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3,083,087 SUBSTITUTED BENZYL ESTERS IN LEADED GASOLINE

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14 Claims. (Cl. 44—69)

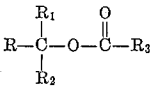
This invention relates to an improved gasoline composition which is of high octane number, which contains a lead compound as an anti-knocking agent and also contains an octane rating booster.

By and large, modern gasolines for use in spark-ignited internal combustion engines, e.g., automotive and airplane engines have an octane number of at least 85 RON, that is, as determined by the research method. Almost without exception producers of gasoline use non-hydrocarbon agents to raise the octane number of the gasoline to suppress knocking. Generally this agent is an alkyl lead compound especially a tetra-lower alkyl lead, usually a small amount within the range from about 0.5 to 3.0 cc. per gallon, or even as much as approximately 5 or 6 cc. per gallon. Tetraethyl lead is the most widely used anti-knock agent, and is effective in raising the octane and thereby reducing the knock caused by poor ignition of gasoline of inferior octane rating. Other lead compounds, such as the lower alkyl lead carboxylates disclosed in copending application Serial No. 855,006, filed Nov. 24, 1958, are useful as anti-knock agents. However, the quantity of lead compound which may be used in a gasoline is limited by decreasing effectiveness at higher percentages, and by the fact that lead compounds cause lead-containing deposits in the cylinders as well as by economic, health and legal considerations.

Several methods are used for determining the octane rating of a gasoline and each method usually gives a different figure; for example, the motor method of determining octane rating generally gives a lower figure than the research method. The spread between the two figures is termed the "sensitivity" of the fuel. Gasolines are sold on the basis of their research octane number but the make of the car and the type of driving determines whether it operates closer to the motor method or research method rating; however, the road octane is usually, numerically, in the space between the two. A gasoline having motor method and research method octane numbers which are closer is less sensitive to variations in operating conditions in its performance.

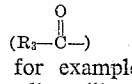
In accordance with this invention, certain gasoline-compatible, i.e. soluble, miscible or dispersible esters are incorporated in a leaded gasoline as an octane booster. The improvement in the gasoline is generally more apparent in the motor method of determining octane rating although some improvement also is observed when the octane is determined by the research method. The fuel, therefore, may even have less spread between its research method number and its motor method number, and would accordingly be considered as less sensitive. Furthermore, the esters usable in gasoline according to this invention can provide a greater increase in the research method octane rating of the gasoline than other esters proposed as gasoline octane rating boosters.

The ester incorporated in gasoline according to this invention is an α,α-organo-substituted benzyl ester such as cumyl acetate; α,α-dimethyl p-methylbenzyl acetate; 1,1-diphenyl ethyl acetate; 1-toluyl-1-methylethyl benzoate, 3-phenyl-3-acetoxypentane, etc. The ester may be represented by the formula

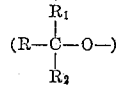


where R is a phenyl group, including substituted phenyl; R_1 is alkyl, including cycloalkyl; R_2 is the same or different R or R_1 group and R_3 is a monovalent hydrocarbon radical of 1 to 9 carbon atoms, e.g. the same or different R_2 group, or hydrogen.

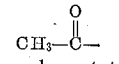
The substituents on the phenyl group, if any, may be, for instance, alkyl, alkoxy or hydroxy. Regardless of where positioned, the alkyl groups advantageously are lower alkyl groups, preferably lower alkyl groups having 1–4 carbon atoms. The acid residue or acyl group



may be derived from for example, formic, acetic or benzoic acid and generally will contain 1–10 carbon atoms, preferably 2 to 5 carbon atoms. The alcohol residue



has 9–20 carbon atoms, advantageously not more than 15 carbon atoms. A preferred acid residue from the standpoint of economy is



a preferred ester is cumyl acetate. Halogens such as chlorine or other materials which might significantly decrease the octane rating of the fuel are usually not a substituent of the ester.

The ester is included in the gasoline composition in the ratio of from 2 to 100 moles of ester per mole of lead compound and sufficient to increase the octane number of the leaded gasoline. The molar ratio of ester to lead compound is preferably about 5 to 75/1. In terms of volume, the fuel usually contains about 0.1 to 3 volume percent of the ester, preferably about 0.2 to 1.5%, an amount sufficient to increase the octane rating of the fuel. The concentration of the additive is important in that larger percentages may decrease the octane rating of the gasoline below the rating of the base fuel. Also, the optimum range of effectiveness of the octane booster varies with the lower-alkyl-lead content of the gasoline. In general, with greater amounts of, for example, tetraethyl lead, not only is the octane increased, but the octane boosting ability of the ester is also increased and the optimum range for this additive is slightly raised.

Gasolines are usually blends of low boiling mineral oil hydrocarbon fractions derived from distillation, cracking and other refining and chemical conversion processes practiced upon crude petroleum. The gasoline will contain varying proportions of paraffins, olefins, naphthenes and aromatics and generally will boil primarily in the range of about 100 to 425° F. The gasoline of this invention has an unsaturated component, i.e., olefinic and/or aromatic, preferably aromatic, which is at least

about 10 volume percent, preferably at least about 25 or 40 percent of the hydrocarbon fuel.

A typical premium gasoline besides a small amount of tetra-lower alkyl lead compound as an anti-knock agent, may also contain small amounts of other non-hydrocarbon constituents used to impart various properties to the gasoline in its use in internal combustion engines, e.g. scavengers, corrosion inhibitors, etc. Such gasolines frequently have a research method octane number of about 90 to 105 and a motor method octane number of about 80–98. The most widely used tetra-lower-alkyl lead compound added to gasolines as an anti-knock agent is tetra-ethyl lead. Frequently, "TEL motor mix" is used in commercial practice to add tetra-ethyl lead and scavengers to the gasoline. "Motor-mix" contains 59.2% tetra-ethyl lead, 13.0% ethylene dibromide, 23.9% ethylene dichloride and 3.9% hydrocarbon diluent, dyes, etc.

Esters suitable for use in the composition of this invention are commercially available or may be prepared as desired. A general procedure is by the reaction at room temperature of about one mole of the tertiary alcohol with one mole of the acid chloride in an organic solvent, such as pyridine, which takes up the HCl of reaction as it is formed, to give the ester. Another procedure involves the reaction of the tertiary alkyl halide with an ammonium or other salt of the acid to yield the ester plus the halide salt which may be removed by filtration. The tertiary alkyl halide may be produced for example, by chlorinating the arylalkane in the presence of ultra-violet light.

EXAMPLES

Cumyl acetate was prepared as follows:

2 moles of α-methyl-styrene was charged to a 500 ml. fluted flask equipped with a stirrer, gas dispersion tube, thermometer, and condenser. Anhydrous HCl was added and the reaction temperature was controlled at 25° C. by means of a water bath. The reaction rate is fast and was complete at the end of 1½ hours. The product was blown with nitrogen to remove any excess HCl. The weight increase was about 75 grams or nearly quantitative for the formation of cumyl-chloride. Sodium acetate was prepared by adding 60 g. NaOH to 600 g. of acetic acid. The solution of sodium acetate in acetic acid was cooled to 45° C. and 200 g. of the cumyl chloride was added during the course of one hour. The mixture was allowed to stir for several hours at room temperature. Then the NaCl was removed by filtration and also about 400 g. of the excess acetic acid which served as a solvent was removed under vacuum from a helices-packed column. The product bottoms was added to water and the organic phase was removed, washed with additional water and dried over $CaSO_4$.

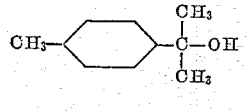
A portion of the product ester was fractionated on a spinning band column at 2 mm. Hg pressure. The major product was cumyl-acetate and only trace quantities of a compound presumed to be cumyl alcohol was found. It is noteworthy that no high-boiling polymeric material was formed. The cumyl acetate was characterized as follows:

Boiling point, ° C. at 2 mm	69.0
Refraction index n_d^{25}	1.4963

	Found	Theory
Percent C	74.3	74.2
Percent H	8.0	7.9
Sap. No.[1]	308	315

[1] Miligrams of KOH required to neutralize 1 gram of sample.

α,α-Dimethyl-methylbenzyl acetate was prepared by adding to a solution of 150 gms. of



and 95 gms. of pyridine in 50 ml. ethyl ether, a solution of 86.9 gms. of acetyl chloride in 50 ml. ether. The acetyl chloride solution was added dropwise over 1½ hours and then the mixture was refluxed for one hour at a maximum temperature of 60° C. After the reaction was complete, an amount of water equal to the reaction mass was added to dissolve the pyridine·HCl complex and removed. The remaining mass was washed first with dilute H_2SO_4, then with dilute $NaHCO_3$, then with water and dried over $MgSO_3$. The ether was stripped off and the product distilled at below 100° C.

A gasoline having an API gravity of 52.6° and an ASTM distillation of:

	° F.
IBP	106
5%	136
20%	172
50%	238
70%	280
EP	385

contained in the following components (±5%):

30% full-range straight run naphtha reformate
30% light fluid catalytically cracked gasoline
30% heavy straight-run naphtha reformate
10% butane

and analyzed as

	Vol. percent
Paraffins	34.3.
Olefins	27.2.
Naphthenes	4.7.
Aromatics	33.8.
Sulfur	0.0213 (wt. percent).

Samples of this base gasoline were obtained and mixed with 2.9 cc. per gallon of "TEL motor mix" (about .002 mole TEL/l.). A different amount of acetate was added to each sample and it was tested by the microoctane method. Table I below records the results of these tests along with the results of tests on samples containing t-butyl acetate. The base-leaded fuel used in samples I to XI had a motor method octane of 88.2 and a research method octane of 99.0. The base fuel used in samples XII to XVI had octanes of 88.5 MM and 99.1 RM.

Table I

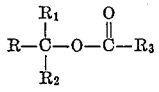
Sample	Volume, percent	Moles/liter	Increase in octane	
			RM	MM
t-Butyl Acetate				
I	0.25	0.0187	0.3	0.9
II	0.50	0.0375	0.6	1.3
III	0.75	0.0562	0.9	
IV	1.00	0.075	0.8	1.5
Cumyl Acetate				
V	0.25	0.012	0.4	
VI	0.50	0.024	0.8	1.1
VII	0.75	0.036	0.9	1.5
VIII	1.00	0.048	1.1	1.6
IX	1.25	0.060	1.4	1.6
X	1.50	0.072	1.4	
XI	2.00	0.096	1.3	
α,α,Dimethyl-p-methylbenzyl Acetate				
XII	0.5		0.5	0.9
XIII	0.75		0.7	1.2
XIV	1.00		0.7	1.4
XV	1.25		0.9	1.5
XVI	1.50		1.2	2.2

The above examples, which are to be considered illustrative only and not limiting, show that the addition of the described benzyl acetate to a leaded gasoline may

boost the octane rating of the fuel by as much as 2.2 numbers according to the motor method and has a greater octane enhancing effect than t-butyl acetate. Also, gasoline samples containing varying amounts as in Table I of, for example, 1,1-diphenyl-ethyl acetate, cumyl formate or 1-toluyl-1-methylethyl benzoate show improved octane enhancing effect.

It is claimed:

1. A leaded gasoline consisting essentially of base hydrocarbon gasoline containing at least about 10 volume percent of unsaturated hydrocarbons, a small amount of lower-alkyl lead anti-knock agent sufficient to reduce knock and about 2 to 100 moles per mole of lead compound of a gasoline compatible ester of the formula



where R is phenyl, R_1 is an alkyl of 1 to 4 carbon atoms, R_2 is selected from the group consisting of R and R_1 and R_3 is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals of 1 to 9 carbon atoms, sufficient to increase the octane rating of the leaded gasoline.

2. Gasoline according to claim 1 containing about 5 to 75 moles of ester per mole of lead compound.

3. Gasoline according to claim 2 where R is a phenyl substituted with a lower alkyl group of 1 to 4 carbon atoms.

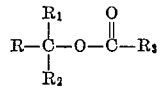
4. Gasoline according to claim 2 where the ester is cumyl acetate.

5. Gasoline according to claim 3 where the ester is α,α-dimethyl-p-methyl benzyl acetate.

6. Gasoline according to claim 1 where the base leaded gasoline has an octane rating by the research method of about 90 to 105.

7. Gasoline according to claim 1, where the unsaturated hydrocarbons are aromatic.

8. A leaded gasoline consisting essentially of base hydrocarbon gasoline containing at least about 25 volume precent of unsaturated hydrocarbons, a small amount of lower-alkyl lead anti-knock agent sufficient to reduce knock and about 2 to 100 moles per mole of lead compound of a gasoline compatible ester of the formula



where R is phenyl, R_1 is an alkyl of 1 to 4 carbon atoms, R_2 is selected from the group consisting of R and R_1 and R_3 is selected from the group consisting of hydrogen and monovalent hydrocarbon radicals of 1 to 9 carbon atoms, sufficient to increase the octane rating of the leaded gasoline.

9. Gasoline according to claim 8 containing about 5 to 75 moles of ester per mole of lead compound.

10. Gasoline according to claim 8 where R is phenyl substituted with a lower alkyl group of 1 to 4 carbon atoms.

11. Gasoline according to claim 8 where the ester is cumyl acetate.

12. Gasoline according to claim 8 where the ester is α,α-dimethyl-p-methyl benzyl acetate.

13. Gasoline according to claim 8 where the base leaded gasoline has an octane rating by the research method of about 90 to 105.

14. Gasoline according to claim 8, where the unsaturated hydrocarbons are aromatic.

References Cited in the file of this patent

UNITED STATES PATENTS

1,692,784	Orelup et al.	Nov. 20, 1928
2,210,942	Lipkin	Aug. 13, 1940
2,228,662	Holm	Jan. 14, 1941
2,360,585	Ross et al.	Oct. 17, 1944
2,384,866	Wiczer	Sept. 18, 1945

FOREIGN PATENTS

837,965	France	Nov. 28, 1938
277,326	Great Britain	Jan. 7, 1929

OTHER REFERENCES

Chem. and Eng. News, Apr. 6, 1959, page 42.

"Improved Motor Fuels Through Selective Blending," by Wagner et al.; paper presented before 22nd. Annual Meeting of the American Petroleum Institute, Nov. 7, 1941, pages 10–13.