In making these tests, the untreated fuel had the following composition:

Paraffin and naphthene -----	61 percent.
Olefins -----	16 percent.
Aromatics -----	23 percent.
Tetraethyl lead -----	3 ml./gallon.

Illustrating the invention, two treated fuels were used in the fleet tests. Approximately three-fourths of the total miles on each car accumulated were with Treated Fuel No. 1, and one-fourth with Treated Fuel No. 2. The compositions of the two treated gasolines were as follows:

Component	Fuel No. 1	Fuel No. 2
Mixed alkyl aryl phosphate (ICC #3). ¹	0.3 theory -----	0.3 theory.
Dibutyl phthalate -----	12.5 lbs./1,000 bbl. -----	12.5 lbs./1,000 bbl.
N-oleyl-N'-β-hydroxyethyl ethylenediamine (MPA). ²	12.0 lbs./1,000 bbl. -----	
Isocetylphenoxytetraethoxy ethanol (Plexol 305).	-----	26.0 lbs./1,000 bbl.

¹Forty-five percent phenyl phosphate, 40% triphenyl phosphate, and 15% methyl diphenyl phosphate in solution in

Table V.—Fleet test—Wear data from individual engines

No.	Fuel	Top ring		2nd ring		Cyl. bore wear in ring area, in.			Intake valve tulip deposit, gms.
		Wt. loss, gms.	Gap inc., in.	Wt. loss, gms.	Gap inc., in.	Top	Center	Bottom	
153-----	Untreated								
	Avg.-----	.6805	.027	.2044	.013	.0004	.0003	.0003	1.0775
	Max.-----	.7279	.030	.2702	.017	.0008	.0005	.0005	2.1425
154-----	Min.-----	.5915	.024	.1336	.008	.0002	.0002	.0000	0.1489
	Treated								
	Avg.-----	.3373	.020	.1255	.011	.0002	.0002	.0002	2.5722
163-----	Max.-----	.4115	.024	.1862	.013	.0006	.0005	.0005	3.9788
	Min.-----	.1854	.019	.0813	.007	.0003	.0000	.0001	0.9721
	Treated								
164-----	Avg.-----	.1835	.009	.0597	.006	.0003	.0002	.0001	2.0600
	Max.-----	.2151	.013	.0893	.009	.0006	.0005	.0005	5.2640
	Min.-----	.1377	.006	.0305	.003	.0001	.0000	.0003	1.6050
165-----	Untreated								
	Avg.-----	.6183	.028	.2638	.014	.0068	.0004	.0003	2.2295
	Max.-----	.9910	.044	.4263	.021	.0012	.0008	.0008	3.3776
166-----	Min.-----	.4529	.021	.1932	.010	.0004	.0001	.0002	1.3409
	Treated								
	Avg.-----	.1814	.010	.0940	.009	.0004	.0002	.0001	1.8094
167-----	Max.-----	.2034	.013	.1206	.013	.0007	.0004	.0005	3.1481
	Min.-----	.1562	.008	.0701	.005	.0003	.0001	.0002	0.9482
	Untreated								
168-----	Avg.-----	.5610	.026	.2236	.014	.0006	.0004	.0003	3.1697
	Max.-----	.6408	.029	.2899	.016	.0011	.0006	.0006	3.9589
	Min.-----	.5292	.023	.1606	.009	.0002	.0001	.0001	2.7805
169-----	Treated								
	Avg.-----	.7098	.033	.1511	.009	.0006	.0004	.0004	3.9609
	Max.-----	1.0156	.039	.2034	.013	.0011	.0007	.0006	5.9075
170-----	Min.-----	.3587	.021	.0698	.007	.0001	.0002	.0002	2.7820
	Untreated								
	Avg.-----	1.4918	.091	.5221	.033	.0014	.0005	.0004	1.6866
171-----	Max.-----	1.5730	.135	1.0512	.063	.0023	.0006	.0008	2.4632
	Min.-----	1.0862	.064	.3170	.022	.0004	.0001	.0000	0.9310

toluene to a content of 11% phosphorus. A theory is defined as that amount of compound containing sufficient phosphorus to completely react with the lead present to form lead phosphate, i.e., the amount of phosphorus necessary to completely react with the lead present to form lead phosphate.
²A solution containing 52% N-oleyl-N'-β-hydroxyethyl ethylenediamine, 31% isopropanol, 7% xylene, and 10% water.

The fleet tests were conducted using modern passenger cars in severe stop-and-go service. The results are shown as follows:

Table IV.—Fleet test—Gasoline utilization

Car No.	Fuel	Test miles	Average miles per gallon
153-----	Untreated	24,788	9.6
154-----	Treated	24,464	10.8
163-----	do	24,890	10.4
164-----	Untreated	24,364	8.3
165-----	Treated	25,960	10.3
166-----	Untreated	25,680	9.6
167-----	Treated	24,437	11.4
169-----	Untreated	24,700	11.3
170-----	Treated	-----	13.4

Table IV shows that the cars operating on untreated fuel during the 25,000-mile test period averaged 9.7 miles per gallon, while the cars operating on treated fuel averaged 10.7 m.p.g. This represents a 10% increase in miles per gallon.

Cars 153 and 154 were 1958 models; cars 167, 169 and 170 were 1959 models; and cars 163, 164, 165 and 166 were 1960 models. The cars were of two makes, all with V-8 engines. All of the cars were operated with the same high-detergency lubricating oil, SAE 20W. All of the test engines were equipped with crankcase-ventilator devices which fed crankcase fumes back into the intake manifold below the carburetor, and all were equipped with either oil-bath or dry-element (paper) air cleaners, and full-flow oil filters. All of the vehicles were operated primarily in dense city traffic, in the same geographic location, and during winter, summer, and fall weather conditions. At the completion of the tests the engines were disassembled for measurement and inspection. The following wear data was accumulated:

In summary, the above data shows that the average top-piston-ring weight loss for the four engines which operated on untreated fuel was 0.8379 gm., while the average for the four engines which operated on the treated fuel of this invention was only 0.3530 gm. In addition, the data shows that the:

Average top-ring gap increase was:

	Inch
Untreated fuel	0.042
Treated fuel	0.018

Average second-compression-ring weight loss was:

	Gram
Untreated fuel	0.3035
Treated fuel	0.1076

Average second-compression-ring gap increase was:

	Inch
Untreated fuel	0.018
Treated fuel	0.009

Average cylinder-wall wear at the top of ring travel was:

	Inch
Untreated fuel	0.0008
Treated fuel	0.0004

Average cylinder-wall wear in the center of ring travel was:

	Inch
Untreated fuel	0.0004
Treated fuel	0.0002

Average cylinder-wall wear at the bottom of ring travel was:

	Inch
Untreated fuel	0.0003
Treated fuel	0.0002

Average intake-valve-tulip deposit was:

	Grams
Untreated fuel	2.0253
Treated fuel	2.8506

This shows that the engine wear, on an average, was reduced by the following values in the engines operating on the treated fuel of this invention:

	Percent reduction
Top-ring weight loss	58
Top-ring gap increase	57
Second-ring weight loss	65
Second-ring gap increase	50
Cylinder bore:	
Top-of-ring travel	50
Middle-of-ring travel	50
Bottom-of-ring travel	33

A separate determination of spark-plug life was made. Spark-plug changes were made when misfire caused loss of engine performance. All changes were made as complete sets of plugs and there was no effort to clean or regap spark-plugs. The results are shown graphically in the drawing. The spark-plug life averaged 6,740 miles with untreated fuel and 11,328 miles with treated fuel. The spark-plug life was increased an average of 68%, on

an overall basis, using the gasoline compositions of this invention.

Carburetor-cleanliness observations showed that in each instance the deposit level was significantly reduced with the treated fuel, particularly in the throttle body.

These test-fleet results show the wear protection afforded the piston rings and cylinder bores through the use of the gasoline compositions of this invention. Wear on these surfaces can cause reduction of compression pressures and increased oil consumption, with resultant loss in power and performance. Although the fleet-test results show that the gasoline compositions of this invention reduce wear on these surfaces, it is logical to recognize that some wear will always occur due to the boundary lubrication conditions. If, based on the data presented herein, it is assumed that 0.0002" wear in the bore normally results from piston travel or motion in 25,000 miles of operation (in excess of 50,000,000 strokes of the piston), the wear attributable to the fuel could be reduced by that quantity. This would result in an average of 0.0006" wear at the top of the ring travel attributable to the characteristics of combustion of the untreated fuel, and 0.0002" attributable to the treated fuel, a reduction in wear of over 66% instead of the 50% value aforementioned. At the center of the ring travel and below, wear attributable to the fuel or its combustion is practically eliminated with the treated gasoline compositions of this invention.

Piston-ring wear is reflected in both weight loss and gap increase, as measured in a ring standard. A ring is subjected to wear on its face, which is exposed to the cylinder wall, and on its sides, which seal against the piston lands. Weight loss reflects wear on all three of these surfaces, while gap increase is associated with face wear only. The wear data reported herein indicate that either protection was being obtained in both respects, or that side wear was not significant, since reductions were obtained in both weight loss and gap increase to about the same degree.

A feature of this invention is the provision of a novel additive composition consisting essentially of dibutyl phthalate, the aforesaid phosphate ester, and the aforesaid surfactant-type carburetor detergent in such proportions that the herein described motor fuel compositions are obtained when sufficient of the additive composition is added to leaded gasoline to provide from about 6 to about 25 pounds of dibutyl phthalate per 1000 barrels of gasoline. Specific examples of additive compositions useful for addition to gasolines in accordance with this invention are:

Table VI

Ingredient	Composition weight, percent			
	1	2	3	4
Dibutyl phthalate.....	10.55	19.09	16.55	31.25
Alkyl aryl phosphate ester ¹	67.51	61.07	66.23	62.50
Surfactant carburetor detergent ²	21.90	19.84	17.22	6.25

¹Forty-five percent dimethyl phenyl phosphate, 40% triphenyl phosphate, and 15% methyl diphenyl phosphate in solution in toluene to a content of 11% phosphorus. A theory is defined as that amount of compound containing sufficient phosphorus to completely react with the lead present to form lead phosphate, i.e., the amount of phosphorus necessary to completely react with the lead present to form lead phosphate.

²A solution containing 52% N-octyl-N'-β-hydroxyethyl ethylenediamine, 31% isopropanol, 7% xylene, and 10% water.

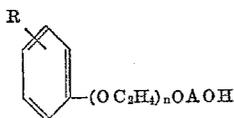
Table VII gives the properties of representative gasolines that may be used with the additive composition of this invention.

Table VII.—Properties of representative gasolines

Gasoline description	Grav-ity, ° API	Reid vapor pressure	ASTM distillation (percent evaporated basis and corrected to 760 mm./Hg)													T.E.L., ml./gal.				
			IBP	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	E.P.		Rec.	Res.	Loss	V/L 20:1
1	61.1	13.2	83	93	112	145	179	203	224	242	260	288	327	369	94.5	1.2	4.3	122.7	2.14	
2	64.9	12.1	85	96	110	127	146	165	189	215	244	250	324	259	409	96.5	1.2	2.3	119.5	2.58
3	64.5	12.7	86	98	108	124	142	163	186	211	235	260	300	330	381	97.2	1.1	1.7	116.5	2.60
4	67.3	12.3	91	102	114	131	150	170	190	212	241	276	309	340	376	97.2	1.1	1.7	119.8	2.03
5	57.0	11.3	91	105	122	152	179	205	228	242	258	274	297	314	365	96.5	1.1	2.4	132.2	2.73
6	61.0	10.8	89	101	112	132	156	180	211	237	264	296	334	355	375	97.1	1.3	1.6	128.4	2.19
7	57.3	11.2	86	100	111	134	162	188	215	242	263	285	314	334	386	98.7	1.2	0.1	127.4	2.78
8	61.2	12.2	96	99	110	130	156	184	211	235	260	288	320	399	95.0	1.0	4.0	123.0	2.63	
9	62.8	12.2	91	102	116	133	155	180	207	238	270	308	360	390	440	97.8	1.1	1.1	123.6	1.60
10	58.4	12.4	96	105	116	138	166	195	226	258	286	314	349	376	466	96.9	1.1	2.0	126.0	2.76
11	63.6	12.2	85	97	106	124	144	168	197	227	260	303	355	384	406	96.9	1.3	1.8	119.8	2.31
12	60.9	12.9	91	97	112	136	164	191	215	240	270	307	364	437	95.0	1.1	3.9	121.8	1.70	
13	62.1	11.9	95	106	116	136	160	186	214	238	260	292	343	383	424	97.8	1.3	0.9	125.7	2.33
14	63.0	11.4	82	102	114	134	158	186	215	238	258	285	337	376	416	97.9	1.3	0.8	127.0	2.64
15	60.9	10.2	87	102	112	130	151	178	209	248	284	316	359	390	419	99.0	0.6	0.4	129.8	2.70
16	60.5	10.8	89	107	128	153	172	196	220	244	279	300	340	366	408	96.0	1.0	3.0	134.0	1.22
17	61.8	11.1	89	109	119	133	153	175	199	225	252	280	310	338	397	99.0	0.8	0.2	126.7	2.72
18	57.5	9.8	92	110	118	132	146	168	199	230	250	272	302	321	394	99.0	0.6	0.4	135.5	2.90
19	61.7	9.5	91	110	121	139	157	176	200	226	256	296	334	356	382	98.0	0.9	1.1	133.4	2.26
20	54.7	11.2	93	107	122	152	176	201	227	246	264	285	311	335	382	97.0	0.9	2.1	132.5	2.99
21	61.4	9.5	93	108	120	138	158	180	204	229	252	278	315	344	382	98.0	0.8	1.2	133.6	1.18
22	57.9	9.5	93	115	125	145	166	189	213	236	259	284	314	342	394	98.7	1.1	0.2	136.4	2.62
23	66.7	7.9	99	125	138	159	181	203	228	245	260	281	314	346	383	98.5	1.4	0.1	149.3	2.89
24	57.7	9.9	95	109	124	151	178	200	220	242	270	322	373	399	427	96.0	1.1	2.9	136.8	0.98
25	59.6	10.1	95	108	121	141	166	191	216	240	266	296	332	362	410	97.0	1.1	1.9	133.5	2.05
26	64.8	10.1	90	108	119	138	162	187	214	234	254	284	318	340	382	98.0	1.2	0.8	132.7	2.78

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A motor-fuel composition consisting essentially of hydrocarbons boiling in the gasoline boiling range, about 6 to 25 pounds as substantially the only wear inhibitor of dibutyl phthalate per 1000 barrels of gasoline, about 2 to 4 milliliter of tetraalkyl lead per gallon of gasoline, about 0.2 to 0.45 theory of a phosphate ester of the group consisting of alkyl aryl phosphates, aryl phosphates and mixtures thereof, about 0.001 to 0.01 weight percent of a surfactant carburetor detergent of the group consisting of an alkylphenoxy polyethoxy alkanol of the formula



wherein R is an alkyl group of 8 to 9 carbon atoms, n is an integer of 4 to 16 and A is an alkylene group of 2 to 4 carbon atoms, the oleic acid salt of N-oleyl trimethylenediamine, fatty acid salts of polyamines containing a total of 16 to 11 carbon atoms and N-oleyl-N'- β -hydroxyethyl-ethylenediamine.

2. A motor-fuel composition in accordance with claim 1 in which the concentration of said dibutyl phthalate is about 12 to 25 pounds per 1000 barrels of gasoline.

3. A motor-fuel composition in accordance with claim 1 in which said phosphate ester is present as a mixture comprising about 45 weight percent of dimethyl phenyl phosphate, about 40 weight percent of triphenyl phosphate and about 15 weight percent of methyl diphenyl phosphate.

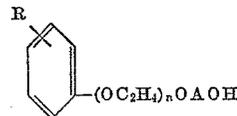
4. A motor-fuel composition in accordance with claim 1 in which said surfactant carburetor detergent is isooctylphenoxytetraethoxy ethanol.

5. A motor-fuel composition consisting essentially of hydrocarbons boiling in the gasoline boiling range, about 3 milliliter of tetraethyl lead per gallon of gasoline about 0.3 theory of a mixture comprising about 45 weight percent of dimethyl phenyl phosphate, about 40 weight percent of triphenyl phosphate and about 15 weight percent of diphenyl phosphate, about 12.5 pounds of dibutyl phthalate as substantially the only wear inhibitor per 1000 barrels of gasoline and about 12 pounds of N-oleyl-N'- β -hydroxyethyl-ethylenediamine per 1000 barrels of gasoline.

6. A motor-fuel composition consisting essentially of hydrocarbons boiling in the gasoline boiling range, about 3 milliliter of tetraethyl lead per gallon of gasoline, about

0.3 theory of a mixture comprising about 45 weight percent of dimethyl phenyl phosphate, about 40 weight percent of triphenyl phosphate and about 15 weight percent of diphenyl phosphate, about 12.5 pounds of dibutyl phthalate as substantially the only wear inhibitor per 1000 barrels of gasoline and about 26.0 pounds of isooctylphenoxytetraethoxy ethanol per 1000 barrels of gasoline.

7. A motor fuel additive composition consisting essentially of the following ingredients: (a) dibutyl phthalate, (b) a phosphate ester selected from the group consisting of alkyl aryl phosphates, aryl phosphates, and mixtures thereof, and (c) a surfactant carburetor detergent selected from the group consisting of an alkylphenoxy polyethoxy alkanol of the formula:



wherein R is an alkyl group of 8 to 9 carbon atoms, n is an integer from 4 to 16, and A is an alkylene group of 2 to 4 carbon atoms, the oleic acid salt of N-oleyl trimethylenediamine, fatty acid salts of polyamines containing a total of 16 to 22 carbon atoms, and N-oleyl-N'- β -hydroxyethyl-ethylenediamine; said ingredients (a), (b) and (c) being present in such proportions that the motor fuel composition defined by claim 1 is obtained when said additive composition is added to a hydrocarbon motor fuel boiling in the gasoline range and containing from about 2 to about 4 milliliters of tetra alkyl lead per gallon, in an amount sufficient to provide from about 6 to about 25 pounds of dibutyl phthalate per 1000 barrels of gasoline.

8. An additive composition in accordance with claim 7 in which said phosphate ester is present as a mixture comprising about 45 weight percent of dimethyl phenyl phosphate, about 40 weight percent of triphenyl phosphate and about 15 weight percent of methyl diphenyl phosphate.

9. An additive composition in accordance with claim 7 in which said surfactant carburetor detergent is isooctylphenoxytetraethoxy ethanol.

10. A gasoline composition consisting essentially of hydrocarbons boiling in the gasoline boiling range containing from 2 to 4 milliliters of tetraethyl lead per gallon of gasoline and from 0.0024 to 0.01 weight percent of dibutyl phthalate as substantially the only wear inhibitor.

11. The method of operating an internal combustion

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engine which comprises using therein as the fuel the composition of claim 10.

12. A gasoline composition consisting essentially of hydrocarbons boiling in the gasoline boiling range containing from 2 to 4 milliliters of lead alkyl per gallon of gasoline and from 0.0024 to 0.01 weight percent of dibutyl phthalate. 5

13. A gasoline composition consisting essentially of hydrocarbons boiling in the gasoline boiling range containing as substantially the only wear inhibitor about 0.0024 to 0.01 weight percent of dibutyl phthalate. 10

14. A gasoline composition in accordance with claim 13 containing about 0.001 to 0.01 wt. percent of isooctyl-phenoxytetraethoxy ethanol.

15. A gasoline composition in accordance with claim 13 containing about 0.2 to 0.45 theory of a phosphate ester of the group consisting of alkyl aryl phosphates, aryl phosphates and mixtures thereof.

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