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GLYCEROL ESTERS 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 anti-knocking agent, and also contains an octane rating booster.

By and large, modern gasolines for use in spark-ignited internal combustion egines, 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 abnormal combustion 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 November 24, 1959, now abandoned, 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 improvement also is usually 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.

The ester incorporated in gasoline according to this invention contains no more than 20 carbon atoms and is a triester of glycerol with a lower aliphatic acid. The ester or acyl groups may be alike or different, straight, branched or cyclic and in general have 1–9 carbon atoms. The glycerol esters of acids having 2 to 5 carbon atoms, such as triacetin, tripropionin and tributyrin are preferred.

The ester is included in the gasoline composition in the ratio of from about 1 to 50 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 2 to 30/1. In terms of volume, the fuel usually contains about 0.2 to 6 volume percent of the ester, preferably about 0.4 to 4%, 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 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 by 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 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 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.

The gasoline blends used in the samples reported in the table below included as a component a naphtha reformate distillation tower bottoms fraction which had an API gravity of 34.1 and contained 25.1% paraffins, 3.2% naphthenes and 71.7% aromatics. The fraction had an ASTM distillation of:

IBP	313° F.	Rec	98.5%
50%	334° F.	Res	1.0%
90%	368° F.	Loss	0.5%
EP	442° F.		

Gasoline blend D comprised 28.4% of these tower bottoms, 28.4% light fluid catalytically cracked gasoline, 19.0% mixed xylenes, 19.0% alkylate fuel and 5.2% butane. This gasoline had an API gravity of 53.0 and a bromine number of 35.0. It analyzed as 34.9% paraffins, 15.1% olefins, 7.1% naphthenes and 42.9% aromatics. Its ASTM distillation was:

IBP	92° F.	Percent rec	98.0
10%	133° F.	Percent res	1.0
50%	256° F.	Percent loss	1.0
90%	329° F.		
EP	403° F.		

Samples of this base gasoline were obtained and mixed with 6 cc. per gallon of TEL as "Motor Mix" (about 0.008 mole TEL/1). A different amount of glycerol triester was added to each sample and it was tested by the Microoctane Method. The base fuel was tested before

each series of tests. The table below records the results of these tests.

TABLE

Sample	Additive, vol. percent	Octane		Change	
		MM	RM	MM	RM
Triacetin					
10	None	95.4	106.7		
11	1.5	96.0	107.5	+0.6	+0.8
12	1.75	95.6	107.5	+0.2	+0.8
13	2.00	95.8	107.6	+0.4	+0.9
14	2.25	96.4	107.8	+1.0	+1.1
Tripropionin					
20	None	95.2	106.1		
21	2.00	97.0	107.4	+1.8	+1.3
22	2.25	97.0	107.6	+1.8	+1.5
23	2.50	97.4	107.8	+2.2	+1.7
24	2.75	97.5	107.6	+2.3	+1.5
Tributyrin					
30	None	95.6	107.1		
31	2.25	96.1	108.0	+0.5	+0.9
32	2.50	96.4	108.1	+0.8	+1.0
33	2.75	96.6	108.1	+1.0	+1.0
34	3.00	97.4	108.1	+1.8	+1.0

It is claimed:

1. A leaded gasoline consisting essentially of base hydrocarbon gasoline containing at least about 10 volume percent unsaturated hydrocarbons, a small amount of lower-alkyl lead anti-knock agent sufficient to reduce knock and about 1 to 50 moles per mole of lead compound of a gasoline-compatible ester containing up to 20 carbon atoms and comprising a glycerol triester of an aliphatic carboxylic acid of 1–9 carbon atoms in an amount sufficient to increase the octane number of the leaded gasoline.

2. Gasoline according to claim **1** where the acid is acetic acid.

3. Gasoline according to claim **1** where the acid is propionic acid.

4. Gasoline according to claim **1** where the acid is butyric acid.

5. Gasoline according to claim **1** containing about 2 to 30 moles of ester per mole of lead compound.

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