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ANTIKNOCK MOTOR FUEL

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6 Claims. (Cl. 44-70)

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This invention relates to novel motor fuels and methods of preparing same, and more particularly it relates to the preparation of stable high octane motor fuels especially adapted for aviation use.

This application is a division of my copending application Serial No. 688,428, filed August 5, 1946, which is a continuation-in-part of my application Serial No. 512,782, filed December 3, 1943, now abandoned.

In the preparation of high octane motor fuels lead tetraethyl is often, if not generally, used to raise the octane number of a hydrocarbon liquid boiling in the gasoline boiling range. However, the storage of certain types of gasoline base stocks containing tetraethyl lead has resulted in the formation of a haze or precipitate in the gasoline, particularly when such fuels are stored at relatively elevated atmospheric temperatures, such as in tropical climates, especially when extended storage periods are involved. The problem has been most serious and perplexing in cases in which the precipitate formed during storage contains only a relatively small proportion of gum, i. e. small enough to pass even fairly strict motor fuel specifications, but contains a major proportion of lead, chiefly in the form of an oxygen-containing compound of lead, which apparently results from the decomposition of the tetraethyl lead. Although the actual amount of tetraethyl lead lost by such decomposition during storage is sometimes small, and, perhaps, entirely negligible, from the point of view of the loss in octane rating, nevertheless the formation of the lead-containing precipitate is serious because even small amounts of such a precipitate tend to clog the strainers in the aviation motor fuel system and it may, therefore, cause faulty operation of the airplane motors.

Although in certain instances formation of a gummy precipitate has appeared to be accelerated in some types of gasoline base stocks, especially cracked gasolines, in the presence of tetraethyl lead, the addition of any of a large number of gum inhibitors was found to overcome such accelerated gum formation; but the present invention involves a very different problem because the precipitate formed in the cases with which this invention is involved contains only a small and unobjectionable amount of gum but

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contains a large proportion of lead. This invention is likewise not related to the problem of discoloration of certain types of gasoline base stocks, even straight-run petroleum distillates, when exposed to sunlight, either when such fuels contain tetraethyl lead or not, because such discoloration is primarily due to chemical changes in some of the organic substituents of the gasoline base stock, whereas in the fuels with which the present invention is concerned there is no substantial discoloration of the base stock and the problem appears to be solely, or at least primarily, one of decomposition of the tetraethyl lead per se, most of the storage being in the dark.

In extensive studies which led to the present invention it was found that straight-run gasoline distillates from highly aromatic crude petroleum could be leaded, i. e., have tetraethyl lead added thereto, and stored without formation of objectionable amounts of lead-containing precipitate. On the other hand, it was found that gasoline basestocks consisting substantially or entirely of aliphatic hydrocarbons, whether natural or synthetic, but particularly synthetic gasoline base stocks made by alkylation, for instance, of butylenes with isobutane, when leaded and stored, resulted in formation of undesirably high amounts of precipitate containing a major proportion of lead oxide. Furthermore, it was found that most of the chemical compounds usually used as gum inhibitors would not prevent such decomposition of the tetraethyl lead.

Although the explanation of these peculiar phenomena is not known with certainty, it is believed that the chief reason why the problem of decomposition of the tetraethyl lead during storage has not become serious until recently may be due to the possible presence of some natural stabilizer present in cracked gasolines and in straight-run distillates obtained from aromatic crudes.

The primary object of the present invention is to stabilize such leaded fuels which are normally unstable with respect to formation of a precipitate containing a major proportion of lead during storage.

Broadly, the invention comprises adding to the leaded fuels described above a small amount of a stabilizer comprising a hydroxy aromatic compound of the hydroxy benzoic acid class. The

preferred representative of this class is salicylic acid, which is the ortho hydroxy benzoic acid, although the meta and para isomers may also be used, as well as esters and salts of these various hydroxy benzoic acids. For instance, alkyl esters such as methyl, ethyl, isopropyl, butyl, amyl, and so forth, esters of ortho hydroxy benzoic acid may be used, and the ammonium salts of ortho hydroxy benzoic acid may be used, such as ammonium salicylate. Similarly, the aryl esters of the ortho, meta, and para hydroxy benzoic acids may be used to advantage as, for example, phenyl, ortho tolyl, meta tolyl, para tolyl, alpha naphthyl and beta naphthyl salicylates.

The amount of stabilizer to be used will vary to some extent according to the particular requirement of the gasoline base stock being used and according to the severity of the conditions under which the motor fuel is to be stored, but normally it will range between the approximate limits of .05-.5 lb. of stabilizer per 1000 gallons of motor fuel, and preferably about 0.1-0.3 lb./1000 gallons of fuel. While the hydroxy benzoic acids per se are not readily soluble in the gasoline base stocks in question and, therefore, should be added thereto in solution in alcohol or similar solvent, the esters of the hydroxy benzoic acids are generally oil soluble and may be readily dissolved directly in the gasoline. However, such esters of the hydroxy benzoic acids as are solids under normal conditions may, advantageously, be dissolved separately in a small quantity of suitable solvent, such as gasoline or alcohol, to make a stock solution. The desired amount of stock solution may then be conveniently added to the main bulk of the gasoline which is to be stabilized. In any event it is preferable to add the inhibitor or solution of inhibitor to the gasoline at or near the time of adding the tetraethyl lead.

Instead of using tetraethyl lead in preparing the motor fuels in question other lead alkyl known anti-knock agents may be used, such as lead tetramethyl, lead dimethyl diethyl, etc. The amount of lead alkyl anti-knock agent to be used will, of course, vary primarily upon the octane requirement of the finished blend, and accordingly may range from relatively small amounts such as 0.5 or 1.0 cc/gallon of fuel, up to relatively large amounts, such as 5 or 6 cc. or more per gallon, as may sometimes be desired for super aviation fuels or other special purposes, but the invention is particularly applicable to motor fuels containing about 3 cc. or more of tetraethyl lead per gallon and is especially applicable to aviation motor fuels now being used for military purposes which require 4 cc. of tetraethyl lead per gallon.

The hydrocarbon or gasoline base stock which, of course, forms the major constituent of the motor fuels in question may be composed of various types of constituents as suggested above, but the invention is particularly applicable to synthetic pure aliphatic hydrocarbon base stocks within the gasoline boiling range, such as those made by alkylation of normal olefins with isoparaffins. Such alkylates generally have an A. S. T. M. octane number of at least 80 and are substantially saturated in respect to hydrogen as shown by a bromine number test in the range of 0.1 to 0.2 and an acid heat value in the range of 1° to 3° F.

In preparing alkylate base stocks of the type preferred, known methods of alkylation may be used, such as reacting isobutane with olefins, such as butylenes or pentylenes or mixtures thereof, in the presence of sulfuric acid of about 90-100%,

preferably 92.98%, concentration, at a temperature of about 0-100° F., preferably 40-70° F. For instance, a liquid mixture consisting of about 58% by volume of isobutane and 20% by volume of butylenes is fed into a reactor containing sulfuric acid of about 96% concentration, using about one volume of hydrocarbon feed per volume of acid, and maintaining the temperature at about 40° F. and at a pressure of about 15 lbs./sq. in. gauge. After a reaction period of about 0.5 hour the hydrocarbon layer is separated from the acid catalyst layer and is washed successively with water, aqueous caustic, and water. In such alkylation processes, in place of isobutane one may use other iso-alkanes, such as isopentane. Also, various olefins may be used, such as isobutene, normal butene-2 or normal butene-3 or a mixture thereof, such as mentioned above, or one or more of the various pentenes, such as pentene-2, pentene-3, or methyl-2-butene-3, or even one or more of the normal hexenes or mixtures of normal olefins having different numbers of carbon atoms, such as 4 and 5 or 4, 5, and 6. It is to be understood, of course, that in such alkylation processes, one may use catalysts other than sulfuric acid such as phosphoric acid, hydrogen fluoride, boron fluoride, etc.

In place of alkylates, such as described above, one may also use synthetic aliphatic base stocks made by reacting normal olefins and iso-olefins in the presence of sulfuric acid and other suitable catalysts; such reaction products are normally referred to as "copolymers." For instance, normal butylene, which may consist of normal butene-2 or butene-3 or a mixture thereof, may be reacted with isobutylene in the presence of sulfuric acid of about 69 to 70% concentration, at a temperature of about 145° to 150° F. and under a pressure of about 145 to 150 lbs./sq. in. above atmospheric. The resulting copolymerization product is separated from the acid catalyst and fractionated to recover a codimer, which is probably a mixture of several branched octenes. Similarly other codimers may be prepared, such as by reacting isobutylene with propylene or even ethylene or with higher olefins, such as one or more of the pentenes or else higher iso-olefins, e. g. isopentene, may be reacted with some of the various olefins referred to. Since these codimers are generally not desirable for use in aviation fuels in their unsaturated or olefinic state, it is preferable for maximum lead susceptibility and other aviation motor fuel characteristics, to hydrogenate the codimers to the corresponding branched paraffins.

The invention also applies to natural petroleum fractions within the gasoline boiling range which consist substantially entirely of aliphatic hydrocarbons, or fractions which are substantially entirely free, or have been separated, from aromatic constituents, for instance, a straight-run gasoline distillate from a Pecos crude, which is an essentially isoparaffinic base stock, or an isopentane fraction distilled or otherwise separated in substantially pure state from any desired crude.

The invention applies to motor fuels comprising mixtures of these various base stocks which are normally unstable in respect to formation of a precipitate containing lead during storage, if stored in the form of a leaded blend. For instance, in preparing high octane aviation motor fuels, especially for military purposes, it is often desired to use an alkylate as the primary constituent of the motor fuel base stock, and to use a small amount of isopentane, isohexane, iso-

heptane or other low boiling substantially pure aliphatic hydrocarbons, such as cyclopentane, in sufficient amount to make a blended fuel having the desired vapor pressure for ease of starting and for operation at suitably low temperatures.

Although the invention applies particularly to aviation motor fuel base stocks consisting substantially or entirely of aliphatic hydrocarbons, either natural or synthetic as described above, it does not exclude the use of other addition agents, particularly antiknock agents consisting of other types of hydrocarbons or various oxygen, nitrogen, or other derivatives thereof, provided that such addition agents do not consist of, or comprise, cracked petroleum fractions or mixed petroleum fractions obtained by straight-run distillation of aromatic containing crudes. In other words, the invention is not intended to apply to the use of mixed aromatic fractions, such as may be obtained by solvent extraction with liquid sulfur dioxide, etc., of aromatic type gasoline base stocks; such mixed aromatic fractions, when leaded, do not need stabilization against decomposition of the tetra-

1941, page 15, and comprised subjecting 200 ml. of the motor fuel sample to oxidation for a period of 5 hours in a glass sample bottle containing strips of carbon steel having an area of 35 square inches. To be considered as passing this test satisfactorily a sample should not form a precipitate exceeding 5 mgs. per 100 ml. of oxidized sample, and the gum value should not exceed 6 mgs. per 100 ml. of oxidized sample, with deduction allowable for lead present in the gum. The sample to be submitted to the accelerated gum test must be protected from direct or diffused light prior to the test.

The alkylate used, when tested without any tetraethyl lead, showed no precipitate and only a very small, practically negligible, amount of gum, namely, about 0.2 mg. in the accelerated gum test, thereby indicating that the alkylate base stock per se is normally stable in respect to precipitate or gum formation during storage.

The results of the accelerated gum test on the leaded blends of this same alkylate are as follows:

TABLE I
Accelerated Gum Tests

Test No.	Sample	T. E. L. Content	Inhibitor Lbs./1000 Gals.	Accelerated Gum Tests			
				Ppt.	Pb+Gum	Pb	Gum
1	Alkylate	Cc.	0	Brown	Mg. 29.7	Mg. 16.3	Mg. 13.4
2	do	3	.1 Salicylic Acid	do	13.4	7.1	6.3
3	do	3	.2 Salicylic Acid	None	1.3	---	1.3

ethyl lead during storage, and furthermore are sufficiently high in octane number and lead susceptibility or octane blending value for the purposes of the present invention. On the other hand, synthetic or substantially pure single aromatic compounds may be used, such as benzene, toluene, isopropyl benzene, tertiary butyl benzene, toluidine, xylidene, etc. Similarly, aliphatic oxygen-containing anti-knock agents may be used, such as di-isopropyl ether, ethyl isopropyl ether, isopropyl tertiary butyl ether, isopropyl alcohol, ethyl alcohol, tertiary butyl alcohol, acetone, methyl isopropyl ketone, etc. These various antiknock addition agents may be used in amounts ranging from about 1% to 40%, preferably about 5% to 20%, or 30%.

The invention and the advantages thereof will be better understood from a consideration of the following experimental data.

3 cc. of tetraethyl lead per gallon were added to an isobutane-butylene alkylate which was made in commercial equipment that was operated substantially according to conditions which have previously been described.

The resulting fuel, which had an A. S. T. M. octane number about 100 was then subjected to the accelerated gum test alone and with addition of salicylic acid in several concentrations. The "accelerated gum test" procedure used was that adopted by the Cooperative Fuel Research Committee of the Society of Automotive Engineers, and published by that Committee in "Test Procedures and General Information in Current Use in the Development and Utilization of Aviation, Motor and Automotive Diesel Fuels," May

Test No. 1 shows that, without inhibitor, the leaded alkylate, containing 3 cc. of tetraethyl lead per gallon, when subjected to the accelerated gum test, forms a brown precipitate and shows a 29.7 mg. total of lead plus gum, of which 16.3 mg. is lead and 13.4 mg. is gum. Tests Nos. 2 and 3 show that the addition of .1 and .2 lbs., respectively, of salicylic acid per 1000 gallons of fuel, reduces (as in Test No. 2) or prevents (as in Test No. 3) the formation of a precipitate and reduces or entirely prevents the presence of lead with the gum in the accelerated gum test. Test No. 3 shows that 0.2 lb. of salicylic acid per 1000 gallons of fuel reduced the gum from 13.4. to 1.3 and reduced the lead from 16.3 to 0.

Another series of tests was made to obtain some approximate estimate of the probable duration of the stability period, assuming by subjecting samples of leaded fuel to the same accelerated gum test, except extending the time of oxidation from 5 hours to 10 hours, to see whether the inhibited samples would have a predicted storage stability life of over three years because the usual 5-hour test oxidation period may be assumed to be equivalent to 18 months of actual storage. In this series of tests the motor fuel used was a 100-octane gasoline which contained 3 cc. of tetraethyl lead per gallon, and the base stock was composed to 7.2% isopentane, 40% isobutane-butylene alkylate, and 52.8% virgin naphtha from Gulf Coast and Pecos crude oils. The motor fuel, before adding the tetraethyl lead had an A. P. I. gravity of 69.3°, a Reid vapor pressure of 6.7 pounds per square inch and an A. S. T. M. octane number of 83.

The results of the accelerated gum tests were as follows:

TABLE II

Effect of different oxidation test periods

Test No.	Time of Oxidation, hours	Ppt.	Pb+Gum	Pb	Gum	Predicted Storage Stability Life ¹
WITHOUT INHIBITOR						
4-----	5	Yellow--	Mg. 10.7	Tr-----	Mg. 10.7	Less than 18 months.
5-----	10	---do---	36.8	13.8 mg--	23.9	
WITH .1 LB. SALICYLIC ACID PER 1,000 GALLONS						
6-----	5	None----	2.6	Nil-----	2.6	Over 3 years.
7-----	10	---do---	2.0	Nil-----	2.0	

¹ Assuming 5-Hour Oxidation Period Equivalent to 18 months storage.

The above tests in Table 2 show that without inhibitor (Tests Nos. 4 and 5) a yellow precipitate is formed in both the 5- and 10-hour tests and that the amount of lead plus gum increases

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ing effect of sunlight. After successive 2 months periods of storage, portions of the large sample

were withdrawn and submitted to the accelerated gum tests. During the latter storage periods, the accelerated gum tests were also supplemented by copper-dish and silica-dish gum tests.

TABLE III

Long-time storage tests

Test No.	Storage Time, Months	Copper Dish Gum	Silica Dish Gum	Accelerated Gum Test			
				Ppt.	Pb+Gum	Pb	Gum
WITHOUT INHIBITOR							
8-----	0	Mg.	Mg.	Yellow-----	Mg. 10.7	Trace-----	Mg. 10.7
9-----	2	-----	-----	do-----	25.3	23.2 mg.	2.1
10-----	4	-----	-----	do-----	23.2	12.1 mg.	11.1
11-----	7	-----	1.5	Brown-----	27.4	15.7 mg.	11.7
12-----	10	-----	2.6	Yellow-----	37.7	34.3 mg.	3.4
13-----	12	2.6	2.7	do-----	30.4	21.1 mg.	9.3
14-----	18	3.0	2.4	do-----	30.4	19.3 mg.	11.1
WITH .1 LB SALICYLIC ACID/1000 GAL.							
15-----	0	-----	-----	None-----	2.6	Nil-----	2.6
16-----	2	-----	-----	do-----	2.6	do-----	2.6
17-----	4	-----	-----	do-----	3.0	do-----	3.0
18-----	7	-----	1.8	do-----	2.4	do-----	2.4
19-----	10	-----	1.8	do-----	2.0	do-----	2.0
20-----	12	2.4	1.3	do-----	2.0	do-----	2.0
21-----	18	2.2	1.6	do-----	5.1	do-----	5.1

from 10.7 at 5 hours to 36.8 at 10 hours, the amount of lead in the gum increasing from a trace at 5 hours to 13.8 in 10 hours; whereas with .1 lb. of salicylic acid per 1000 gallons (Tests Nos. 6 and 7) no precipitate was formed even with the 10-hour oxidation period, in which tests the small amount of salicylic acid used resulted in reducing the total amount of lead plus gum from 36.8 to 2.0, the lead being reduced from 13.8 to 0. These tests indicate that .1 lb. of salicylic acid per 1000 gallons of leaded fuel is sufficient to stabilize the fuel for over three years.

Another series of tests was made to determine the behavior of similar leaded fuel blends in actual storage over a long time, up to 18 months, making test observations at intermediate periods of 2, 4, 7, 10 and 12 months. In this series of tests, the fuel used was the same as that used for tests 4 to 7 (Table 2) and contained 3 cc. of tetraethyl lead per gallon.

In this series of tests large samples were stored in contact with an iron strip (having a total area of 4 sq. inches) in brown glass bottles enclosed in brown paper bags to prevent interfer-

These tests show that without inhibitor (Tests Nos. 8 to 14) the leaded fuel formed a yellow or brown precipitate in the accelerated gum test both without storage and at all periods up to the 18 months, whereas the fuel inhibited with salicylic acid (Tests No. 15 to 21) did not form any precipitate at any time throughout the 18 months test. Also, as indicated in previous tests, the leaded fuels without inhibitor showed large amounts of lead plus gum ranging from 10.7 initially to 30.4 at 18 months, in the accelerated gum test, whereas salicylic acid maintained the lead plus gum figure to a value ranging between 2.6 and 5.1, with no lead present at any test period through the 18 months. The copper-dish and silica-dish gum tests were not substantially affected by the presence of salicylic acid in the leaded fuel. The accelerated gum tests therefore showed that salicylic acid, in a concentration of .1 lbs. per 1000 gallons of fuel, inhibited the leaded fuel against formation of a precipitate, and against the decomposition of the tetraethyl lead during actual storage up to the 18 months.

In still another series of tests, a 100-octane

number aviation gasoline base stock was prepared by blending together 16.5% of isopentane, 14.5% of isohexane, 29.0% of isoheptane, 27.0% of isobutane-butylene alkylate, 5.0% of virgin naphtha from Pecos crude oil, and 8.0% of low boiling aromatics extracted from a Gulf Coast virgin naphtha. The isopentane, isohexane, and isoheptane were derived from crude petroleum naphtha by careful fractionation. When a sample of this base stock was submitted to the accelerated gum test, no precipitate and less than about 0.2 mg. of gum per 100 cc. of sample was formed in the absence of tetraethyl lead. Upon blending 5 cc. of tetraethyl lead per gallon into the base stock and submitting samples of the leaded fuel to the accelerated gum test, both with and without methyl salicylate or phenyl salicylate added to the mixture, the following results were obtained:

TABLE IV

Test No.	Sample	T. E. L. Content	Inhibitor Lbs./1000 Gallons	Accelerated Gum Test	
				Ppt.	Pb+Gum
22	100 Oct. No. Gas.	Cc. 5	0	Mg. 1.7	Mg. 10.1
23	do	5	0.2 Methyl Salicylate.	0.7	3.3
24	do	5	0.2 Phenyl Salicylate.	1.2	2.9

Test number 22 shows that, although less than the allowable amount of precipitate was formed in the uninhibited sample, the quantity of lead and gum exceeded the amount that is considered acceptable. Test number 23 shows that the addition of 0.2 pound of methyl salicylate to the gasoline inhibited formation of precipitate and the deposition of lead compounds and gum so that the inhibited fuel satisfactorily met the required specifications. Test number 24 similarly shows the addition of 0.2 pound of phenyl salicylate to the leaded gasoline reduced both the amount of precipitate formed during the oxidation step and the amount of lead and gum deposited in the evaporating dish during evaporation of the gasoline; the amount of lead compounds and gum was less than the amount considered allowable in the specification of the test.

As an indication that the invention applies not only to synthetic hydrocarbon fuels such as made by alkylation, etc., but also to natural substantially pure aliphatic hydrocarbons, it is noted that a sample of isopentane when submitted to the accelerated gum test showed no precipitate and only 1.1 gum when tested without tetraethyl lead, but, when tested with an addition of 3 cc. of tetraethyl lead per gallon, gave a heavy brown precipitate and 18.5 lead plus gum, the lead per se being 16.3. It is thus apparent that although leaded isopentane is unstable in

respect to formation of a precipitate containing lead during storage, this instability is overcome by the addition of salicylic acid as shown in the tests set forth in Table 3 involving a 100-octane fuel containing 7.2% isopentane and 3 cc. of tetraethyl lead.

Although the invention is intended to apply primarily to fuels whose hydrocarbon base stock is composed substantially or entirely of aliphatic hydrocarbons, either natural or synthetic, with or without addition of various anti-knock agents which are oxygenated or other types of derivatives of hydrocarbons, in its broader sense the invention also comprises blends of such relatively pure aliphatic base stocks with minor amounts of aromatic-containing petroleum fractions in such low or non-stabilizing proportions that the mixed fuel blend when leaded is still normally unstable in respect to formation of a precipitate containing lead during storage.

It is not intended that this invention be unnecessarily limited by any theory suggested as to the mechanism of the operation of the invention nor by any of the specific examples which have been given merely for the sake of illustration, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as well as all modifications coming within the spirit and scope of the invention.

I claim:

1. A motor fuel consisting essentially of a lead alkyl anti-knock agent and a predominant amount of a hydrocarbon base stock within the gasoline boiling range consisting essentially of a hydrogenated copolymer of a normal olefin having from 2 to 6 carbon atoms and an iso-olefin having 4 to 5 carbon atoms, said fuel being stabilized against deterioration during storage by having added thereto a small amount of an inhibitor selected from the class consisting of hydroxy benzoic acid and esters and salts thereof.

2. A motor fuel according to claim 1 in which the inhibitor is salicylic acid.

3. A motor fuel according to claim 1 in which the inhibitor is an alkyl ester of salicylic acid.

4. A motor fuel according to claim 1 in which the inhibitor is methyl salicylate.

5. A motor fuel according to claim 1 in which the inhibitor is an aryl ester of salicylic acid.

6. A motor fuel according to claim 1 in which the inhibitor is phenyl salicylate.

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