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MOTOR FUELS

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

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 lead oxide, 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 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 not 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

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distillates from highly aromatic crude petroleums could be leaded, i. e., have tertaethyl lead added thereto, and stored without formation of objectionable amounts of lead-containing precipitate. On the other hand, it was found that gasoline base stocks 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 a small amount of hydroxy aromatic hydrocarbon of the hydroquinone class to such motor fuels which are normally unstable with respect to formation of a haze or precipitate and containing a major proportion of lead during storage. Hydroquinone, p—HO—C_6H_4—OH, itself has been found to be a most effective stabilizer, although other compounds within the hydroquinone class may be used, such as quinhydrone, $C_6H_4O_2$—$C_6H_4(OH)_2$, which may be considered as a quinone substituent of hydroquinone.

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. This stabilizer is not readily soluble in the gasoline base stocks in question and, therefore, should be added thereto in solution in alcohol or similar solvent either at or near the time of adding the tetraethyl lead thereto. 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 require-

ment 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 iso-paraffins. Such alkylates generally have an ASTM 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 isopentanes. 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. iso-pentene, 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, isoheptane or other low boiling substantially pure aliphatic hydrocarbon, 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 anti-knock 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 tetraethyl lead during storage, and furthermore are more 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 anti-knock 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 ASTM octane number above 100 was then subjected to the accelerated gum test alone and with addition of hydroquinone or quinhydrone 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 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 1

Accelerated gum tests

Test No.	Sample	T. E. L. content	Inhibitor, lbs./1,000 gals.	Accelerated gum tests			
				Ppt.	Pb+gum	Pb	Gum
		Cc.			*Mg.*	*Mg.*	*Mg.*
1	Alkylate	3	0	Brown	29 7	16.3	13.4
2	do	3	.1 hydroquinone	None	2.6		2.6
3	do	3	.2 hydroquinone	do	2.8		2.8
4	do	3	.1 quinhydrone	do	1.8		1.8
5	do	3	.2 quinhydrone	do	2.0		2.0

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 hydroquinone per 1000 gallons of fuel, completely prevents the formation of any precipitate and reduces the gum to a satisfactorily low amount, 2.6 mg. and 2.8 mg. (both below the allowed maximum of 6 mg.), with no lead present with the gum. Tests Nos. 4 and 5 show similarly satisfactory results upon the use of quinhydrone in place of hydroquinone.

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 of 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 ASTM octane number of 83.

The results of the accelerated gum tests were as follows:

TABLE 2

Effect of different oxidation test periods

Test No.	Time of oxidation, hours	Ppt.	Pb+gum	Pb	Gum	Predicted storage stability life [1]
WITHOUT INHIBITOR						
			Mg.	*Mg.*	*Mg.*	
6	5	Yellow	10.7	Tr.	10.7	Less than 18 months.
7	10	do	36.8	13.8	23.0	
WITH .1 LB. HYDROQUINONE PER 1,000 GALLONS						
8	5	None	1.8	Nil	1.8	Over 3 years.
9	10	do	2.3	Nil	2.3	
WITH .1 LB. QUINHYDRONE PER 1,000 GALLONS						
10	5	do	2.0	Nil	2.0	Over 3 years.
11	10	do	3.5	Nil	3.5	

[1] Assuming 5-hour oxidation period equivalent to 18 months storage.

The above tests in Table 2 show that without inhibitor (tests Nos. 6 and 7) a yellow precipi-

tate is formed in both the 5- and 10-hour tests and that the amount of lead plus gum increases 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. hydroquinone per 1000 gallons (tests Nos. 8 and 9) and with .1 lb. quinhydrone (tests Nos. 10 and 11), no precipitate was formed even with the 10-hour oxidation period, and the amount of lead plus gum increased only slightly from 1.8 to 2.3 in the case of hydroquinone and 2.0 to 3.5 in the case of quinhydrone, both being considerably below the 6.0 maximum permitted, there being no lead present in the gummy residue called "lead + gums." In other words, these tests indicate that .1 lb. of inhibitor per 1000 gallons of leaded fuel is sufficient in the case of hydroquinone or quinhydrone 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 6 to 11 (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 interfering 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.

gum test both without storage and at all periods up to the 18 months, the fuel inhibited with hydroquinone (tests Nos. 19–25) did not form any precipitate at any time throughout the 18-month test, and the fuel inhibited with quinhydrone (tests Nos. 26–32) was stabilized against precipitate formation throughout the 4-month period but developed a slight brown or yellow precipitate during longer storage periods. Also, as indicated in previous tests, the leaded fuel without inhibitor showed large amounts of lead plus gum ranging from 10.7 initially to 30.4 at 18 months, in the accelerated gum tests, whereas hydroquinone maintained the lead plus gum figure to a value ranging between 1.8 and 3.6, with no lead present, while the quinhydrone showed satisfactory lead plus gum values, with no lead, for the first 7 months. Thus the quinhydrone shows a substantial stabilizing effect against formation of a precipitate containing lead during storage, although hydroquinone is superior in stabilizing the leaded fuel for a much longer period. The copper-dish and silica-dish gum tests indicate that long-time storage of the leaded fuels did not have any substantial effect on either the copper-dish gum or silica-dish gum.

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

TABLE 3

Test No.	Storage time, months	Copper dish gum	Long-time storage tests				
			Silica dish gum	Accelerated gum test			
				Ppt.	Pb+gum	Pb	Gum
			WITHOUT INHIBITOR				
		Mg.	*Mg.*		*Mg.*	*Mg.*	*Mg.*
12	0			Yellow	10.7	Trace	10.7
13	2			do	25.3	23.2	2.1
14	4			do	23.2	12.1	11.1
15	7		1.5	Brown	27.4	15.7	11.7
16	10		2.6	Yellow	37.7	34.3	3.4
17	12	2.6	2.7	do	30.4	21.1	9.3
18	18	3.0	2.4	do	30.4	19.3	11.1
			WITH .1 LB. HYDROQUINONE/1000 GAL.				
19	0			None	1.8	Nil	1.8
20	2			do	1.8	Nil	1.8
21	4			do	3.4	Nil	3.4
22	7		1.4	do	3.2	Nil	3.2
23	10		1.2	do	3.6	Nil	3.6
24	12	3.0	1.8	do	2.8	Nil	2.8
25	18	2.0	1.6	do	2.3	Nil	2.3
			WITH .1 LB. QUINHYDRONE/1-000 GAL.				
26	0			None	2.0	Nil	2.0
27	2			do	2.0	Nil	2.0
28	4			do	4.2	Nil	4.2
29	7		1.0	Sl. brown	4.4	Nil	4.4
30	10		2.0	Yellow	8.0	7.1	0.9
31	12	0.9	1.5	do	9.2	Trace	9.2
32	18	1.0	1.7	do	4.0	Trace	4.0

These tests show that whereas, without inhibitor (tests Nos 12–18), the leaded fuel formed a yellow or brown precipitate in the accelerated leaded isopentane is unstable in respect to formation of a precipitate containing lead during storage, this instability is overcome by the addi-

tion of hydroquinone or quinhydrone 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 comprising a hydrocarbon mixture normally stable against gum formation and composed predominately of saturated aliphatic hydrocarbons and containing a small amount of a lead alkyl anti-knock agent which in the presence of said hydrocarbons tends during storage to form lead-containing precipitates and a hydroxy aromatic hydrocarbon of the class consisting of hydroquinone and quinhydrone in an amount sufficient to inhibit the formation of a lead-containing precipitate during storage.

2. Motor fuel according to claim 1 in which the hydrocarbon fuel base stock has an octane number of at least 80.

3. Motor fuel according to claim 1 in which the hydrocarbon fuel base stock consists entirely of saturated aliphatic hydrocarbons and without tetraethyl lead is normally stable against precipitate and gum formation during storage.

4. Motor fuel according to claim 1 containing at least 3 cc. of tetraethyl lead per gallon of fuel.

5. A motor fuel comprising a lead alkyl anti-knock agent and a hydrocarbon base stock which is normally stable against precipitate and gum formation during storage in the absence of lead alkyl compounds, said hydrocarbon base stock consisting substantially entirely of synthetic liquid hydrocarbons within the gasoline boiling range made by alkylation of normal olefins with isoparaffins, together with a small amount of saturated C_5 hydrocarbon to obtain the desired vapor pressure, said fuel being stabilized against deterioration during storage by having added thereto a small amount of hydroquinone.

6. Motor fuel according to claim 5 in which the alkylate base stock is made by alkylation of an olefin selected from the group consisting of butylenes and pentylenes with isobutane, and the fuel contains at least 3 cc. of tetraethyl lead and about .05–0.5 lb. of hydroquinone per 1000 gallons of fuel.

7. A motor fuel comprising a lead alkyl anti-knock agent and a hydrocarbon base stock which is normally stable against precipitate and gum formation during storage in the absence of lead alkyl compounds, said hydrocarbon base stock comprising 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 hydroquinone.

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