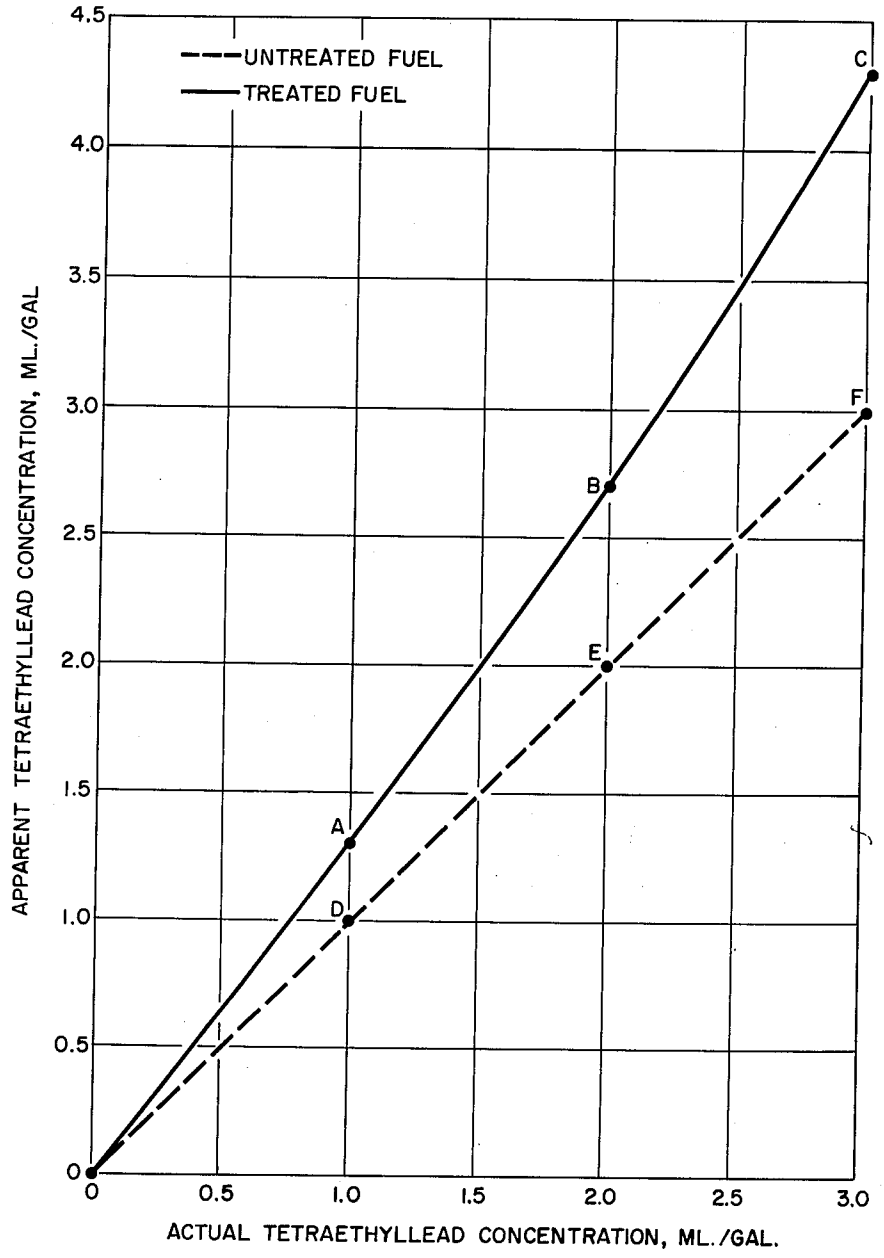
April 17, 1962 F. J. DYKSTRA 3,030,196

HYDROCARBON FUELS CONTAINING BORON ESTERS

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FIGURE 1



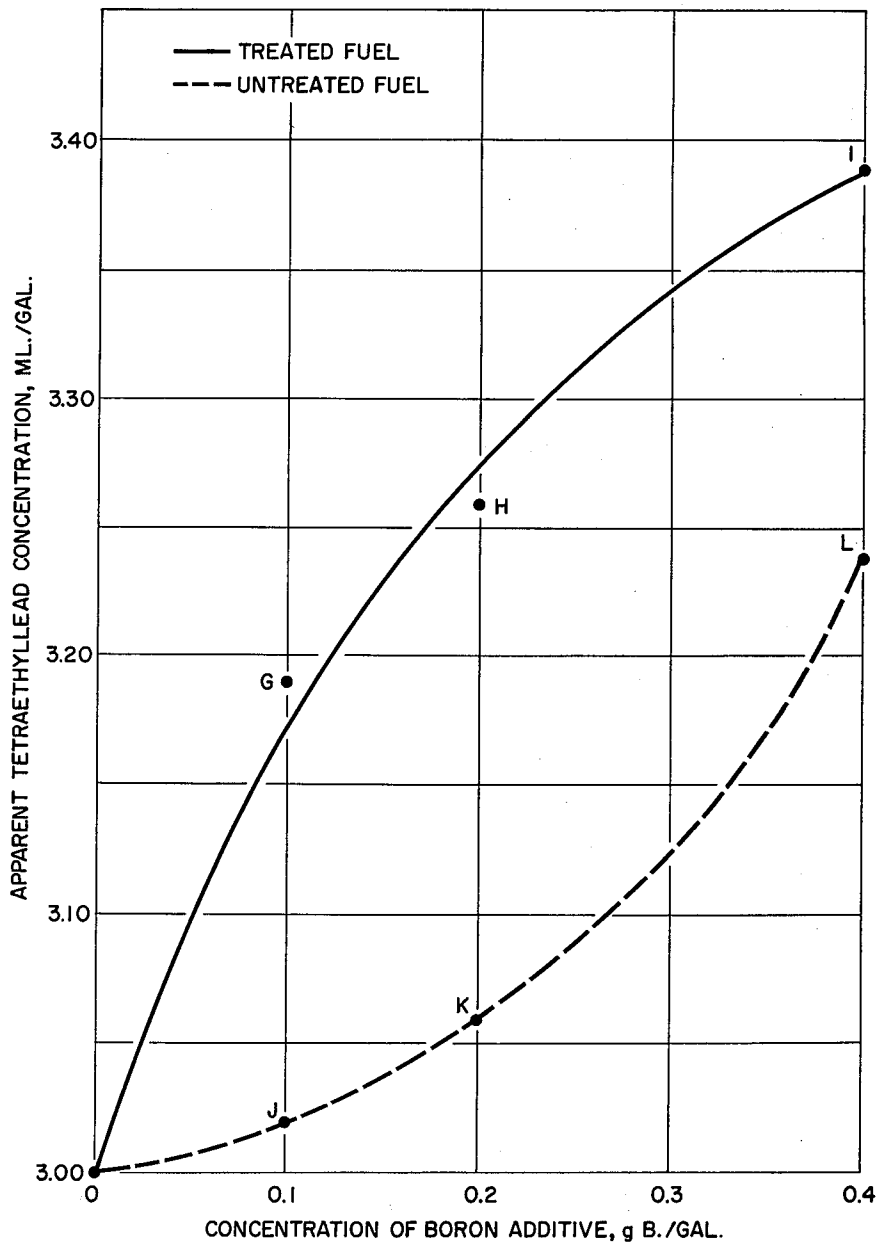
FRED J. DYKSTRA, *INVENTOR.*

BY Kenneth Swartwood

HYDROCARBON FUELS CONTAINING BORON ESTERS

Filed April 9, 1956 3 Sheets-Sheet 2

FIGURE 2



FRED J. DYKSTRA, *INVENTOR.*

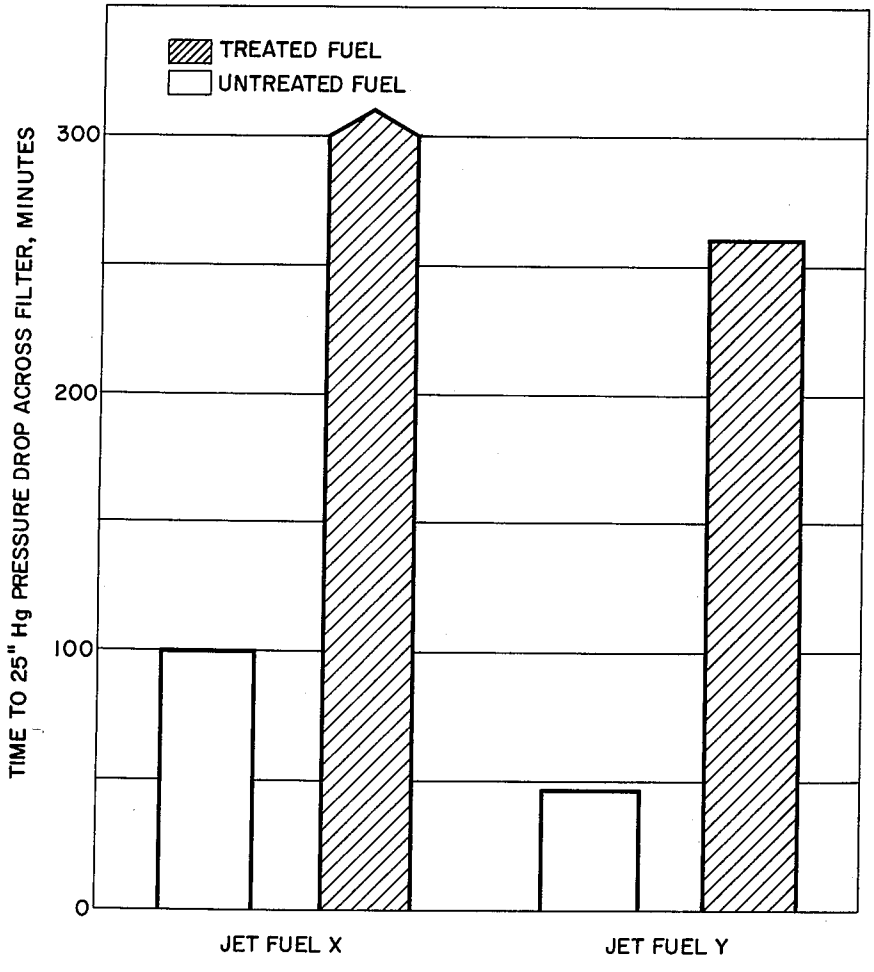
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HYDROCARBON FUELS CONTAINING BORON ESTERS

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FIGURE 3



FRED J. DYKSTRA, *INVENTOR.*

BY Kenneth Swartwood

United States Patent Office 3,030,196 Patented Apr. 17, 1962

3,030,196 HYDROCARBON FUELS CONTAINING BORON ESTERS

Fred J. Dykstra, Detroit, Mich., assignor to Ethyl Corporation, New York, N.Y., a corporation of Delaware

Filed Apr. 9, 1956, Ser. No. 577,030
7 Claims. (Cl. 44—69)

This invention relates to treating and improving liquid hydrocarbons.

An object of this invention is to provide a process of treating light liquid hydrocarbons. Another objects is to provide a process of treating liquid hydrocarbons derived from mineral sources, such as gasoline, jet fuel, and light distillates—viz., kerosene, domestic fuel oil, and diesel fuel. A further object is to provide improved liquid hydrocarbons derived from mineral sources as described above. A particular object is to provide a process of treating gasoline and jet fuel whereby these hydrocarbon fuels are substantially improved in performance characteristics. A still further object is to provide gasoline and jet fuel improved by the process of this invention. Another object is to provide novel and useful treating agents used in the process of this invention and also novel and valuable products formed during such process. An additional object is to provide new chemical compounds. Still another object is to provide methods of employing the liquid hydrocarbon compositions of this invention. Other objects will be apparent from the ensuing description.

The above and other objects of this invention are accomplished by a process which comprises contacting a liquid hydrocarbon with an ester of a metaboric acid, said hydrocarbon having a kinematic viscosity of less than about 4.28 centistokes, an API gravity at 60° F. of not less than about 32° API, and a mid-boiling point of up to about 580° F., at least a portion of said hydrocarbon being non-aromatic, said ester being (1) soluble in said hydrocarbon and (2) resistant to oxidative deterioration.

The liquid hydrocarbon used in the process of this invention is preferably derived from mineral sources. Thus, this liquid hydrocarbon is derived from petroleum, coal, shale, tar sands, natural gas, lignite and gilsonite. This hydrocarbon is a liquid hydrocarbon fuel, at least a portion of which is non-aromatic. The improvements from the process of this invention are of greatest magnitude where such hydrocarbon contains at least a trace amount of at least one non-hydrocarbon substance—e.g., sulfur compounds, nitrogen compounds, oxygen compounds (peroxides, hydroperoxides, etc.), or the like. Moreover, very substantial improvements are effected when using a mixture of liquid hydrocarbons meeting the above requisites. Thus, this invention is applicable to liquid petroleum gas, gasoline, jet fuel, kerosene, diesel fuel, domestic fuel oil and related light fuels.

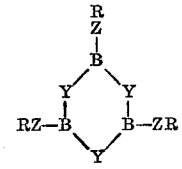
An ester of a metaboric acid is used as the treating agent in this invention. These esters must meet two requirements: (1) They must be soluble in the hydrocarbon being treated and (2) they must be resistant to oxidative deterioration. As to the first requirement, the ester functions when dissolved in the hydrocarbon being treated. Preferably the ester of a metaboric acid used should have sufficient solubility in the hydrocarbon being treated such that on bringing the metaborate ester in contact with the hydrocarbon, a solution of the former in the later occurs almost immediately. However, in the instant process esters of a metaboric acid which dissolve in the hydrocarbon more slowly or less completely can be used successfully. Physical agitation, such as stirring, is helpful when using these less-soluble esters. In most cases, that portion of the ester dissolved in the hydrocarbon is consumed in effecting improvements therein. This enables additional treating agent to pass into solution and exert its function. The treating agent used should be soluble in the liquid hydrocarbon being treated to the extent that a solution containing at least 0.0004 percent by weight of boron can be achieved.

The second requirement of the treating agents is that they be resistant to oxidative deterioration. Resistance to oxidative deterioration can be readily measured by subjecting the treating agents to Test Procedure D–525 of the American Society for Testing Materials. This procedure measures the extent to which the test material is degraded by oxygen when the material is placed in a test bomb maintained under oxygen pressure of 100 p.s.i.g. at a temperature of 100° C. In short, the esters used in the process of this invention must not be deteriorated when in contact with air and, for this reason, my treating agents are nitrogen-free. An attempt to employ an oxygen-sensitive ester of a metaboric acid in the process of this invention would be futile because the treating agent would be decomposed or otherwise chemically modified to the extent that it could not exert its beneficial function.

There are four metaboric acids which form esters which are suitable in the practice of this invention. These acids have the empirical formulas HOBO, HOBS, HSBO and HSBS. Thus, esters of these metaboric acids, which esters meet the above requirements for use as treating agents pursuant to this invention, have the empirical formula

RYBZ

wherein R is selected from the group consisting of alkyl, aralkyl, cycloalkyl, aryl, alkaryl, alkoxyalkyl, poly(alkoxy)-alkyl, and aryloxy alkyl; and Y and Z are selected from the group consisting of oxygen and sulfur. It is preferable that the R groups contain no more than about 18 carbon atoms, although in most cases, R groups containing up to about 8 carbon atoms give the best results and, for this reason, are particularly preferred. Under normal conditions—i.e., ambient temperatures and pressures—the above esters of metaboric acids exist as trimers having the formula



wherein R, Y and Z are as designated above.

The most particularly preferred treating agents used in this invention are esters of metaboric acid. In other words, Y and Z in the above formula are both oxygen in these most preferred compounds. Esters of metaboric acid are not only very effective treating agents, but provide very clean-burning, treated hydrocarbons because these esters are sulfur-free. Isopropyl metaborate is an excellent example. Moreover, this compound is readily prepared from cheap starting materials.

The treating agents of this invention can be mixed with esters of other boric acids, such as orthoborate esters. Advantages of using such mixtures are that they are easily prepared and that orthoborate esters are good drying agents. Thus, these easily-prepared mixtures, when contacted with liquid hydrocarbons as defined above which contain small smounts of water, possess the feature that the orthoborate ester portion of the mixture is consumed in drying the hydrocarbon thereby enabling the metaborate ester to better exert its beneficial function. These advantages are somewhat offset by the fact that esters of boric acids other than esters of metaboric acids do not

exert the beneficial function exhibited by the metaboric esters themselves. This means that only a portion of the mixture is capable of bringing about the improvements in the hydrocarbons. Thus, it is desirable that when a mixture of esters of boric acids is used, at least about 10 percent by weight of the mixture is an ester of a metaboric acid as defined above. Preferably, these mixtures contain a major proportion of an ester of a metaboric acid. By using such mixtures, the total amount of treating agent needed is reduced to a satisfactorily small amount. Under no circumstances can the process of this invention be carried out with a mixture of boric acid esters which does not contain an ester of a metaboric acid.

The process of this invention is simple and economical. The treating agent is readily handled and is free from obnoxious or dangerous characteristics. For example, most of the treating agents of this invention are normally solids having low vapor pressures. They are relatively non-toxic and can be used without the necessity of stringent safety precautions. No gas is used or formed during the process. High temperatures are not necessary.

Not only is the process of this invention relatively simple, economical and non-hazardous, but the achieved results are substantial. The combustion characteristics of the hydrocarbon fuels treated by this invention are greatly improved. Other improvements in these hydrocarbons are also effected. For example, gasolines treated by this invention have (1) improved tetraethyllead susceptibility, (2) reduced surface ignition rate, (3) improved boron additive response, (4) greater stability, (5) improved color and appearance, (6) reduced water content, (7) cleaner burning characteristics; jet fuels of the invention have high temperature stability and improved combustion properties; and diesel fuels of the invention have reduced smoke-forming tendencies. The nature and importance of the above and other improvements brought about by this invention are considered hereinafter.

With the vast majority of the liquid hydrocarbons amenable to the treatment of this invention, a flocculent precipitate is formed as the treating agent is contacted with the hydrocarbon. Because the liquid hydrocarbon used in the process of this invention has a viscosity and an API gravity as set forth above, this flocculent precipitate rapidly coalesces and if the hydrocarbon is maintained in the quiescent state, the precipitate rapidly settles to the bottom of the treating vessel. This precipitate can thus be readily separated by decantation, filtration, centrifugation and like procedures. Many improvements are brought about in the hydrocarbons in which the above precipitate is formed. For example, the peroxide and hydroperoxide content of the treated hydrocarbon is reduced frequently to zero, when this precipitation occurs. Thus, the hydrocarbon possesses enhanced resistance against oxidative deterioration. This is surprising because the treating agents themselves, particularly the esters of metaboric acids, are not antioxidants. The nitrogen content of the hydrocarbons being treated is also reduced. This reduction in nitrogen content is apparently tied in with the substantial improvements brought about in the hydrocarbons, such as those discussed above.

A highly important feature of the present process is that there is only a negligible loss in hydrocarbon volume sustained. Thus, unlike various conventional refinery processes, the process of this invention brings about substantial improvements in the hydrocarbon without sacrificing significant amounts of the hydrocarbon in the course of the treatment. Generally speaking, the losses in hydrocarbon volume sustained when practicing the present process are less than about one-half of one percent. The importance of this to the petroleum refiner will be immediately apparent.

The foregoing relates to a preferred embodiment of the invention, namely, a process which comprises contacting a liquid hydrocarbon with an ester of a metaboric acid—preferably an ester of metaboric acid—said hydrocarbon having a kinematic viscosity of less than about 4.28 centistokes, an API gravity at 60° F. of not less than about 32° API, and a mid-boiling point of up to about 580° F., at least a portion of said hydrocarbon being non-aromatic, said ester being (1) soluble in said hydrocarbon and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said hydrocarbon; and separating said precipitate and said hydrocarbon.

Any excess quantities of the treating agent can be left in the liquid hydrocarbon or it can be removed therefrom.

With a few types of liquid hydrocarbons, no precipitate is formed on dissolving the treating agent therein. Such hydrocarbons are normally those which have been extensively treated during refinery operations, particularly by acid washings. Even though a precipitate does not form in such hydrocarbons, the process of this invention still further improves their performance characteristics. For example, certain gasolines containing sulfur compounds exhibit improved tetraethyllead susceptibility when treated by this invention. The nature and importance of this improvement are considered hereinafter. However, such improvements are believed to result, at least in part, from the ability of the treating agents of this invention to render these sulfur compounds innocuous even though no precipitate is formed.

In carrying out the process of this invention, the treating agent is contacted with the hydrocarbon being subjected to treatment. Ordinarily, the treating agent is added to and blended with the hydrocarbon, although the reverse procedure can be used. This contacting is done at a temperature less than the boiling temperature of the hydrocarbon at the prevailing pressure. With most hydrocarbons the treatment temperature is room temperature—i.e., in the range of about 20 to 30° C. To insure that the treating agent comes in intimate contact with the body of the hydrocarbon, physical agitation—such as stirring, shaking or the like—is helpful. As pointed out above, the majority of hydrocarbons when subjected to this treatment yield a quantity of flocculent precipitate which rapidly forms in the hydrocarbon. When this precipitate formation occurs, it is advantageous to add the treating agent in incremental portions until the continued addition of the heating agent causes no more precipitate to form. Such precipitate is then separated from the hydrocarbon by conventional methods. In most cases, this separation is most easily effected by allowing the hydrocarbon to stand for a period of time sufficient to permit the precipitate to settle to the bottom of the treating vessel. A settling aid, such as active clay or the like, may be used to speed up the rate at which this precipitate settles. After the precipitate has settled, the hydrocarbon can be removed from the reaction vessel by decantation. If desired, the precipitate can then be filtered in order to recover therefrom additional quantities of the treated hydrocarbon. Other methods of separating the precipitate and the hydrocarbon include centrifugation, filtration, decantation, distillation, or various combinations thereof.

With certain hydrocarbons, the addition of the treating agent does not cause the formation of a precipitate. In this case, a small amount of the treating agent is simply blended with the hydrocarbon and the solution is agitated to insure homogeneity.

The methods of carrying out this invention will be still further apparent from the following specific examples in which all parts and percentages are by weight. In these examples, the general procedure described above is carried out. Thus, for the sake of brevity, most of these examples are presented in abbreviated form. Where the results of chemical analyses for nitrogen and boron contents of hydrocarbons are presented, it will be understood (1) that weight percent of nitrogen refers to the

content of complex nitrogenous compounds present in the hydrocarbon expressed in terms of elemental nitrogen, and (2) that weight percent of boron refers to the boron content of the hydrocarbon expressed in terms of elemental boron, although the boron is actually present in the form of boron compounds, chiefly metaborate esters. All treatments were carried out at room temperature (about 25 to about 30° C.) unless otherwise specified. The properties of the gasolines used in the following examples are shown in Table I.

TABLE I.—PROPERTIES OF REPRESENTATIVE GASOLINES

	A	B	C	D	E	F	G	H	I	J	K
Hydrocarbon Type, Percent Vol.:											
Paraffins	[a] 45.2	[a] 39.7	[a] 35.3	-------	[a] 70.1	[a] 49.9	[a] 49.7	[a] 73.7	[a] 44.0	39.1	-------
Olefins	28.4	27.7	24.2	-------	15.6	15.9	22.3	14.5	17.9	21.0	-------
Aromatics	25.4	32.6	30.5	-------	14.3	34.2	28.0	11.8	38.1	17.1	-------
Naphthenes	-------	-------	-------	-------	-------	-------	-------	-------	-------	22.8	-------
Distillation, F.:											
Barometer, In Hg	29.3	29.7	29.1	29.1	29.3	29.3	29.7	29.3	-------	29.2	-------
Initial, ° F	98	92	90	86	94	111	81	110	94	88	-------
Percent Evaporated, ° F.:											
5	114	119	-------	101	116	138	97	139	119	-------	-------
10	134	135	-------	115	132	156	109	153	140	-------	-------
15	151	146	-------	135	144	171	119	164	157	-------	-------
20	167	160	-------	-------	155	184	130	173	171	-------	-------
30	193	186	-------	-------	175	205	155	188	196	140	-------
40	213	213	-------	-------	192	227	183	202	216	-------	-------
50	228	236	-------	205	208	250	211	216	233	-------	-------
60	240	255	-------	-------	223	271	237	230	247	-------	-------
70	253	272	-------	-------	242	291	263	250	262	240	-------
80	274	287	-------	275	267	313	291	279	281	270	-------
85	288	297	-------	-------	286	325	309	303	295	-------	-------
90	310	309	-------	301	309	339	328	337	309	334	-------
95	341	331	340	321	342	358	354	387	330	393	-------
Final	390	369	378	378	385	394	410	411	366	426	-------
Existent Gum, mg./100 ml.	2.6	-------	-------	-------	-------	-------	-------	-------	2.8	0.6	-------
Oxidation Stability, min.	480	-------	-------	-------	-------	-------	-------	-------	720	375	-------
Sulfur Content, wt. percent	0.028	-------	-------	0.063	0.035	0.096	-------	0.035	0.050	0.34	-------
Gravity, ° API	59.0	56.6	56.2	65.8	64.4	51.5	62.3	60.7	54.6	6.14	60.2
Vapor Pressure, p.s.i.	8.9	8.1	8.1	11.4	-------	-------	13.0	-------	7.8	11.7	-------

[a] Includes naphthenes.

Example 1

To a reaction vessel containing 186 parts of Fuel A was added 0.16 part of benzyl metaborate. A flocculent red precipitate rapidly formed in the body of this fuel and settled to the bottom of the reaction vessel. This precipitate (0.35 part) was separated from the fuel. The treated fuel was subjected to chemical analysis and found to contain less than 0.0001 percent of nitrogen, whereas the untreated fuel contained 0.0008 percent of nitrogen.

Example 1 demonstrates that upon contacting a typical treating agent of this invention with a representative gasoline, a flocculent precipitate is formed therein. Once this precipitate is removed, the gasoline possesses a much lower nitrogen content than it did before treatment. This example also shows that the treating agents of this invention can be used without recourse to solvent. However, it is particularly advantageous to dissolve an appropriate quantity of treating agent in a suitable solvent, such as toluene, xylene, mesitylene, or like aromatic hydrocarbon, in which the treating agents of this invention do not form precipitates. Other suitable solvents include pure paraffinic hydrocarbons, such as pure 2,2,4-trimethylpentane, n-heptane; organic esters, such as phthalates, sebacates; and the like. By using the treating agents in a preformed solution, the blending procedures used in the instant process are simplified, more rapid and more uniform. Moreover, such preformed solutions are advantageous because the treating agents are less susceptible of hydrolytic degradation when dissolved in such a solvent.

Examples 2 Through 9

	Fuel (Parts)	Treating Agent (Parts)	Solvent (Parts)	Precipitate Formed	Nitrogen Content, Percent		Boron Content, Percent	
					Before	After	Before	After
2[a]	A (140,000)	Benzyl metaborate (140)	Toluene (130)	Floc. red	0.0010	0.0002	None	0.000035
3	A (186)	n-Butyl metaborate (0.10)	Toluene (0.21)	do	0.0010	0.0001	None	0.0015
4	A (186)	Isopropyl metaborate (0.095)	Toluene (0.140)	do	0.0010	0.0001	None	0.00042
5	A (74)	Ethyl metaborate (0.04)	n-Heptane (0.53)	do	0.0010	0.0001	None	0.0033
6	A (74)	Cyclohexyl metaborate (0.07)	n-Heptane (9.17)	do	0.0010	0.0001	None	0.0030
7	A (744)	Mix. of benzyl metaborate and tribenzyl orthoborate (0.8).[b]	None	do	0.0010	0.0001	None	0.0009
8	A (186)	Tri-n-butyl orthoborate (0.43)	None	None	0.0010	0.0009	None	-------
9	A (186)	Triisopropyl orthoborate (0.34)	None	None	0.0010	0.0010	None	-------

[a] Before treatment Fuel A had a yellow color, whereas after treatment it was water white. A portion of this treated fuel was exposed to sunlight for one week, and it was found to be more stable against sunlight-induced deterioration than was the untreated fuel.

[b] The treating agent used in this experiment contained 66% of benzyl metaborate with the remainder being predominantly tribenzyl orthoborate. This mixture was prepared by heating a mixture of 240 parts of boric acid and 672 parts of benzyl alcohol to 230° C. for two hours.

Examples 1–7 show that various treating agents of this invention cause the formation in the fuel of precipitates containing nitrogen. Also shown by these examples are that the treating agents can be used with or without a solvent and that good results are achieved when using a mixture of esters of boric acids, so long as the mixture contains an ester of a metaboric acid. That it is essential to employ an ester of a metaboric acid or a mixture of esters of boric acids, at least a portion of which is an ester of a metaboric acid, is established by the results presented in Examples 8 and 9. When pure orthoborate esters were used, no precipitate was formed and the nitrogen content of the fuel was unchanged.

Example 10

Hydrocarbon ---------- Fuel A (186 parts).
Treating agent ---------- n-Butyl metaborate (0.20 part).
Solvent for treating agent -- Toluene (0.42 part).
Precipitate formed -------- Flocculent red.

In this example, Fuel A before treatment contained 3.0 milliliters of tetraethyllead per gallon as a commercial antiknock fluid. Samples of the treated and the untreated gasoline were analyzed to determine the extent by which the treatment of this invention affected the initial concentrations of the ingredients of this antiknock fluid. The results are as follows:

	Tetraethyllead, ml./gal	Ethylene Dibromide, T	Ethylene Dichloride, T
Untreated	3.0	0.54	1.00
Treated	3.0	0.54	0.97

In the above table, T stands for "theory," a theory of halogen being the quantity theoretically required to react with the lead during engine combustion to form the corresponding lead halide.

It will be seen from Example 10 that a feature of this invention is the fact that the treatment can be conducted on gasoline which has been previously leaded without affecting the concentrations of the tetraethyllead or its normal scavenger complement.

Examples 11 through 16

Example	Fuel (Parts)	Treating Agent (Parts)	Solvent (Parts)	Precipitate Formed	Nitrogen Content, Percent		Boron Content, Percent	
					Before	After	Before	After
11	B (1408)	n-Butyl metaborate (0.65)	Toluene (1,18)	Brownish-yellow.	0.0008	0.0001	None	0.0016
12	C (1400)	n-Butyl metaborate (0.81)	Toluene (1,39)	Floc. brown.	0.0011	0.0006	None	0.0017
13	D (1414)	n-Butyl metaborate (0.23)	Toluene (0,69)	Floc. pale yellow.	0.00034	0.00009	None	0.002
14	E (1378)	n-Butyl metaborate (0.84)	Toluene (1,55)	Floc. brownish-yellow.	0.0012	0.0005	None	0.002
15	F (1435)*	n-Butyl metaborate (5,5)	Toluene (10.1)	Floc. yellowish-brown.	0.0134	0.0061	None	0.010
16	G (1400)	n-Butyl metaborate (0.71)	Toluene (1,31)	do	0.0012	0.0003	None	0.0017

* This fuel before and after treatment contained 3.0 milliliters of tetraethyllead per gallon as the commercial antiknock fluid described in connection with Example 10.

Example 17

In this example the effect of different concentrations of treating agent on the peroxide and nitrogen content of a representative gasoline was studied. In each of three separate reaction vessels was placed 1372 parts of Fuel H, which contained 3.0 milliliters of tetraethyllead per gallon as a conventional anti-knock fluid. To the first gasoline sample was added a solution of 2.8 parts of n-butyl metaborate dissolved in 5.1 parts of toluene. The second gasoline sample was treated with a solution of 4.3 parts of n-butyl metaborate dissolved in 7.8 parts of toluene. A solution of 7.0 parts of n-butyl metaborate dissolved in 12.8 parts of toluene was added to the third gasoline sample. In all cases a flocculent reddish-brown precipitate was formed in the gasoline. After separating this precipitate from the gasoline samples, portions thereof together with a sample of the same but untreated gasoline were each washed with 1000 parts of water. In this manner the three untreated gasoline samples no longer contained any boron dissolved therein. The untreated gasoline was washed in the same fashion to insure that each of the samples was handled in the same manner with the exception of the metaborate treatment. Chemical analysis of these samples revealed the following:

Sample	Amount of n-butyl metaborate used, parts	Peroxide Number	Nitrogen Content, Percent
1	None	0.70	0.0063
2	2.8	0.45	0.0029
3	4.3	0.39	0.0019
4	7.0	0.37	0.0005

Example 18

Hydrocarbon ---------- Fuel A (372 parts).
Treating agent ---------- n-Butyl metaborate (0.39 part).
Solvent for treating agent - Toluene (0.71 part).
Precipitate formed -------- Flocculent red.
Observed changes -------- The peroxide number of Fuel A before treatment was 0.37. After treatment, the peroxide number of this fuel was zero.

The results presented in Examples 17 and 18 show, inter alia, that the treatment of this invention causes a reduction in the peroxide number of the hydrocarbon being treated. As shown by Example 18, this peroxide number is reduced in some fuels to zero.

Example 19

210 parts of isopropyl metaborate dissolved in 396 parts of toluene was added to 140,000 parts of Fuel I. The flocculent red precipitate which formed in the body of the gasoline was separated therefrom and a portion of the treated gasoline subjected to chemical analysis to determine its boron content. It was found to contain 0.0055 percent of boron. To the remainder of the treated gasoline was then added 34,000 parts of water. The resulting water-gasoline mixture was agitated for 10 minutes. Then, the gasoline was allowed to stand for 10 minutes, during which time the water settled to the bottom of the treating vessel. The gasoline was separated from this water phase by decantation and dried with calcium sulfate. A portion of this water-washed, boron-treated gasoline was then subjected to chemical analysis to determine its boron content. It was found to contain less than 0.0003 percent of boron.

Example 20

To 1785 parts of Fuel A was added 1.75 parts of n-butyl metaborate dissolved in 3.20 parts of toluene. The resulting flocculent red precipitate was separated from the gasoline. This boron-treated gasoline, which contained approximately 0.005 percent of boron, was then vigorously stirred with 400 parts of water at 25° C. for 10 minutes. The water was separated from the gasoline which was then subjected to chemical analysis to determine its boron con-

tent. The water-washed, boron-treated gasoline contained less than 0.0003 percent of boron.

Examples 19 and 20 demonstrate that many of the treating agents of this invention can be separated from the hydrocarbon after treatment by means of water washing. Some of the treating agents of this invention are not affected by water, and to separate these compounds from the treated hydrocarbon, other procedures are resorted to. Thus, to remove these water-insensitive treating agents, recourse can be had to distillation, the use of strong acids or bases to decompose the treating agent, or like procedure. Thus, an additional embodiment of this invention is the process which comprises contacting a liquid hydrocarbon with an ester of a metaboric acid, said hydrocarbon having a kinematic viscosity of less than about 4.28 centistokes, an API gravity at 60° F. of not less than about 32° API, and a mid-boiling point of up to about 580° F., at least a portion of said hydrocarbon being non-aromatic, said ester being (1) soluble in said hydrocarbon and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said hydrocarbon, said ester being present in said hydrocarbon in excess of the amount required to form said precipitate; separating said precipitate and said hydrocarbon; and separating from said hydrocarbon said excess amount of said ester.

Example 21

A mixture of benzyl borates containing benzyl metaborate was prepared by digesting boric oxide with 55 percent of the theoretical amount of benzyl alcohol necessary to make tribenzyl orthoborate. The temperature of this digestion was 200° C. The resulting mixture of benzyl borates contained approximately 70 percent by weight of benzyl metaborate. This mixture was dissolved in half its weight of dibutyl phthalate as a solvent. This treating agent was then added in incremental portions to 141,000 parts of a commercially available gasoline. The above treating agent was added until no additional precipitate formed in the body of the gasoline and this required a total of 276 parts of treating agent. To aid settlement and filtration of the precipitate, 403 parts of an active clay was added to the gasoline on completion of the addition of the treating agent. The gasoline was then allowed to stand for 1.5 hours. Then the gasoline was separated from the precipitate by decantation followed by filtration. Inspection data on this gasoline are as follows:

	Untreated	Treated
API Gravity	58.4	57.8
Reid Vapor Pressure, p.s.i.	9.7	8.7
Distillation, ° F.:		
Initial	94	97
5% Evaporated	102	117
10% Evaporated	129	136
50% Evaporated	244	249
90% Evaporated	361	363
Final, ° F	413	416
Recovery, percent	97.8	97.8
Residue, percent	1.1	1.1
Oxidation Stability, min	190	195
G.M. Sludge Number	106	67

There was a significant change in the General Motors sludge number caused by the above treatment of the gasoline. The General Motors sludge number is a research technique intended to determine relative varnish- and sludge-forming tendencies of fuels by the density of color developed in the fuels upon addition of p-nitrophenyl diazonium fluoborate. Higher numbers indicate greater varnish-forming tendencies and thus metaborate treatment brought about a reduction in the varnish- and sludge-forming tendencies of the treated fuel.

Example 22

Hydrocarbon ---------- Fuel J (14,100 parts).
Treating agent ---------- Mixture of benzyl metaborate and tribenzyl orthoborate (28 parts).
Solvent for treating agent --- Dibutyl phthalate (26 parts).
Precipitate formed ------- Brownish-red.

Example 23

Hydrocarbon ---------- Fuel K (14,100 parts).
Treating agent ---------- Mixture of benzyl metaborate and tribenzyl orthoborate (16.7 parts).
Solvent for treating agent --- Dibutyl phthalate (16.5 parts).
Precipitate formed --------- Brown.

Example 24

In this example, the effect of temperature on treatment was studied. To 110 parts of Fuel H maintained at 28° C. was added 0.20 part of isopropyl metaborate dissolved in 0.71 part of toluene. It was observed that during the first minute after the addition of the treating agent, the fuel developed a turbidity. After this time, the flocculent brownish-yellow precipitate developed, coalesced and began to settle. The identical procedure was repeated with the exception that the sample of Fuel H was maintained at 50° C. In this instance the turbidity which developed as soon as the treating agent was added to the fuel lasted for about 30 seconds after which the development of the flocculent, yellowish-brown precipitate commenced. Thus, with this fuel an increase in the treating temperature shortened the time required for precipitate formation. Furthermore, the use of the higher temperature in this fuel caused a greater degree of coalescence as compared with the lower temperature.

Example 25

To 2630 parts of isooctane containing 6.1 parts of ethyl disulfide, 14.6 parts of butyl sulfide and 14.6 parts of octyl mercaptan is added 2.5 parts of isopropyl metaborate dissolved in 4.0 parts of toluene. No precipitate formation occurs, but the isooctane is markedly improved for use as a fuel for spark ignition engines because it has improved tetraethyllead susceptibility (discussed hereinafter).

Example 26

1.60 parts of methyl metaborate is blended with 2774 parts of a shale oil gasoline having a specific gravity of 0.73 at 20° C., an initial boiling point of 47° C., a 10 percent boiling point at 66° C., a 50 percent boiling point at 121° C., a 90 percent boiling point at 171° C., and a final boiling point of 207° C.

Example 27

To individual samples of Fuels A–K, inclusive, each sample weighing 750 parts, is added 0.89 part of phenyl metaborate.

Example 28

The procedure of Example 27 is repeated using 1.57 parts of dodecyl metaborate as the treating agent.

Example 29

The procedure of Example 27 is repeated using 1.05 parts of diisopropyl carbinyl metaborate, i.e., the metaborate ester derived from 2,4-dimethyl pentanol-3.

Example 30

The procedure of Example 27 is repeated using 1.27 parts of S-isooctyl metaborate.

Example 31

Hydrocarbon	Jet Fuel X (15,035 parts).
Treating agent	n-Butyl metaborate (2.27 parts).
Solvent for treating agent	Toluene (4.16 parts).
Precipitate formed	Flocculent red.

Example 32

Hydrocarbon	Jet Fuel Y (13,914 parts).
Treating agent	n-Butyl metaborate (3.23 parts).
Solvent for treating agent	Toluene (5.84 parts).
Precipitate formed	Flocculent brownish-pink.
Observed changes	Initial nitrogen content 0.0005%; after treatment, 0.0001%. After ment this fuel contained 0.0007% of boron.

Jet Fuel X was a JP–4 San Joaquin crude jet fuel, whereas Jet Fuel Y was a JP–4 referee fuel. The inspection data of these fuels are shown in Table II.

TABLE II.—PROPERTIES OF TYPICAL JET FUELS

	Jet Fuel X	Jet Fuel Y
Gravity, °API	47.3	48.5
Vapor Pressure	2.8	2.8
Distillation, ° F.:		
Initial		
5		
10	221	
15		268
20	263	287
50	327	354
80	359	
90	379	460
Final	480	516
Existent Gum, mg./100 ml	1.0	1.4
Potential Gum, mg./100 ml	1.0	9.6
Total Sulfur, percent	0.06	0.193
Mercaptan Sulfur, percent	0.0007	0.001
Freezing Point, ° F	−76	−67
Aromatic, vol. percent	12.5	14.6
Olefins, vol. percent	0.3	1.2

Example 33

To 3177 parts of a commercially available diesel fuel having a cetane number of 51.7, an API gravity of 37.0, a heat content of 19,620 B.t.u. per pound, a 50 percent boiling point of 509° F., and a nitrogen content of 0.0019 percent was added 3.0 parts of isopropyl metaborate dissolved in 6.1 parts of toluene. The diesel fuel containing this treating agent was shaken to insure homogeneity. A flocculent reddish-brown precipitate rapidly formed and was allowed to settle to the bottom of the treating vessel. Then the precipitate was separated from the diesel fuel by filtration. 1588 parts of this treated fuel was then water washed at 28° C. so as to remove therefrom the excess isopropyl metaborate. This water-washed, boron treated sample contained no detectable quantity of boron and had a nitrogen content of 0.0006 percent. The sample of the treated, but unwashed fuel, contained 0.0039 percent of boron and 0.0007 percent of nitrogen.

Example 34

To 2142 parts of LPG (composed chiefly of propane, butane, propylene, and butylene) maintained at −50° C. is added 2.40 parts of isopropyl metaborate dissolved in 4.88 parts of toluene.

Example 35

3.7 parts of p-tolyl metaborate is blended with 3040 parts of a domestic fuel oil having a 10 percent boiling point of 436° F., a 50 percent boiling point of 486° F., a 90 percent boiling point of 550° F., an API gravity of 38.5° and a viscosity of 2.60 centistokes.

Example 36

3.2 parts of diethylcarbinyl metaborate, i.e., the metaborate ester derived from pentanol-3, is blended with 3040 parts of a diesel fuel having a viscosity of 3.80 centistokes, an API gravity of 33.0°, and a 50 percent boiling point of 580° F.

Example 37

4.7 parts of o-octyl thiometaborate is blended with 3040 parts of a power kerosene derived from shale oil and having a specific gravity at 20° C. of 0.87, an initial boiling point of 188° C., a 50 percent boiling point of 215° C. and a 90 percent boiling point of 236° C.

Example 38

The procedure of Example 37 is repeated using 8.2 parts of octadecyl metaborate.

The mechanism by which the process of this invention functions is obscure. It is known, however, that this process functions at least in part by chemical reaction between the metaborate esters and certain deleterious constituents originally present in the hydrocarbon. By means of this chemical reaction some of these deleterious constituents are removed from the body of the hydrocarbon because they enter into the formation of the flocculent precipitate. On the other hand, some of the benefits afforded by this invention result from chemical reactions occurring within the body of the hydrocarbon leading to chemical changes which are not accompanied by the formation of precipitates. Where a flocculent precipitate is formed, it is probable that both types of reactions occur concurrently and it is also possible that this precipitate is capable of adsorbing or otherwise reacting with still other trace quantities of deleterious ingredients in the hydrocarbon so as to remove them or render them innocuous. It has been observed that the nitrogen content, if any, of the hydrocarbons being subjected to treatment is reduced to an extremely low concentration, even where the initial nitrogen content of the hydrocarbon was itself very low. In addition, peroxides and hydro-peroxides have also been found to be totally or partially destroyed when carrying out the instant process.

The improvements effected by this invention depend in part upon the nature of the hydrocarbon being treated. We consider first the improvements brought about in gasoline.

Gasoline subjected to the process of this invention manifests, when leaded, octane quality which is higher than would be expected. When gasoline is used as a fuel for spark ignition internal combustion engines, it is generally leaded—i.e., the gasoline contains a small amount of a lead alkyl antiknock agent, such as tetraethyllead, and its normal scavenger complement (ethylene dibromide, a mixture of ethylene dibromide and ethylene dichloride, etc.). Such antiknock agents raise the octane quality of the gasoline and thereby prevent knocking or detonation. With the advent of the high compression spark ignition engine is has become necessary for the petroleum refiner to supply gasolines having very high octane numbers. The unexpectedly higher octane quality of leaded gasolines brought about by this invention results from a substantial improvement in susceptibility of the fuel for the lead alkyl antiknock agent—for convenience referred to herein as tetraethyllead susceptibility.

Tetraethyllead susceptibility may be defined as the response which a gasoline exhibits to the addition of tetraethyllead in terms of the magnitude of the increase of octane number thereby produced. Thus, the gasoline has improved tetraethyllead susceptibility when the addition

of tetraethyllead thereto causes a larger increase in octane quality of the fuel than would otherwise be obtained by the addition of the identical quantity of tetraethyllead.

To demonstrate the improvements in tetraethyllead susceptibility brought about by treating gasoline in accordance with this invention, recourse was had to the standard ASTM Research Method, Test Procedure D–908 (which can be found in the 1953 edition of "ASTM Manual of Engine Test Methods for Rating Fuels"). In one series of engine tests, unleaded portions of Fuel A were treated substantially as described in Example 2. After treatment, Fuel A contained 0.038 gram of boron as benzyl metaborate per gallon. To individual portions of this treated fuel were added differing concentrations of the commercial antiknock fluid described in connection with Example 10. Individual portions of Fuel A, which had not been treated in accordance with this invention, were likewise leaded in the same fashion. Thus, a series of treated and untreated fuels was prepared containing 1.0, 2.0 and 3.0 milliliters of tetraethyllead per gallon. Each of these individual fuels was then subjected to the above ASTM test procedure and the octane quality of the fuel obtained. The results of this series of tests are depicted in FIGURE 1.

Referring to FIGURE 1, the abscissa represents the actual concentration of tetraethyllead employed in the respective gasoline samples, both treated and untreated. The ordinate of FIGURE 1 shows the apparent tetraethyllead concentration of these gasoline samples. The broken, straight line passing through points D, E and F represents the untreated samples of Fuel A. It can be seen that the actual and apparent concentrations of tetraethyllead coincide. In other words, the samples of untreated Fuel A gave an antiknock rating which coincided with the expected octane quality brought about by employed tetraethyllead in this fuel. The samples of Fuel A which were treated pursuant to this invention exhibited an improved tetraethyllead susceptibility as shown by the solid curve passing through points A, B and C. For example, the sample of Fuel A which has been metaborate treated and which actually contained 1.0 milliliter of tetraethyllead per gallon gave an antiknock rating equivalent to that produced by adding 1.3 milliliters of tetraethyllead per gallon to the same fuel when untreated. Compare points A and D. Similarly, at an actual concentration of 2.0 milliliters of tetraethyllead per gallon, the treated sample of Fuel A exhibited an octane quality equivalent to 2.7 milliliters of tetraethyllead per gallon in the untreated fuel. Thus, by comparing points B and E in FIGURE 1, it can be seen that at an actual concentration of 2.0 milliliters of tetraethyllead per gallon the treatment of this invention caused Fuel A to exhibit the octane quality produced by the addition of another 0.7 milliliter of tetraethyllead per gallon to the untreated fuel. Furthermore, at an actual tetraethyllead content of 3.0 milliliters of tetraethyllead per gallon, the treatment of this invention caused the fuel to have an apparent tetraethyllead concentration of 4.3 milliliters of tetraethyllead per gallon. Thus, in this instance the treatment of this invention raised the octane quality of the fuel by the amount equivalent to the addition to the untreated fuel of another 1.3 milliliters of tetraethyllead per gallon.

Another series of engine tests as described above was conducted on various commercially available gasolines. In these tests five different gasolines were used. Research octane numbers at a single tetraethyllead concentration were obtained on four of these gasolines, both treated and untreated. Samples of the fifth gasoline—treated and untreated—were engine rated unleaded and also when leaded at two concentrations of tetraethyllead. This latter group of tests thus shows the magnitude of the improvements in tetraethyllead susceptibility exhibited at different concentrations of tetraethyllead. The treating agent used on the present series of gasolines was n-butyl metaborate. The results of these tests are shown in Table III.

TABLE III.—EFFECT OF TREATMENT ON TETRAETHYLLEAD SUSCEPTIBILITY OF VARIOUS GASOLINES

Gasoline	Treated as in Example	Boron Content, g.B/gal.	TEL Conc., ml./gal.	Research Octane Number
Fuel F	15	0.280	6.0	98.7
Fuel F	Untreated	none	6.0	98.2
Fuel H	17	0.140	6.0	93.9
Fuel H	Untreated	none	6.0	92.5
Fuel B	11	0.035	3.0	[a] 100.3
Fuel B	Untreated	none	3.0	[a] 100.0
Fuel G	16	0.048	2.9	[a] 103.9
Fuel G	Untreated	none	2.9	[a] 103.4
Fuel A	3	0.190	0.0	91.7
Fuel A	Untreated	none	0.0	91.8
Fuel A	3	0.190	1.5	97.8
Fuel A	Untreated	none	1.5	97.0
Fuel A	3	0.190	3.0	100.0
Fuel A	Untreated	none	3.0	98.6

[a] Performance Number.

Referring to the data presented in Table III, it is clear that in all cases the gasolines, when treated in accordance with this invention, exhibited improvements in tetraethyllead susceptibility. The size of these improvements is especially significant because they were brought about in high octane quality gasoline in which it is normally very difficult and expensive to effect such an improvement.

That the present process greatly improves the tetraethyllead susceptibility of gasolines was further demonstrated by additional comparative engine tests. A sample of Fuel I was treated with isopropyl metaborate and the precipitate which formed separated from the fuel. The amount of isopropyl metaborate used in this treatment was such that after treatment the fuel contained 0.155 gram of boron per gallon. To another and untreated portion of Fuel I was added the identical concentration of boron as the 2-methyl-2,4-pentanediol ester of n-butyl boronic acid, no precipitate forming. This ester is a typical boron additive as disclosed in U.S. Patent 2,710,252. Both of these boron-containing samples contained 3.00 milliliters of tetraethyllead per gallon as the commercial antiknock fluid described in connection with Example 10. Both of these fuels were then subjected to the ATSM Research Method discussed above. The results of these tests are shown in Table IV.

TABLE IV.—EFFECT OF BORON COMPOUNDS ON TETRAETHYLLEAD SUSCEPTIBILITY

Boron Compound	Conc. of B, g./gal.	Apparent TEL Conc., ml./gal.
Isopropyl metaborate	0.155	3.62
2-methyl-2,4-pentanediol ester of n-butyl boronic acid	0.155	3.04

As shown in Table IV the use in the gasoline of a boron additive described in the prior art had no appreciable effect on tetraethyllead susceptibility. On the other hand, a substantial improvement in tetraethyllead susceptibility was brought about by practicing this invention. This improvement probably results from the removal of deleterious ingredients from the gasoline by means of the flocculent precipitate and also the presence in the gasoline of an exceptionally effective boron additive, namely, isopropyl metaborate. It is believed that the residual additive remaining dissolved in the fuel when treated pursuant to this invention contributes, for the most part, to the enhancement of tetraethyllead susceptibility of gasolines.

Treated and untreated gasoline samples as described in Example 21 were subjected to the standard ASTM Designation D–357. These tests, the results of which are presented in Table V, still further demonstrate the improvements in tetraethyllead susceptibility brought about by practicing this invention.

TABLE V.—EFFECT OF TREATMENT ON TETRAETHYLLEAD SUSCEPTIBILITY

Conc. of TEL, ml./gal.	Motor Octane Number	
	Untreated	Treated
1.5	76.3	76.8

Gasolines of this invention when leaded exhibit reduced surface ignition rate. Surface ignition—i.e., wild ping—is erratic engine combustion caused by glowing engine deposits. It is currently a severe problem in the operation of high-compression spark ignition engines.

That gasolines treated pursuant to this invention are greatly improved in resistance to surface ignition was shown by conducting a series of standard engine tests. The test equipment and procedure used are as described in U.S. Patent 2,728,648. To portions of Fuel A treated as described in Example 2 and containing 0.038 gram of boron as benzyl metaborate per gallon was added 3.0 milliliter of tetraethyllead per gallon as the antiknock fluid described in connection with Example 10. These treated fuels were then subjected to the above surface ignition test procedure. For comparative purposes, untreated samples of Fuel A which contained the identical concentration of the same antiknock fluid were subjected to this engine test procedure. The results of these tests are shown in Table VI.

TABLE VI.—EFFECT OF TREATMENT ON SURFACE IGNITION RATE

Boron Content, g./gal.	Surface Ignition Rate	
	Number per Hour	Percent of Baseline
None (untreated)	72	100
0.038	41	57
None (untreated)	65	100
0.038	35	54

The results presented in Table VI show that typical gasolines of this invention are greatly improved from the standpoint of reduced surface ignition. In another series of similar engine tests, it was noted that the fuel samples which had been treated in accordance with this invention had reduced deposit-forming tendencies. This was shown by the fact that the exhaust valve deposit weights were 70 percent and 79 percent of baseline values, i.e., as compared with the same but untreated fuel.

Other engine tests were conducted to determine the effect of treatment per this invention on surface ignition rate. In all cases the fuels, both treated and untreated, contained 3.0 milliliters of tetraethyllead per gallon. The results of these tests are shown in Table VII.

TABLE VII.—EFFECT OF TREATMENT ON SURFACE IGNITION RATE

Test Number	Gasoline	Treated as in Example	Surface Ignition Rate	
			Number Per Hour	Percent of Baseline
1	Viz Example 21	Untreated	52.8	100.0
2	Viz Example 21	21	18.4	34.8
3	Fuel J	Untreated	11.7	100.0
4	Fuel J	22	1.3	11.1
5	Fuel K	Untreated	13.9	100.0
6	Fuel K	23	3.1	22.3

The data in Table VII again show that in all cases the metaborate treated fuels gave lower surface ignition rates. In Tests 3–6, inclusive, the engines were operated under severe operating conditions—full load, constant speed—which provided high engine surface temperatures. Under these conditions, the severity of surface ignition is reduced.

The Lauson engine cleanliness test was applied in Tests 1 and 2 described in Table VII. As the name of this test implies, it is a measure of the burning quality of the fuel. Thus, a piston rating of 10 on completion of the engine test means that the piston is clean. The lower the number, the dirtier was the engine. In Test 1 in Table VII, the piston rating was 4.0. However, in Test 2 using a fuel of this invention, the piston rating was 5.5 showing that the treatment of this invention provided a cleaner-burning fuel.

Gasolines treated in accordance with this invention possess improved boron additive response. As pointed out above, the treating agents of this invention, when dissolved in leaded gasoline, cause a substantial improvement in tetraethyllead susceptibility. It has been found that treatment of gasolines by the instant process produces a gasoline in which conventional organoboron additives bring about an improvement in tetraethyllead susceptibility. This completely unexpected phenomenon is demonstrated by a series of engine tests using the Research Method discussed above.

The fuel used in these tests was Fuel I treated as described in Example 19. Thus, this commercially available gasoline contained essentially no boron because the treating agent, isopropyl metaborate, had been removed therefrom by water washing. This gasoline was then leaded to a concentration of 3.0 milliliters of tetraethyllead per gallon as the antiknock fluid described in connection with Example 10. To this boron-treated, leaded gasoline was added the 2-methyl-2,4-pentanediol ester of n-butyl boronic acid as disclosed in U.S. Patent 2,710,252. Several concentrations of this additive were employed. For comparative purposes, the same concentrations of the 2-methyl-2,4-pentanediol ester of n-butyl boronic acid were blended with untreated samples of Fuel I which contained 3.0 milliliters of tetraethyllead per gallon as the same antiknock fluid. Thus, the only difference between the respective series of gasoline samples was that one set had been treated in accordance with this invention and the other series had not been so treated. It is emphasized that the treated series of gasoline samples contained essentially no metaborate ester and, therefore, the effects produced resulted from the removal from these gasolines of deleterious constituents by way of the flocculent precipitate formed during the treatment.

The above series of gasolines were then subjected to the ASTM Research Engine test procedure. The results of these tests are shown in FIGURE 2.

Referring to FIGURE 2, the abscissa is the concentration of the boron additive employed in the gasolines—this additive being the 2-methyl-2,4-pentanediol ester of n-butyl boronic acid. The ordinate of FIGURE 2 represents the apparent tetraethyllead concentration exhibited when these fuels, which actually contained 3.00 milliliters of tetraethyllead per gallon, were engine rated. The broken curve passing through points J, K and L shows the amount by which the tetraethyllead was enhanced by using the above boron additive in the untreated gasoline. The solid curve represents the corresponding effect brought about by the above boron additive when used in the same but treated gasoline containing the same concentration of tetraethyllead. In the untreated gasoline the conventional boron additive produced a small enhancement of tetraethyllead susceptibility when employed at concentrations of 0.1 and 0.2 grams of boron per gallon. Thus, points J and K show that this boron additive at these concentrations caused the fuel to have apparent tetraethyllead concentrations of 3.02 and 3.06 milliliters per gallon, respectively. Point L shows that at the rela-

tively high concentration of 0.4 gram of boron per gallon in the untreated fuel, this boron additive made 3.00 milliliters of tetraethyllead appear as if 3.24 milliliters were present. In contrast, points G, H and I show that with the treated fuel the extent of this enhanced tetraethyllead susceptibility was much greater. Thus, at concentrations of 0.1, 0.2 and 0.4 gram of boron per gallon, the above boron additive in the treated fuel caused the actual 3.00 milliliters of tetraethyllead per gallon concentration to appear as if 3.19, 3.26 and 3.39 milliliters, respectively, were present. Simply stated, the treatment of this invention transformed the fuel into one which possessed an improved boron additive response in terms of tetraethyllead susceptibility.

The above relates to another embodiment of this invention. This embodiment is the process which comprises contacting gasoline, at least a portion of which is non-aromatic, with an ester of metaboric acid, said ester being (1) soluble in said gasoline and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said gasoline, said ester being present in said gasoline in excess of the amount required to form said precipitate; separating said precipitate and said gasoline; separating from said gasoline said excess amount of said ester; and blending with said gasoline (1) an antiknock quantity of a lead alkyl antiknock agent and (2) a small amount of a gasoline-soluble, organic-boron compound. Likewise, another embodiment of this invention is the leaded, boron-containing gasoline just described.

The gasoline-soluble, organic-boron additive used in the above embodiment of this invention can be any organic boron compound or mixture of such compounds which improves the performance quality of the leaded gasoline. Thus, this additive can be of the type disclosed in U.S. Patent 2,151,432 and in Industrial and Engineering Chemistry, vol. 43, No. 12, December 1951, pages 2842–2843. However, it is preferable to employ a gasoline-soluble, organic-boron additive which is stable toward moisture, i.e., a boron compound which resists hydrolysis. Such additives are disclosed in U.S. Patents 2,710,251; 2,710,252; 2,720,448 and 2,720,449, which are incorporated herein by the foregoing reference. Thus, the gasoline-soluble, organic-boron additives used in the above embodiment of this invention are preferably (1) an alkyl boronic acid in which the alkyl group has from 6 to 8 carbon atoms; (2) an ester of an alkane diol having from 2 to 8 carbon atoms and an alkyl boronic acid having from 4 to 10 carbon atoms; (3) a borinate ester of the formula R_2BOR which contains 9 to 18 carbon atoms and wherein each R is a hydrocarbon radical of 1 to 7 carbon atoms, and preferably wherein at least one R is an alkyl radical; and (4) a boronate ester of the formula $RB(OR)_2$ which contains 10 to 15 carbon atoms and wherein each R is a hydrocarbon radical of 2 to 7 carbon atoms, and preferably wherein at least two of these R groups are aliphatic. The concentrations of the above and other gasoline-soluble, organic-boron additives used in the above embodiment are as set forth in the above U.S. patents.

Summarizing, it has been found that the gasolines of this invention exhibit:

(1) Improved tetraethyllead susceptibility,
(2) Reduced surface ignition rate,
(3) Improved boron additive response,
(4) Greater stability against sunlight-induced deterioration,
(5) Improved color and appearance,
(6) Greater stability through destruction of peroxide and hydroperoxides,
(7) Reduced water content,
(8) Clean-burning characteristics, hence, reduced deposit-forming tendencies, and
(9) Reduced varnish- and sludge-forming tendencies.

We turn to the improvements brought about in jet fuels of this invention.

Jet fuels of this invention possess high-temperature stability.

The development of new jet aircraft power plants has focused attention on the necessity of providing jet fuels having thermal stability. For example, it has been found that presently available jet fuels of the JP–4 and and JP–5 type form severe deposits in the fuel systems of advanced jet engines during operations for which the power plant has been designed.

At supersonic flight the jet aircraft is subjected to high temperatures. This heat must be removed. In many types of jet aircraft the fuel is used as a heat sink for cooling vital aircraft components, such as engine oil. It has been found, however, that when jet fuels are heated in aircraft fuel systems, fuel degradation occurs. The result of this degradation is the production of sediment which plugs filters and deposits lacquers on such vital engine parts as heat exchanger surfaces.

It has been pointed out that such factors as new jet engine design, higher engine pressure ratios and the use of the fuel as a heat sink have increased the temperature environment of the fuel to the point that it has been stressed beyond its capabilities. The tendency of the fuel to form deposits at fuel temperatures below the cracking level has been termed a fuel property and described as High Temperature Stability. This property is measured by tests using the Erdco Jet Fuel Coker (see Petroleum Processing, December 1955, pages 1909–1911).

To demonstrate the substantial improvements in high temperature stability brought about in jet fuels by the practice of this invention, recourse was had to the Erdco Coking test. Samples of Jet Fuels X and Y which had been treated as described in Examples 31 and 32 were subjected to the Erdco Coking test. These jet fuels had been treated with n-butyl metaborate. Jet Fuel X contained no detectable quantity of n-butyl metaborate after treatment, whereas Jet Fuel Y contained 0.021 gram of boron per gallon as this metaborate ester. For comparative purposes, untreated samples of Jet Fuels X and Y were subjected to the same test. The conditions used in this test were as follows: Unit operated at 150 p.s.i. with the preheater temperature at 325° F., the filter temperature at 500° F., and a residence time of 30 seconds.

The results of the above comparative tests are shown graphically in FIGURE 3. Referring to this figure, the ordinate represents the time in minutes required to obtain a pressure drop across the filter of the Erdco Jet Fuel Coker, amounting to 25 inches of mercury. On the abscissa of this figure are designated the jet fuels subjected to the test. The unshaded bars represent the untreated fuels. The cross-hatched bars represent the treated fuels. In particular, the untreated sample of Jet Fuel X caused severe coking during the test because a pressure drop of 25 inches of mercury across the filter was achieved in 100 minutes. In contrast, the treated sample of Jet Fuel X possessed greatly-improved, high-temperature stability, because at the end of 300 minutes the pressure drop across the filter was only 8.8 inches of mercury. Hence, during this test a 25 inches of mercury pressure drop across the filter was not achieved even after 300 minutes. Untreated Jet Fuel Y resulted in a 25 inches of mercury pressure drop across the filter in less than 50 minutes. However, the treated sample of Jet Fuel Y required over 250 minutes to reach this pressure drop. Consequently, these data show that treatment of jet fuels pursuant to this invention greatly improves their high-temperature stability characteristics.

Diesel fuels treated by the instant process exhibit greatly improved performance characteristics. For example, diesel fuels so treated have considerably reduced smoke-forming tendencies. This is significant because

these treated fuels increase the smoke limited power output of compression ignition engines. To demonstrate this improvement, the diesel fuel samples described in Example 33 were subjected to an engine test. The test equipment comprised a direct injection, single-cylinder diesel engine equipped with means to assay the amount of smoke formed during operation of this engine under smoke-forming operating conditions and also the power output of the engine. For comparative purposes, a sample of the same, but untreated diesel fuel was subjected to the same engine test. The results of these engine tests are shown in Table VIII.

TABLE VIII. — EFFECT OF TREATMENT OF SMOKE-FORMING TENDENCIES OF DIESEL FUEL

Fuel	Smoke Formed, percent of Baseline	Power Output, IMEP [1]
Untreated	100	101.1
Treated—Unwashed	94	102.0
Treated—Washed	86	101.1

[1] Indicated Mean Effective Pressure.

The data presented in Table VIII show that the diesel fuels of this invention had considerably reduced smoke-forming tendencies at a given power output. This means that, as compared with the untreated fuel, the treated fuels produce a greater power output at a given smoke level and thus result in more efficient diesel engine operation.

Substantial improvements are brought about in other hydrocarbons treated by this invention. For example, liquid petroleum gas (LPG) is effectively dried and freed of impurities by the present process. Thus, treated LPG is a superior fuel. Light distillates, such as diesel fuels, domestic heating oils, kerosenes, etc., treated pursuant to this invention possess greater stability, are cleaner burning and manifest improved color characteristics.

The precipitates usually formed during the process of this invention are novel and useful compositions of matter. Thus, another embodiment of this invention relates to these precipitates formed when carrying out the process as described hereinabove.

These precipitates are valuable as a source of fuel additives. To obtain such additives, the precipitates are contacted with water whereby two separate phases are formed. One phase is an aqueous solution which contains most of the boron initially present in the precipitate. The other phase is normally a darkly-colored oil which contains only a small amount of boron. Unexpectedly, this oil is a particularly effective additive when used in leaded gasoline.

To illustrate the preparation of such fuel additives, a flocculent precipitate, formed during a treatment similar to that described in Example 21, was contacted with water. A deep-brown oil having a characteristic odor was liberated and separated from the water phase. This oil had a specific gravity of 0.783 at 20° C. and boiled above 130° C. Most of the boron which had been present in the original precipitate was contained in the water extract.

To demonstrate the effectiveness of this oil as a fuel additive, small amounts thereof were blended with leaded samples of the treated and untreated gasoline described in Example 21. These two gasoline samples were subjected to an engine test procedure in which the effect of these fuels on surface ignition was determined. In addition, samples of the treated and untreated gasoline as described in Example 21 were subjected to this same test procedure. In all cases, the gasoline samples contained 3.0 milliliters of tetraethyllead per gallon. The results of these tests are shown in Table IX.

TABLE IX.—EFFECT OF ADDITIVES ON SURFACE IGNITION RATE

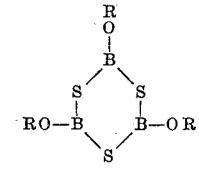
Test Number	Gasoline Treated	Additive	Surface Ignition Rate	
			Number Per Hour	Percent of Baseline
1	No	None	53	100
2	No	Oil from precipitate	44	83
3	Yes	None	15	28
4	Yes	Oil from precipitate	10	19

By comparing Tests 1 and 2, it can be seen that the addition of an additive of this invention—the oil derived from the precipitates of this invention—to an untreated gasoline caused a reduction in surface ignition rate. From Tests 3 and 4, it is clear that the addition of such an additive to a treated gasoline still further reduces its surface ignition rate.

The foregoing relates to still another embodiment of the present invention; namely, as a new composition of matter, the oil product obtained by contacting water and a precipitate formed by the process of this invention. Leaded gasolines containing such oil products in amounts from about 0.1 to about 5 percent by weight are also within this invention.

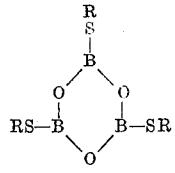
The hydrocarbons used in this invention are derived from mineral sources. These hydrocarbons can be individual hydrocarbons or mixtures thereof provided they meet the requisites set forth hereinabove. Thus, the process of this invention is applicable to LPG; light straight-run gasoline; straight-run gasoline; virgin naphtha; distillates, such as kerosene, domestic fuel oil and diesel fuel (light, medium and high speed); cracked-gasolines, cracked-naphthas and cracked-distillates produced by such cracking methods as thermal, catalytic and coking; thermally and catalytically reformed gasoline; thermally and catalytically reformed naphthas; isomate prepared by isomerizing gasoline hydrocarbons; polymer or "poly-gasoline"; alkylates; natural or "wild" gasoline; jet fuel, such as mixtures of gasolines, naphthas and/or distillates; synthine; shale oil gasoline; tractor fuel; petroleum spirits; and the like. The invention is particularly applicable to mixtures of hydrocarbons meeting the above requisites which are used as or in the formulation of motor and aviation gasoline, jet fuel, domestic fuel oil or diesel fuel. Generally speaking, this invention is applicable to any hydrocarbon meeting the above requisites which is derived from mineral sources and has an endpoint of up to about 725° F.

Typical treating agents of this invention having the formula



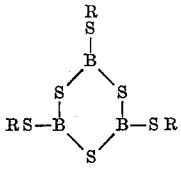
include O-methyl thiometaborate; O-ethyl thiometaborate; O-n-propyl thiometaborate; O-isopropyl thiometaborate; the various O-butyl thiometaborates; O-amyl thiometaborates; O-hexyl thiometaborates; O-heptyl thiometaborates; O-octyl thiometaborates; O-nonyl thiometaborates; O-decyl thiometaborates; O-undecyl thiometaborates; O-dodecyl thiometaborates; O-octadecyl thiometaborates; O-cyclohexyl thiometaborate; O-methylcyclohexyl thiometaborate; O-phenyl thiometaborate; O-o-, m-, and p-tolyl thiometaborates; O-xylyl thiometaborates; O-benzyl thiometaborate; O-(β-ethoxyethyl) thiometaborate; O-(β-(β-ethoxyethoxy)ethyl) thiometaborate; O-(β-phenoxyethyl) thiometaborate; and the like.

Treating agents having the formula



include such compounds as S-methyl metaborate; S-ethyl metaborate; S-n-propyl metaborate; S-isoproyl metaborate; the various S-butyl metaborates; S-amyl metaborates; S-hexyl metaborates; S-heptyl metaborates; S-octyl metaborates; S-nonyl metaborates; S-decyl metaborates; S-undecyl metaborates; S-dodecyl metaborates; S-octadecyl metaborate; S-cyclohexyl metaborate; S-methylcyclohexyl metaborate; S-phenyl metaborate; S-o-, m-, and p-tolyl metaborates; S-xylyl metaborates; S-benzyl metaborates; S-(β-ethoxyethyl) metaborate; S-(β-(β-ethoxyethoxy)ethyl) metaborate; S-(β-phenoxyethyl) metaborate; and the like.

Those treating agents having the formula



include S-methyl thiometaborate; S-ethyl thiometaborate; S-n-propyl thiometaborate; S-isopropyl thiometaborate; the various S-butyl thiometaborates; S-amyl thiometaborates; S-hexyl thiometaborates; S-heptyl thiometaborates; S-octyl thiometaborates; S-nonyl thiometaborates; S-decyl thiometaborates; S-undecyl thiometaborates; S-dodecyl thiometaborates; S-octadecyl thiometaborate; S-cyclohexyl thiometaborate; S-methylcyclohexyl thiometaborate; S-phenyl thiometaborate; S-o-, m-, and p-tolyl thiometaborates; S-xylyl thiometaborates; S-benzyl thiometaborates; S-(β-ethoxyethyl) thiometaborate; S-(β-(β-ethoxyethoxy) ethyl) thiometaborate; S-(β-phenoxyethyl) thiometaborate; and the like.

Preferred treating agents include such compounds as methyl metaborate; ethyl metaborate; n-propyl metaborate; isopropyl metaborate; the various butyl metaborates; amyl metaborates; hexyl metaborates; heptyl metaborates; octyl metaborates; nonyl metaborates; decyl metaborates; undecyl metaborates; dodecyl metaborates; octadecyl metaborates; cyclohexyl metaborate; methylcyclohexyl metaborate; phenyl metaborates; o-, m- and p-tolyl metaborates; xylyl metaborates; benzyl metaborate; β-ethoxyethyl metaborate; β-(β-ethoxyethoxy)ethyl metaborate; β-phenoxyethyl metaborate; and the like. Of these compounds, those in which the R groups contain up to about 8 carbon atoms are particularly preferred.

To prepare the above treating agents, the following reactions are used:

O-substituted thiometaborates:

(1) $3HSBS+B(OR)_3 \rightarrow (ROBS)_3+B(SH)_3$

S-substituted metaborates:

(2) $3HOBO+3RSH \rightarrow (RSBO)_3+3H_2O$ or

(3) $3H_3BO_3+3RSH \rightarrow (RSBO)_3+6H_2O$

S-substituted thiometaborates:

(4) $3HSBS+3RSH \rightarrow (RSBS)_3+3H_2S$

O-substituted metaborates:

(5) $3HOBO+3ROH \rightarrow (ROBO)_3+3H_2O$ or

(6) $3H_3BO_3+3ROH \rightarrow (ROBO)_3+6H_2O$ or

(7) $(RO)_3B+B_2O_3 \rightarrow (ROBO)_3$

Reactions 1 and 4 are preferably carried out in refluxing carbon disulfide. Reactions 2, 3, 5 and 6 are conveniently carried out in refluxing toluene. Reaction 7 does not require a solvent; the reaction temperature is from 100 to 150° C.

The following specific examples illustrate the preparation of treating agents of this invention. In these examples all parts and percentages are by weight.

Example 39

In a reaction vessel equipped with heating and condensing means were placed 130.5 parts of orthoboric acid and 433 parts of toluene. This mixture was refluxed at about 110° C. whereby 39 parts of water was removed from the system as a toluene azeotrope. To the resultant slurry was slowly aded 132 parts of isopropanol over a period of 4.5 hours. The mixture was then refluxed at about 110° C. so that 45.5 parts of water-isopropanol mixture was removed as a toluene azeotrope. The solution remaining in the reaction vessel was subjected to chemical analysis which showed the presence of 3.82 percent of boron. Infrared analysis showed this solution to contain a maximum of 4 percent of triisopropyl orthoborate with the remainder being isopropyl metaborate. The toluene was then removed from this solution by distillation and isopropyl metaborate was recovered by recrystallization from a mixture of benzene and petroleum ether. The isopropyl metaborate so recovered was a white solid having a melting point of 50° C. Chemical analysis showed this solid to contain 12.5 percent of boron and to have a molecular weight of 253, which corresponded to the theoretical values of 12.6 percent of boron and a molecular weight of 258.

Example 40

To 86 parts of toluene were added 25 parts of cyclohexanol and 15.5 parts of orthoboric acid. This mixture was heated to about 110° C. until 9 parts of water was removed from the reaction system as a toluene azeotrope. Reaction was completed in 30 minutes. The toluene was removed by distillation from the clear solution remaining in the reaction vessel, leaving a white, fluffy product—cyclohexyl metaborate—melting at approximately 140° C.

Example 41

A mixture of 80 parts of orthoboric acid and 224 parts of benzyl alcohol was heated to 230° C. for one hour. 49 parts of water was evolved and removed from the system. The resulting solution was dissolved in an equal volume of benzene and then 10 times this volume of petroleum ether was added. A heavy liquid phase consisting of benzyl metaborate separated. Found—8.05 percent of boron, 5.29 percent of hydrogen, 62.5 percent of carbon, molecular weight 391. Theory for benzyl metaborate—8.10 percent boron, 5.27 percent of hydrogen, 62.9 percent of carbon, molecular weight 402.

Example 42

22.6 parts of β-ethoxy ethanol, 15.5 parts of orthoboric acid and 86 parts of toluene were heated at about 110° C. for 40 minutes. 10 parts of water was evolved and removed from the system as a toluene azeotrope. At this point the reaction vessel contained a clear solution of β-ethoxyethyl metaborate dissolved in toluene. 86 percent of the toluene was removed from this solution by distillation at 110° C., leaving a clear, water-white, oily liquid consisting of β-ethoxyethyl metaborate dissolved in a small amount of toluene.

The treating agents of this invention can be used singly or in admixture. Moreover, the treating agents can be mixed with esters of other acids of boron, such as orthoboric acid, mesoboric acid, dihydrodiboric acid, hexahydrotetraboric acid, hydrotetraboric acid, hexahydrohexaboric acid, dihydrohexaboric acid, hexahydrooctoboric acid, dihydrooctoboric acid, dihydrodecaboric acid, dihydrododecaboric acid, etc.

Solvents which can be used in conjunction with the above treating agents include pure paraffin hydrocarbons, such as pentane, n-decane, etc.; aromatic hydrocarbons, such as benzene, toluene, xylene, mesitylene, etc.; cyclohexane; cyclohexene; halogenated hydrocarbons, such

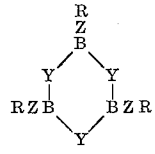
as chloroform, carbon tetrachloride, methylene dichloride, amyl chloride, bromobenzene, etc.; esters, such as ethyl acetate, amyl acetate, butyl phthalate, octyl sebacate, etc.; ethers; ketones, such as acetone, methylethyl ketone, etc.; and other organic solvents which are inert to the treating agents.

In carrying out the treatament of this invention, the ratio of treating agent to hydrocarbon being treated varies depending upon the nature of the hydrocarbon used. Thus, with relatively pure hydrocarbons, relatively small amounts of treating agents are used. When the hydrocarbon being treated contains a large amount of impurities, a correspondingly greater amount of treating agent is used. Generally speaking, the weight ratio of treating agent to hydrocarbon being treated ranges from about 0.00002:1 to about 0.05:1.

The temperature at which the process of this invention is conducted is also dependent upon the particular hydrocarbon being treated. For example, when the hydrocarbon is LPG, temperatures as low as about —50° C. are useful. With gasoline and similar hydrocarbons, the temperature is usually from about 20 to about 50° C. Thus, the temperature of this treatment is a temperature less than the boiling temperature of the hydrocarbon being treated at the prevailing pressure.

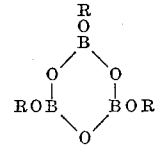
I claim:

1. A process for improving the combustion characteristics of gasoline which comprises adding to said gasoline an ester of a metaboric acid, said ester having the empirical formula



wherein R is a radical of one to 8 carbon atoms and is selected from the group consisting of alkyl, aralkyl, cycloalkyl, aryl, alkaryl, alkoxyalkyl, poly(alkoxy)-alkyl and aryloxy alkyl; and Y and Z are selected from the group consisting of oxygen and sulfur; at least a portion of said gasoline being non-aromatic, the weight ratio of said ester to said gasoline ranging from 0.00002/1 to 0.05/1, said ester being (1) soluble in said gasoline and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said gasoline; and separating said precipitate and said gasoline.

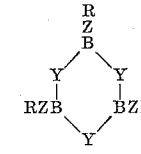
2. The process of claim 1 wherein said ester is an ester of metaboric acid having the following formula



wherein R is a radical of one to 8 carbon atoms and is selected from the group consisting of alkyl, aralkyl, cycloalkyl, aryl, alkaryl, alkoxyalkyl, poly(alkoxy)-alkyl and aryloxy alkyl; at least a portion of said gasoline being non-aromatic, the weight ratio of said ester to said gasoline ranging from 0.00002/1 to 0.05/1, said ester being (1) soluble in said gasoline and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said gasoline; and separating said precipitate and said gasoline.

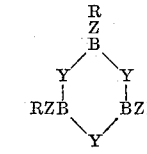
3. A process for improving the combustion characteristics of gasoline which comprises adding to said gasoline

an ester of a metaboric acid, said ester having the empirical formula



wherein R is a radical of one to 8 carbon atoms and is selected from the group consisting of alkyl, aralkyl, cycloalkyl, aryl, alkaryl, alkoxyalkyl, poly(alkoxy)-alkyl and aryloxy alkyl; and Y and Z are selected from the group consisting of oxygen and sulfur; at least a portion of said gasoline being non-aromatic, the weight ratio of said ester to said gasoline ranging from 0.00002/1 to 0.05/1, said ester being (1) soluble in said gasoline and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said gasoline; said ester being present in said gasoline in excess of the amount required to form said precipitate; separating said precipitate and said gasoline; and separating from said gasoline said excess amount of said ester.

4. A process for improving the combustion characteristics of gasoline which comprises adding to said gasoline an ester of a metaboric acid, said ester having the empirical formula



wherein R is a radical of one to 8 carbon atoms and is selected from the group consisting of alkyl, aralkyl, cycloalkyl, aryl, alkaryl, alkoxyalkyl, poly(alkoxy)-alkyl and aryloxy alkyl; and Y and Z are selected from the group consisting of oxygen and sulfur; at least a portion of said gasoline being non-aromatic, the weight ratio of said ester to said gasoline ranging from 0.00002/1 to 0.05/1, said ester being (1) soluble in said gasoline and (2) resistant to oxidative deterioration, whereby a precipitate is formed in said gasoline; said ester being present in said gasoline in excess of the amount required to form said precipitate; separating said precipitate and said gasoline; and separating from said gasoline said excess amount of said ester; and blending with said gasoline (1) an antiknock quantity of a lead alkyl antiknock agent and (2) a small amount of gasoline-soluble, organic boron compound.

5. The gasoline composition produced by the process of claim 1.

6. The gasoline composition produced by the process of claim 2.

7. The gasoline composition produced by the process of claim 4.

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