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N-PROPYL N-BUTYRATE IN LEADED GASOLINE

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This invention relates to an improved gasoline composition which is of high octane number, which contains a lead compound as an antiknocking 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 reasearch 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 a tetraalkyl lead, especially tetraethyl lead, usually a small amount within the range from about 0.5 to 3 cc. per gallon, or even as much as approximately 5 or 6 cc. per gallon. Tetraethyl lead is the most widely used antiknock agent, and is effective in raising the octane and thereby reducing the knock caused by poor ignition of gasoline of inferior octane rating. 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 but 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 considered to be less sensitive to variations in operating conditions in its performance.

In accordance with this invention n-propyl butyrate is incorporated in a leaded gasoline as an octane rating booster. The improvement in the gasoline is sometimes more apparent in the research method of determining octane rating and sometimes more improvement is observed when the octane rating is determined by the motor method. The fuel, therefore, may even have less spread between its research method number and its motor method number and may accordingly be less sensitive.

The composition of this invention comprises leaded gasoline in which has been incorporated about 5 to 50 moles of n-propyl butyrate per mole of lead compound and sufficient to increase the octane number of the leaded gasoline. Although it has been reported that certain tertiary alkyl esters are effective octane rating boosters, we have found that this particular normal ester is an effective octane rating booster while closely related esters do not exhibit such advantageous properties.

From our data we believe that the preferred ratio of ester to lead compound is about 10 to 35. The greatest octane rating increase seems to be obtained at an additive to, for example, tetraethyl lead molar ratio of about 30 to 1; however, economically it may be desirable to use a ratio somewhat below 30 to 1. In terms of volume about 0.2 to 3 volume percen of the additive may be contained in the fuel, preferably about 0.8 to 2.5% and

sufficient to raise the octane rating of the fuel. The effectiveness of the booster is greatly dependent upon its concentration; too high a concentration may actually decrease octane rating below that of the base fuel. In general, with greater amounts of, for example, tetraethyl lead, not only is the octane rating increased, but the octane rating boosting ability of the ester is also increased.

Gasolines are usually blends of hydrocarbon mineral oil fractions boiling primarily in the approximate range of about 100 to 425° F. The gasoline will contain varying proportions of paraffins, olefins, naphthenes and aromatics derived by distillation, cracking and other refining and chemical conversion processes practiced upon crude petroleum fractions. Straight run gasolines, gasolines derived from cracking gas oil, gasolines or reformate from reforming straight run naphtha over a platinum-alumina catalyst in the presence of free hydrogen, etc., are components frequently used in making up a gasoline composition. A typical premium gasoline, besides a small amount of tetra-lower-alkyl lead compound as an antiknock agent, may also contain small amounts of other non-hydrocarbon constituents used to impart various properties to the gasoline in its use in internal combusiton engines, e.g. scavengers, corrosion inhibitors, etc. Such gasolines frequnetly have a research method octane number of about 90 to 105 and a motor method octane number of about 80 to 98.

Examples

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

typically contains the following components:

Components—	Approximate boiling range, ° F.
30% full-range straight run naphtha reformate	100 to 380
30% light fluid catalytically cracked gasoline	100 to 230
30% straight-run naphtha heavy reformate	260 to 395
10% butane.	

Analyzing:	Volume percent
Paraffins	34.3.
Olefins	27.2.
Naphthenes	4.7.
Aromatics	33.8.
Sulfur	0.0213 (Wt. percent).

The most widely used tetra-lower-alkyl lead compound added to gasolines as an antiknock agent is tetraethyl lead. Frequently, "TEL motor mix" is used in commercial practice to add tetraethyl lead and scavengers to the gasoline. "Motor mix" containings 59.2% tetraethyl lead, 13.0% ethylene dibromide, 23.9% ethylene dichloride and 3.9% hydrocarbon diluent, dyes, etc.

Compositions illustrative of this invention, but not to be considered as limiting its scope were prepared and tested.

100 cc. samples of the base gasoline described above, containing 3 or 6 ml. per gallon of tetraethyl lead (added as "motor mix") were tested by the microoctane method. Each sample also contained a different amount of ester. The octane rating of the base fuel containing the motor mix was measured before each test and varied between

88 and 89.5 motor method and 98 and 99 research method. Tests on these samples gave the following results:

Sample	TEL (ml./gal.)	Additive	cc./100 cc. Fuel	Octane Rating Change	
				M. Method	R. Method
I	6	Methyl propionate	1.0	+0.1	+0.3
II	3	Ethyl propionate	1.0	−0.2	+0.1
III	3	n-Propylpropionate	1.0	+0.1	0
IV	3	Isopropylpropionate	1.0	+0.2	+0.3
V	3	Isobutylpropionate	1.0	+0.2	+0.3
VI	3	Methylbutyrate	1.0	−0.1	+0.1
VII	3	Ethylbutyrate	1.0	−0.1	+0.1
VIII	3	n-Propyl-n-butyrate	0.25	−0.2	−0.1
IX	3	do	0.5	−0.4	+0.1
X	3	do	1.0	+0.7	+0.8
XI	3	do	2.0	+2.3	+1.9
XII	6	do	0.25	0	+0.3
XIII	6	do	0.5	+0.4	+0.3
XIV	6	do	1.0	+0.9	+1.2

These results show that n-propyl butyrate is a far more effective octane rating booster than other non-tertiary alkyl esters.

We claim:

1. A leaded gasoline consisting essentially of base hydrocarbon gasoline, a small amount of tetra-lower-alkyl lead antiknock agent sufficient to reduce knock and about 5 to 50 moles per mole of lead compound of n-propyl n-butyrate, sufficient to increase the octane rating of the leaded gasoline.

2. The gasoline composition of claim 1 containing about 10 to 35 moles of n-propyl n-butyrate per mole of lead compound.

3. The gasoline composition of claim 1 where the base leaded gasoline has an octane rating of about 90 to 105 by the research method.

4. The gasoline composition of claim 2 where the base leaded gasoline has an octane rating of about 90 to 105 by the research method.

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