

UNITED STATES PATENT OFFICE

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MOTOR FUELS

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1 Claim. (Cl. 44-69)

1 This invention relates to novel motor fuels and to methods of preparing same and more particularly it relates to the preparation of stable high octane motor fuels such as are especially adapted for aviation purposes. In the preparation of high octane motor fuels, lead tetraethyl is often, if not generally, used to raise the octane number of a gasoline base stock. However, the storage of gasolines con-

2 tively protected against both haze and gum formation. This is illustrated by the results given in the attached table, which presents data on the storage of an alkylate motor fuel base stock alone and in various combinations with hydroquinone and a commercial gum inhibitor herein referred to as inhibitor A, consisting of 50% n-butyl p-aminophenol in 30% isopropyl alcohol and 20% dry methanol.

TABLE 1

Inspection of aviation gasoline base stock made by alkylation of normal butylene with isobutane + 4 ml. of tetraethyl lead per gallon

Column Number.....	1	2	3	4	5	6	7	8	9	10
Sample Number.....	I	II			III			IV		
Stock and Procedure.....	Leaded Alkylate Without Additive	Stock+0.1 lb. Hydroquinone per 1000 gals.			Stock+0.2 lb. Gum Inhibitor A per 1000 gals.			Stock+0.2 lb. Gum Inhibitor A and 0.1 lb. Hydroquinone per 1000 gals.		
Storage Period.....	Initial	Init.	1 mo.	3 mos.	Init.	1 mo.	3 mos.	Init.	1 mo.	3 mos.
Army Gum:										
Gum+Pb.....	34	17	3	3	4	2	2	5	3	3
Precipitate.....	74	48	0.8	0.6	1	0.2	None	1	0.2	0.2
Modified Army Gum:										
Gum+Pb.....	41	36	50	62	4	4	2	5	6	6
Precipitate.....	64	96	16	38	2	0.7	0.9	2	0.2	0.2
Nitrogen Bomb Test.....	¹ DNP	Pass	Pass	Pass	Pass	Pass	DNP	Pass	Pass	Pass
Precipitate, mgs./200 ml.....	13	None	None	None	None	None	17	None	None	None

¹ DNP=Does not pass. Storage Conditions: 5 gallons in 10 gallon steel drums (dry) at 100° F.

taining relatively large quantities of tetraethyl lead fluid, particularly where extended storage periods are involved, frequently results in the formation of a haze or precipitate insoluble in the gasoline. This insoluble material results from the decomposition of a small amount of the tetraethyl fluid, and its formation is accelerated by heat and by the presence of minute quantities of oxygen and other impurities and also by the use of lead fluid which has been aged in storage for extended periods prior to adding to the gasoline. Aviation gasolines, which contain 4 cc. of lead fluid, are extremely susceptible to the formation of this haze or precipitate. The insoluble material formed in these stocks tends to clog the strainers in fuel systems and the contaminated stock cannot be safely used without extensive reconditioning. In addition, precipitate formation may be accompanied by a corresponding loss in octane rating. According to this invention it has been found that leaded gasolines may be effectively protected against this haze or precipitate formation, without affecting any other properties, by the addition of a small amount of hydroquinone or quinhydrone. When used in conjunction with a suitable gum inhibitor, the gasoline is effec-

35 The original alkylate, containing no addition agents other than 4 cc. of tetraethyl fluid, showed a high gum content and according to the nitrogen bomb test, haze or precipitate would be formed on storage. The addition of 0.1 lb. of hydroquinone per 1,000 gals. of the leaded base reduced the Army gum value, particularly after storage at 100° F. but did not affect the modified Army gum. This blend, however, was stable to haze formation (nitrogen bomb test) even after three months' storage at 100° F. The addition of 0.2 lb. of gum inhibitor A per 1,000 gals. of the leaded alkylate effectively reduced the gum but did not stabilize the lead. The nitrogen bomb test run on this material after three months' storage showed that haze or precipitate would develop on further storage. The addition of both hydroquinone and inhibitor A effectively reduced the gum and protected the blend from lead decomposition. The nitrogen bomb test referred to above is a test which has recently been developed for the particular purpose of determining whether a leaded motor fuel has a tendency to form haze or precipitate due to decomposition of the lead tetraethyl during storage. Briefly described, the test consists in placing 200 ml. of the motor fuel into an 8-ounce glass bottle, covering it with a

loose fitting cover and placing the covered bottle in a clean, dry test bomb identical with, or similar to, the United States Army Air Corps bomb at room temperature, charging the bomb with nitrogen under 100 lbs./sq. inch pressure and exhausting it and repeating this operation three times to displace oxygen and finally charging with nitrogen to about 100-102 lbs./sq. inch and placing the bomb in a water or steam bath at $212 \pm 0.5^\circ$ F. for 16 hours, after which it is removed from the bath and cooled to room temperature, the nitrogen exhausted gradually and the contents of the bottle carefully examined to see if any precipitate or bloom or haze can be discerned in the motor fuel, for example, by visual inspection. If so, it is reported as "not passing." If desired, especially if a precipitate or haze is noticeable, the contents of the bottle are filtered through a weighed Gooch crucible, rinsing the bottle twice with 20 ml. portions of 86° Bé. naphtha to remove all precipitate and washing the precipitate in the crucible with another 20 ml. portion of the naphtha, then drying in an oven at 221° F. for one hour, cooling and re-weighing, reporting the precipitate in mgs. per 200 ml. of fuel.

Although in the tests discussed above a gasoline base stock made by alkylation was used, it is not intended that the invention be limited to that particular type of base stock. Other types of liquid hydrocarbon fuels of the motor fuel boiling range may be used, such as straight run or cracked gasoline or stocks made by polymerization of lower olefins with or without subsequent hydrogenation, e. g., by polymerizing isobutylene to a dimer and hydrogenating to produce essentially 2,2,4-trimethyl pentane, or stocks made by isomerization, hydroforming or by any combination of these and other known processes. However, the invention is particularly applicable to motor fuels prepared from a gasoline base stock having an octane number at least as high as 80 (by the A. S. T. M. method), and preferably at least as high as 85, and particularly to such base stocks which are highly refined and substantially free from olefins. It is also preferred to use base stocks which are distilled or fractionated to a proper boiling range for aviation fuel purposes, i. e., having a boiling range of $100-350^\circ$ F. and preferably $150-300^\circ$ F.

Instead of using tetraethyl lead, one may use other lead alkyl anti-knock agents, such as lead tetramethyl or some of the mixed lead alkyl compounds, such as lead dimethyl, di-ethyl, etc. The amount of the lead alkyl anti-knock agent used is an important feature of this invention because the problem involved in this invention does not occur to much extent, or at least not seriously, if amounts of lead tetraethyl less than 3 ml. per gallon are used. In other words, the invention is particularly applicable to fuels containing at least 3 ml. and perhaps 4 ml. or even 6 or higher ml. per gallon.

In place of n-butyl p-amino phenol, one may also use other gum inhibitors, such as various mono hydroxy phenols, e. g., alpha naphthol, alkyl phenols, such as p-amyl phenol, p-tertiary butyl phenol, etc., or other compounds selected from the class of amino phenols, particularly, the alkyl p-amino phenols, e. g. tertiary amyl p-amino phenol, isobutyl p-amino phenol, benzyl p-amino phenol, etc.

The amount of the gum inhibitor to be used will, of course, vary to a certain extent with the type of motor fuel base stock and the severity of

the storage conditions to which the fuel is likely to be subjected, but normally will range between the approximate limits of .01-0.5 lb./1,000 gallons, and generally about .05-0.2 lb./1,000 gallons.

The hydroquinone, which of course has the chemical formula $\text{HO}-\text{C}_6\text{H}_4-\text{OH}$, or the quinhydrone which is presumed to have the formula $\text{HO}-\text{C}_6\text{H}_4-\text{O}-\text{O}-\text{C}_6\text{H}_5=\text{O}$, may be used in various amounts, depending primarily upon the amount of lead alkyl anti-knock agent used as well as the temperature, time and other storage conditions to which the fuel is likely to be subjected, but generally the amount of stabilizer should be between about .01 and 0.5 lb./1,000 gallons of fuel, the preferred limits being similar to those of the gum inhibitor, namely, about .05 to about 0.2 or 0.3 lb./1,000 gallons. Thus the preferred type of motor fuel composition according to this composition is one comprising a major proportion of an aviation gasoline base stock having an octane number of at least 80, containing at least 3 ml. of lead tetraethyl (or other lead alkyl anti-knock agent) and a sufficient amount of gum inhibitor to make the thus compounded fuel normally substantially stable in respect to gum formation, although still unstable in respect to decomposition of the lead tetraethyl during storage, this fuel then being stabilized against decomposition of the lead tetraethyl by addition thereto of about .01-0.5 lb. of hydroquinone per 1,000 gallons of fuel.

To further emphasize the outstanding importance and effectiveness of hydroquinone as a stabilizer in this invention, the following additional tests are reported.

A number of chemical compounds coming within the general class of hydroxy and/or amino derivatives of aromatic hydrocarbons, a number of which are known to be good gum inhibitors, were tested as stabilizers or precipitate inhibitors in a concentration of 2 mg. per 100 ml. (.167 #/1000 gal.) in an aviation gasoline base stock consisting of catalytic naphtha, alkylate and isopentane, to which 4 ml. of tetraethyl lead was added per gallon of fuel. These samples were then subjected to the nitrogen bomb test described above and also, for comparison, to the modified Army gum test. The results were as follows:

TABLE 2

Inhibitor Added, 2 mg./100 ml.	Modified Army Gum		Nitrogen Bomb Test	
	Gum+ Pb	Precipitate	Rating	Precipitate, mg./200 ml.
None.....	17	20	DNP ¹	5.1
Phenyl ether of hydroquinone.....	11	16	do.....	5
Catechol.....	13	23	do.....	11
Phloroglucinol.....	23	37	do.....	4
Resorcinol.....	6	11	do.....	9
Alpha-naphthol.....	5	5.6	do.....	7.2
Beta-naphthol.....	4	3.4	do.....	6.3
Alpha-naphthylamine.....	3	0.7	do.....	2.4
Phenyl alpha-naphthylamine.....	3	0.2	do.....	2.4
Alpha-tetrahydro-naphthol.....	3	1.4	do.....	5.1
Hydroquinone.....	22	31	Pass.....	None

¹ DNP= Does not pass.

These tests show that hydroquinone is the only one of the hydroxy and amino aromatic compounds tested which gave satisfactory stabilization of the tetraethyl lead as determined in the nitrogen bomb test. It is interesting to note that several of the materials, such as catechol, alpha-

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naphthol, etc., actually very slightly increased the amount of precipitate above the 5.1 mg. obtained without any addition agent. It should also be noted that even materials, such as alpha-naphthylamine and phenyl alpha-naphthylamine which reduced the modified Army gum precipitate to the lowest figure, did not make the fuel pass the nitrogen bomb test. It should also be noted that although the hydroquinone does pass the nitrogen bomb test, it not only did not reduce the amount of modified Army gum but actually increased it over the amount obtained without any addition agent (31 compared to 20). These data therefore indicate that there is no reliable relation between gum inhibiting and stabilization against precipitate or haze formation due to decomposition of lead tetraethyl as determined in the nitrogen bomb test. According to the present invention, therefore, both hydroquinone and a gum inhibitor must be incorporated into the leaded gasoline in order to stabilize it against precipitate and haze formation during storage.

Another series of tests were made using as base stock a butene-isobutane alkylate containing 4 ml. of tetraethyl lead per gallon. Comparative tests were made on the base stock containing some hydroquinone, some quinhydrone, or some of the same gum inhibitor referred to as inhibitor "A" in the previous series of tests. These various blends were then subjected to the nitrogen bomb test with the following results indicated in Table 3. Although numerical figures are not available for the gum formation, two columns are added in the table to indicate in a general way whether the gum was high or low. It is understood of course that for a leaded aviation motor fuel to be satisfactory during storage, the nitrogen bomb test must show a passing rating and no precipitate formation, and the gum test should show low gum formation.

TABLE 3

Test No.	Lbs./1000 gal.			Nitrogen Bomb Test		Gum
	Inhib. "A"	Hydroquinone	Quinhydrone	Rating	Ppt., mgs./200 mls.	
1.				DNP	16	High.
2.	0.2			do	7.7	Low.
3.	0.4			Pass	None	Do.
4.		0.1		do	None	High.
5.			0.1	do	None	Do.
6.	0.2	0.1		do	None	Low.
7.	0.2		0.1	do	None	Do.

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The tests in Table 3 show that 0.2 lb. of inhibitor "A" per 1000 gallons gave a satisfactory reduction in gum formation but did not give satisfactory results in the nitrogen bomb test, and on the other hand 0.1 lb. of either hydroquinone or quinhydrone satisfactorily passed the nitrogen bomb test with no precipitate formation, but still permitted high gum formation. 0.4 lbs. per 1,000 gallons was required of inhibitor "A" in order to both pass the nitrogen bomb test and give satisfactory low gum formation. On the other hand, as shown in tests 6 and 7, 0.1 lb. of hydroquinone or quinhydrone, when used together with 0.2 lbs. of inhibitor "A," gave unexpectedly superior results by passing the nitrogen bomb test with no precipitate formation, and at the same time giving only low gum formation.

It is not intended that the invention be limited to any particular materials which have been given merely for the sake of illustration, nor unnecessarily by any theory as to the mechanism of the operation of the invention.

I claim:

A motor fuel consisting essentially of an alkylate gasoline base stock and a lead alkyl antiknock agent, normally characterized by substantial gum formation and lead precipitation on prolonged storage, said fuel containing about 0.1 pound of normal butyl para aminophenol per 1000 gallons of fuel, and about 0.1 pound of hydroquinone per 1000 gallons of fuel.

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