

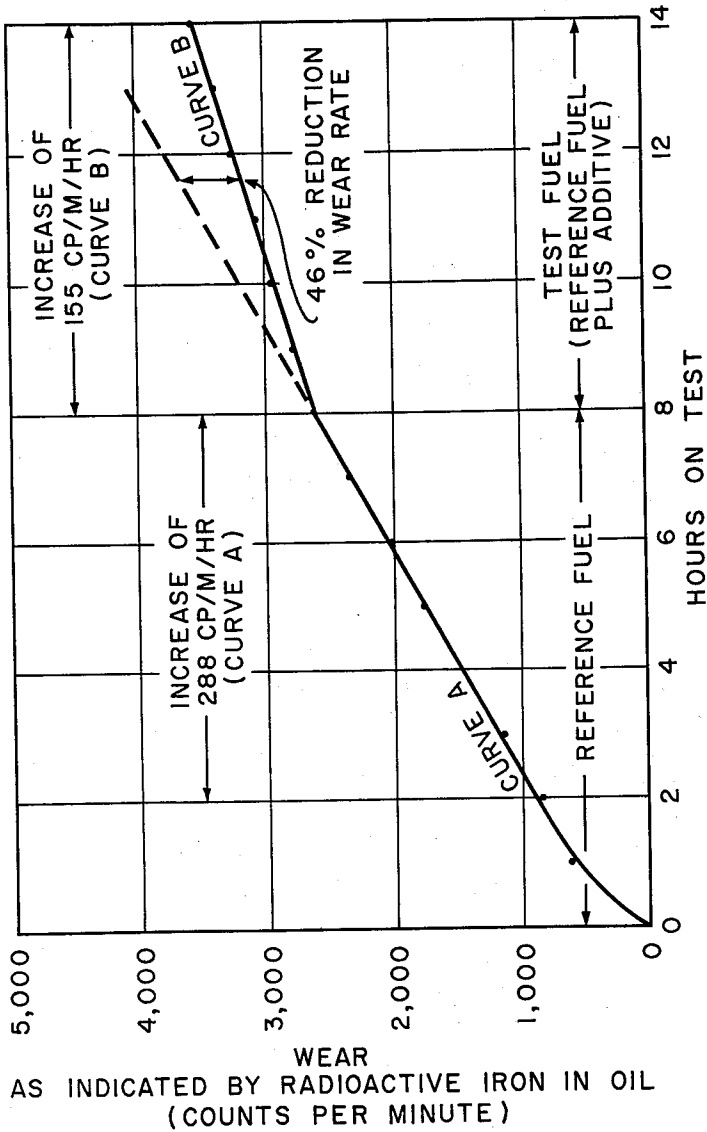
Jan. 26, 1960

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2,922,706

GASOLINE COMPOSITIONS

Filed May 31, 1957



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GASOLINE COMPOSITIONS

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Application May 31, 1957, Serial No. 662,643

6 Claims. (Cl. 44—58)

This invention relates to improved gasoline compositions and more particularly to additive compositions which are effective in modifying combustion-chamber deposits and reducing piston-ring wear when incorporated in a gasoline.

It is well known to those familiar with this art that gasoline of higher antiknock rating is necessary for satisfactory operation of the high compression gasoline engines which have been manufactured in the last few years. Tetraethyl lead, which is added to gasoline to improve the antiknock rating, contributes to the accumulation of engine deposits, especially the hard, adherent deposits which form in the combustion chamber. These deposits appear to consist mainly of solid lead oxides and a resinous polymeric substance. Unfortunately these deposits increase the octane requirements of the engine and lower its efficiency. Various halogen-containing compounds are normally incorporated in gasoline compositions along with tetraethyl lead so that a portion of the lead is converted to volatile lead halides and is removed from the combustion chamber in the exhaust gases. It has not been possible to remove all the lead compounds in this manner and the use of various additives have been suggested for the purpose of modifying the combustion chamber deposits to render them less conductive of electricity, more friable and less adherent. Of the various additives suggested the most successful has been tricresyl phosphate. No additive has been found, however, which will eliminate the formation of the resinous organic material which serves as binder or adhesive in combustion chamber deposits. Methods which will reduce deposit formation are consequently the objects of continuing research. It is the failure to solve this problem which has mainly delayed further increases in the compression ratios of modern gasoline engines.

Another problem which is becoming more serious, particularly in modern automobile engines, is that of rapid wear of piston rings. It is well known that compression rings appear to wear out in succession rather than simultaneously; that is, the second ring does not begin to wear rapidly until after failure of the top ring. Obviously if the top ring can be prevented from wearing excessively, the situation can be kept under control. In the past, attempts have been made to reduce top-ring wear by addition of lubricants of various kinds to the gasoline. In general, this has resulted in formation of deposits in the ring grooves which interfere with the action of the ring; and the beneficial effects of "upper cylinder lubricants," if any, have always been subjects of controversy. The results of research in recent years have shown that the major portion of top-ring wear occurs during periods in which the engine is operating at low temperatures. Our own findings corroborate these results. We are also of the opinion that the increase noted in the rate of top-ring wear in some of the newer high compression engines is not associated with higher compression pressures and the higher piston temperatures brought about by these

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higher pressures. We believe that the phenomenon is more likely low temperature corrosive wear associated with the larger size of the new engines, which causes them to warm up more slowly. Larger engines, especially in passenger cars, are usually operated at a small fraction of their rated output, so that low engine temperatures prevail.

We have discovered that the performance of gasoline with respect to both engine cleanliness and piston-ring wear may be significantly improved by the addition thereto of small amounts, preferably from about 0.01 percent to 0.1 percent by volume, of esters of acyclic aliphatic dicarboxylic acids. We have observed beneficial effects at concentrations as low as 0.001 percent and suspect some benefit may exist at even lower concentrations, although our test methods are not sufficiently sensitive and precise for us to state positively that this is true. At concentrations of about 0.2 percent by volume, further addition of ester is not sufficiently beneficial to be economically feasible. We have also observed that some esters exert an undesirable influence upon the volatility and ignitability of the fuel at higher concentration levels.

Although we do not wish to be limited by specific examples disclosed or by any particular theory of operation, we wish to set forth certain principles which we believe should be followed in choosing esters of dicarboxylic acids for the purposes explained herein. First of all, the compounds should possess a high flash point; otherwise they will burn quickly and may never reach the piston ring area. If possible, they should have low vapor pressure so that the esters will have an opportunity to exist at least partially in the liquid state in the cylinder. We suspect that this condition is necessary in order to assist in reducing the formation of engine deposits. We believe the esters should have good chemical stability at high temperatures so that they will not promote the formation of resinous or coke-like deposits. The esters should possess lubricity at both high and low temperatures, as any compound which exists as a liquid in the engine cylinder is likely to cause wear if it does not lubricate. A desirable characteristic of the esters is the ability to soften or dissolve resinous deposit-forming substances which may accumulate in the lubricating oil. Finally, the ester should be available at low cost.

We have found that beneficial effects are exhibited by many esters, both individually and in various blends, among which are the following:

- Di-2-ethylhexyl succinate
- Di-C₈ oxo alcohol succinate
- Ditetradecyl glutarate
- Di-2-ethylhexyl adipate
- Isooctyl adipate
- Nonyl adipate
- Dibutoxyethyl adipate
- Di-3,5,5-trimethylhexyl adipate
- Isooctyl 2-ethylbutyl adipate
- Di-2-ethylhexyl beta-methyladipate
- Dicyclohexyl beta-methyladipate
- Diisooctyl azelate
- Di-2-ethylhexyl azelate
- Di-2-ethylbutyl azelate
- Di-2-ethylhexyl sebacate
- Di-1-methyl-4-ethyloctyl sebacate
- Diisooctyl sebacate

In general, the diesters we have found to be useful have molecular weights between 200 and 600 and are represented by the formula $\text{ROOC}-(\text{C}_n\text{H}_{2n})-\text{COOR}'$ in which R and R' are saturated alkoxyalkyl or saturated hydrocarbon substituent groups having from 2 to 18 carbon atoms and in which n may vary from 2 to 8. The bene-

ficial effects vary, of course, from one ester to another, and in many instances a blend of esters gives better results than those obtainable with any individual component of the blend. We prefer not to use solid esters, as there is a possibility that they will cause deposits to form in the fuel induction system. Solid esters can be tolerated in small percentages and traces of solid esters present as impurities in commercial samples cause no apparent undesirable effects. We prefer to use esters which are liquids and which also have the lowest pour points consistent with other physical properties. When a choice is available, for example, between esters of straight chain alcohols and branched chain alcohols we often find the branched chain esters are to be preferred because they have lower pour points. Fortunately in most instances they are also cheaper. Although we have established the fact that unsymmetrical esters such as isooctyl 2-ethyl-butyl adipate can be used in practicing our invention, we prefer not to use them for economic reasons. Esters of substituted acids such as methyladipic acid are also suitable and in some instances they are more desirable than the corresponding esters of unbranched acids. Generally, however, they are more expensive.

Briefly, we find the adipates possess outstanding polymer-softening ability and satisfactory flash point, low vapor pressure, thermal stability, and low temperature lubricity, all at a reasonable cost. By addition of selected esters to liquid adipates, for example, diisooctylazolate, the property of lubricity at high temperatures is imparted to the composition, which is desirable. It is more economical to obtain the desired properties by blending low-priced esters than it would be to select a single ester with all the desired properties and manufacture it especially for this purpose. As for example, with a blend consisting of di-isooctylazolate and di-isooctyladipate, the relative amounts of the two may vary from 1 to 99 percent by volume of di-isooctylazolate and from 99 to 1 percent by volume di-isooctyladipate.

Two different types of engine tests were used in evaluating the effects of our novel gasoline compositions. Some of the tests were conducted in a Chevrolet engine operated under the following conditions:

Engine speed	-----r.p.m.-----	2,000
Engine load	-----B.M.E.P.-----	18
Water temperature	-----° F-----	100
Oil temperature	-----° F-----	140

The top compression rings of cylinders 2, 3, 4, 5, and 6 were made radioactive by exposure to neutron radiation in an atomic pile. Five radioactive rings were used in order to make the test as sensitive as possible. No radioactive ring was used on the No. 1 piston because the No. 1 cylinder is near the cold water inlet, resulting in cylinder wall temperatures which are not uniform.

The rate of wear was determined by measuring the amount of radioactive iron worn off the rings and suspended in the lubricating oil. At the end of each thirty minutes of running, a 10-minute count of radioactivity was made with scintillation detecting and counting equipment. During the first few hours of continuous operation, the results of these counts were plotted to determine the rate of wear. At the end of about six hours of continuous running at a constant rate of wear the engine was switched over to operation on the sample of gasoline to be tested, without changing any of the other operating conditions. Counts of radioactivity were made every half hour for four hours, and a new wear curve was plotted by the same technique as described above. The final result is the change in the slope of the wear curve, or in rate of wear, expressed in percent. A commercial premium grade gasoline was used as the standard fuel in all tests. The experimental gasolines were prepared by addition of esters to measured quantities of the same fuel.

A similar test procedure was used with a one-cylinder valve-in-head co-operative oil test engine with a radio-

active top piston ring, operated under the following conditions:

Engine speed	-----r.p.m.-----	2,000
Engine load	-----B.M.E.P.-----	18.7
Water temperature	-----° F-----	100
Oil temperature	-----° F-----	140

Example 1

A gasoline composition on which extensive tests were made for deposit modification and piston-ring wear contained 0.7 ml. per gallon (approximately 0.018 percent by volume) of a mixture of 95 percent by volume diisooctyl adipate and 5 percent by volume diisooctyl azelate.

A series of tests was made in the Chevrolet engine using a premium motor oil and premium gasoline as the standard for comparison. A typical set of wear curves is shown in the drawing.

In this particular test a constant rate of wear was obtained after two hours of running time had elapsed. In the drawing, curve A was plotted by averaging 10-minute counts made every half hour. As the slope of the curve indicates, the rate of wear corresponded to an increase of 288 counts per minute per hour. After changing to the test fuel the wear rate was shown to correspond to an increase of only 155 counts per minute per hour (curve B). The reduction in rate of wear was then

$$\frac{133}{288} = 46 \text{ percent}$$

for this particular test run. This test was continued another two hours, as indicated, without any significant variation in the rate of wear. Under the stated test conditions, the reduction in rate of wear obtained with the test sample containing 0.7 ml. per gallon of a mixture of 95 volume percent diisooctyl adipate and 5 volume percent diisooctyl azelate was 45 to 50 percent for the entire series of tests.

In a series of tests with the C.O.T. single cylinder engine, using the same fuels and premium motor oil, the reduction in wear was 20 to 25 percent. When a supplement 1 level alkaline reserve detergent motor oil was used, the reduction in wear was 10 to 12 percent. This type of motor oil is recommended for use in diesel engines and is known to reduce corrosive wear. Apparently our novel gasoline compositions also reduce corrosive wear and to an even greater extent than the supplement 1 oil, although at present we are unable to give an adequate explanation of the mechanism of this action. We have some evidence of adsorption of the esters on metal surfaces, which may offer a partial explanation. We have no knowledge of any previously reported corrosive wear inhibiting effect of these diesters. Some reduction in high temperature piston ring wear might be expected to result from a lubricating effect, but the rate of wear at high temperatures is so low that any improvement would probably lie within the limits of experimental error.

Example 2

A test run was made with the Chevrolet engine by the same procedure as outlined above, using a premium grade motor oil and a gasoline composition containing 0.35 ml. per gallon of diisooctyl azelate. A 33 percent reduction in piston ring wear was observed.

Example 3

A test run was made with the Chevrolet engine by the procedure described above, using a premium grade motor oil and a gasoline composition containing 1.4 ml. per gallon of a composition containing 95 percent by volume diisooctyl adipate and 5 percent by volume diisooctyl azelate. A 62 percent reduction in piston ring wear was observed.

Example 4

A test run was made with the Chevrolet engine by the same procedure as in Example 1, using a premium grade motor oil and a gasoline composition containing 0.35 ml.

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per gallon of diisooctyl adipate. This run showed a 10 percent reduction in piston ring wear.

Our improved gasolines containing non-aromatic, liquid esters of aliphatic dicarboxylic acids have been stored in steel containers, used in a high speed endurance run in an automobile, and subjected to numerous other tests in an effort to discover undesirable characteristics. We find these fuels burn clean, leave significantly less deposits in combustion chambers, and do not corrode containers on storage. Their performance has been satisfactory in every practical test to which they have been put. The anti-knock rating appears to be virtually unaffected by the esters in the proportion used. There likewise appears to be no significant effect upon volatility or any of the other important characteristics of gasoline. The percentages of additive necessary to obtain beneficial results are so small as to be quite feasible economically.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A motor fuel composition consisting essentially of a major proportion of gasoline to which is added from 0.001 percent to 0.2 percent by volume of a composition consisting essentially of at least one liquid ester represented by the formula $\text{ROOC}-(\text{C}_n\text{H}_{2n})-\text{COOR}'$ having a molecular weight between about 328 and about 524 in which R and R' are selected from the class consisting of saturated hydrocarbon substituent groups having from 2 to 18 carbon atoms and saturated alkoxyalkyl substituent

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groups, and in which n may vary from 2 to 8, as an agent for reduction of low-temperature wear.

2. A motor fuel composition consisting essentially of a major proportion of gasoline to which is added from 0.001 percent to 0.2 percent by volume of dibutoxyethyl adipate as an agent for reduction of low-temperature wear.

3. A motor fuel composition consisting essentially of a major proportion of gasoline to which is added from 0.001 percent to 0.2 percent by volume of di-2-ethylhexyl azelate as an agent for reduction of low-temperature wear.

4. A motor fuel composition consisting essentially of a major proportion of gasoline to which is added from 0.001 percent to 0.2 percent by volume of di-2-ethylhexyl sebacate as an agent for reduction of low-temperature wear.

5. A motor fuel composition consisting essentially of a major proportion of gasoline to which is added from 0.001 percent to 0.2 percent by volume of diisooctyl sebacate as an agent for reduction of low-temperature wear.

6. A motor fuel composition consisting essentially of a major proportion of gasoline to which is added from 0.001 percent to 0.2 percent by volume of a composition comprising 5 percent by volume of diisooctylazelate and 95 percent by volume of diisooctyladipate as an agent for reduction of low temperature wear.

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