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STABILIZED LEADED GASOLINES

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4 Claims. (Cl. 44—69)

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This invention relates to the manufacture of stabilized leaded gasolines, and more particularly to the inhibition of gum formation, prevention of haze formation and prevention of lowering of octane rating in "anti-knock" gasolines containing tetra-alkyl lead compounds.

It is customary in the production of high grade "anti-knock" gasolines to add to a good grade of gasoline, a small amount of a tetra-alkyl lead compound, usually tetra-ethyl lead, to reduce the tendency to cause knocking in high compression gasoline engines. The tetra-ethyl lead is added to the gasoline in a quantity sufficient to produce the desired anti-knock rating. In some cases a relatively small amount may be required while in other cases, for example, in the preparation of certain aviation grades of gasoline, a relatively large amount may be added. Gasoline to which a large amount of tetra-ethyl lead or other tetra-alkyl lead has been added is often referred to as a "heavily leaded" gasoline.

Although tetra-alkyl lead compounds, and in particular tetra-ethyl lead, are efficient for imparting anti-knock properties to gasoline, their employment is not entirely free from disadvantage. For one thing, leaded gasoline tends to develop a hazy appearance upon standing, particularly in the presence of strong sunlight. For example, in direct sunlight in the summertime, leaded gasoline may develop a perceptible haziness after an hour or two of exposure, and longer periods of exposure result in a very marked haziness and precipitation. The formation of haze in gasoline is objectionable because the gasoline is not as marketable as a clear product; customers prefer a product which is crystal clear. A further and more important objection is that a reduction in the octane rating of the gasoline is frequently associated with haze formation; furthermore, damage is likely to occur in the fuel lines and carburetor.

In addition to haze formation in leaded gasolines, there is a tendency to deposit gummy or resinous materials on standing, this tendency being particularly noticeable under the influence of air and light. Gum formation, as with haze formation, is usually attended by a lowering in anti-knock rating and development of a yellow or brownish color. Gum formation is also observed in engines burning the leaded gasoline, with the result that ring and valve sticking occur.

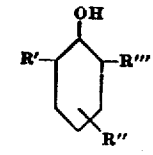
This invention has as an object the stabilization of leaded gasolines, especially heavily leaded gasolines, against haze formation.

It is a further object of this invention to protect leaded gasoline against the deposition of gum and resinous matter.

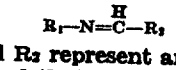
A still further object of this invention is the prevention of lowering of anti-knock rating in leaded gasolines.

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These and other objects are accomplished by the present invention wherein there is added to gasolines containing a tetra-alkyl lead compound stabilizing amounts of (1) at least one phenol represented by the structural formula:



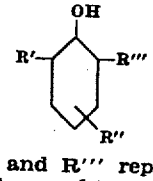
wherein R', R'' and R''' represent alkyl substituents, at least one of R' and R''' having at least 3 carbon atoms; and (2) at least one azomethine compound represented by the structural formula:



wherein R_1 and R_2 represent an aromatic group.

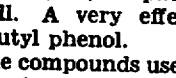
We have found that the addition to gasolines of trisubstituted alkyl phenol compounds of the above type in conjunction with the aromatic azomethine compounds shown impart characteristics which could not be predicted from the separate use of each inhibitor.

The alkyl phenols used in accordance with our invention have the formula:



wherein R', R'' and R''' represent alkyl substituents, at least one of R' and R''' having at least 3 carbon atoms. Examples of such phenols are 2,4,6-tritertiarybutyl phenol; 2,6-ditertiarybutyl-4-secondarybutyl phenol; 2,6-ditertiarybutyl-4-methyl phenol; 2,6-ditertiarybutyl-3-methyl phenol; 4,6-ditertiarybutyl 2-methyl phenol; 2-isopropyl-4,6-dimethyl phenol; 2-tertiarybutyl-4,6-dimethyl phenol; 2-tertiary amyl-4,6-dimethyl phenol; 4-methyl-2,6-diisopropyl phenol; 2,4,6-triisopropyl phenol; 2,4,6-tritertiaryamyl phenol; and 2-tertiarybutyl-4,6-ditertiaryamyl phenol. Either individual phenols or mixtures thereof may be used, especially the mixture of alkylated phenols obtained in accordance with U. S. Patent 2,149,759 patented March 7, 1937, to Cantrell. A very effective phenol is 2,4,6-tritertiarybutyl phenol.

The azomethine compounds used in accordance with our invention have the formula:



wherein R_1 and R_2 are aromatic groups. They are preferably made in accordance with the procedure shown in U. S. Patent 2,388,903 patented November 13, 1945, to Cantrell and Peters by con-

densing a primary aryl amine with an aromatic aldehyde in the presence of a small amount of

gasoline. A comparison of the uninhibited and inhibited gasolines follows:

	Uninhibited Base Gasoline	Motor Fuel I	Motor Fuel II	Motor Fuel III
Oxygen Gum, mg./100 cc.: AN Method	3	3	3	2.
Precipitate, Mg./200 cc.	1	1	1	nil.
Sunlight Stability, 5 Hrs.: Appearance	heavy ppt.	heavy ppt.	slight haze	bright.
Height in inches of column of oil through which elite type can be read.	opaque	opaque	4	6.
Ultra Violet Light Stability, Quarts Tube, 1 hr.: Appearance.	heavy ppt.	heavy ppt.	slight haze	bright.

dicyclohexylamine. Representative azomethine compounds are benzalaniline, benzalxylidine, benzal-betanaphthylamine, benzal-alphanaphthylamine, benzal-o-toluidine, benzal-p-toluidine, benzal-o-anisidine, benzal-p-anisidine, benzal-p-aminoazobenzene, p-dimethylaminobenzalxylidine, 2-hydroxy-5-methylbenzalaniline, p-dimethylaminobenzal-p-dimethylaminoaniline, p-dimethylaminobenzalaniline, dibenzal-p-phenyleneediamine, dibenzal-o-tolidine, cinnamylideneaniline, cinnamylidenexylidine, furfuralaniline, furfuralxylidine, furfural-p-toluidine, furfural-o-tolidine, furfural benzal-o-tolidine, and furfuracrylideneaniline.

For inhibiting haze formation, gum formation and lowering of octane rating in leaded gasolines, small amounts of the above described phenols and azomethine compounds are sufficient. Generally, from 0.001 to 0.1 per cent by weight of the phenols and from 0.001 to 0.1 per cent by weight of the azomethine compounds, or from 3 to 300 pounds of the phenol per 1000 barrels of gasoline and from 3 to 300 pounds of the azomethine compound per 1000 barrels of gasoline are added. A barrel is equivalent to 42 gallons.

The following examples further illustrate our invention:

Example I.—Twenty pounds of a mixture consisting of 60 per cent by weight of the mixture of alkylated phenols obtained in accordance with U. S. Patent 2,149,759 and 40 per cent by weight of benzalxylidine were added to 1000 barrels of a motor fuel containing tetraethyl lead. The resulting motor fuel was stabilized against gum and haze formation.

Example II.—Fifty pounds of a mixture consisting of 10 pounds of the mixture of alkylated phenols obtained in accordance with U. S. Patent 2,149,759 and 40 pounds of benzalxylidine were added to 1000 barrels of a leaded gasoline. Not only was haze formation eliminated, but the formation of gummy decomposition products or solid deposits on the spark plugs, piston rings and valves of a test engine operating on the inhibited gasoline was virtually eliminated. The inhibited gasoline thus permitted operation of the engine without the usual ring and valve sticking and eliminated gum and carbon deposits.

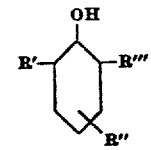
Example III.—From an aviation gasoline base having an octane rating of 91 and containing 4.0 cc. of tetraethyl lead per gallon, three inhibited motor fuels were made up as follows: Motor fuel I containing 12 pounds of 2,4,6-tritertiarybutyl phenol per 1000 barrels of base gasoline; motor fuel II containing 50 lbs. of benzalxylidine per 1000 barrels of base gasoline; and motor fuel III containing 12 pounds of 2,4,6-tritertiarybutyl phenol per 1000 barrels of base gasoline and 50 pounds of benzalxylidine per 1000 barrels of base gasoline. A comparison of the uninhibited and inhibited gasolines follows:

The marked improvement of motor fuel III, prepared in accordance with our invention, over the uninhibited gasoline base as well as over the other inhibited motor fuels containing only a phenol or an azomethine compound is clear. It is also clear that the properties of motor fuel III are not merely a summation of the properties of the other inhibited motor fuels. Motor fuel III, in accordance with our invention, exhibits unexpected improved properties which could not have been predicted from the properties of the other inhibited motor fuels.

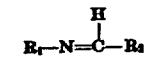
While we do not desire to be bound by any theory as to the action of our inhibitor, we believe that the synergistic effects of the phenol and azomethine compound on each other are due to the formation of addition products between the compounds.

We claim:

1. A leaded gasoline containing stabilizing amounts of (1) at least one phenol having the formula:



wherein R', R'' and R''' represent alkyl substituents, at least one of R' and R''' having at least 3 carbon atoms; and (2) at least one azomethine compound having the formula:



wherein R_1 and R_2 represent aromatic groups.

2. A leaded gasoline in accordance with claim 1, wherein the phenol is present in an amount of from 0.001 to 0.1 per cent by weight of the gasoline, and the azomethine compound is present in an amount of from 0.001 to 0.1 per cent by weight of the gasoline.

3. A leaded gasoline containing stabilizing amounts of 2,4,6-tritertiarybutyl phenol and benzalxylidine.

4. A leaded gasoline containing per 1000 barrels of gasoline 12 pounds of 2,4,6-tritertiarybutyl phenol and 50 pounds of benzalxylidine.

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