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STABILIZATION OF TETRAALKYL LEAD AND COMPOSITIONS CONTAINING THE SAME

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This invention relates to the stabilization of tetraalkyl lead, unmixed with anything but its normal impurities, and to the stabilization of tetraalkyl lead compositions containing hydrocarbons and/or halogen derivatives of hydrocarbons.

It is known that ordinary commercial tetraalkyl lead compounds, particularly tetraethyl lead, decompose slowly on standing with the formation of a precipitate, and that this decomposition is accelerated in the presence of halogen derivatives of hydrocarbons. This decomposition also takes place in hydrocarbon motor fuels which contain tetraethyl lead compounds. Ordinarily, tetraalkyl lead compounds, such as tetraethyl lead are incorporated in gasoline in the form of a liquid called "ethyl fluid" which usually is a solution containing a mixture of tetraethyl lead and a halogenated hydrocarbon, such as ethylene dibromide or ethylene dichloride, or both. Sometimes a small amount of dye is present in the "ethyl fluid" to impart a distinctive color. The "ethyl fluid" is, of course, added to the gasoline to produce an improved anti-knock rating. In some cases, only a relatively small amount of "ethyl fluid" is added, but sometimes, as with certain aviation grades of gasoline, a larger amount is used. Motor fuels to which a relatively large amount of tetraethyl lead or other tetraalkyl lead compound has been added, are often referred to as "heavily leaded" gasolines.

Hydrocarbon motor fuels containing such tetraalkyl lead compounds tend to develop a hazy appearance upon standing, especially when contact between these fuels and the oxygen of the air occurs, as is inevitable in the ordinary handling and storage of commercial motor fuels. Perceptible haziness may become apparent within a few hours and after longer periods of time, the haziness may become very marked and precipitation may occur. These hazing and precipitation phenomena sometimes occur in the "ethyl fluid" itself, and the haze or precipitate is, of course, imparted to the motor fuel upon blending the hazed "ethyl fluid" with the fuel.

The formation of haze and precipitate in gasoline is objectionable from two standpoints. One involves the reaction of the customer, since invariably the customer prefers a product which is clear and transparent. The second and more important objection is that a reduction in octane rating often develops with these haze precipitation phenomena and the precipitate may tend to clog the carburetor system of the combustion engine in which the fuel is used.

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It is known that this decomposition of tetraalkyl lead compounds can be retarded by means of aliphatic amines, including alkyl amines and hydroxyalkyl amines. To improve the solubility of these amines in tetraalkyl lead compositions and particularly in hydrocarbon motor fuels containing tetraalkyl lead compounds, it has been proposed to employ the amines in the form of their salts with long-chain fatty acids, i. e. fatty acids containing a lipophilic group, e. g. oleic, stearic or lauric acids. This type of compound is not always a desirable addition to motor fuels, particularly fuels containing unstable olefinic hydrocarbons and which have been inhibited against gum formation, because many gum inhibitors are adversely affected by the presence of acidic substances.

We have now found that the decomposition of tetraalkyl lead compounds can be retarded by incorporating in the tetraalkyl lead compounds or compositions containing the same an aromatic compound which is a derivative of a phenylenediamine in which one hydrogen atom of each amino group is replaced by a secondary or a tertiary alkyl group. The secondary alkyl or tertiary alkyl groups (which all contain at least three carbon atoms) can be alike or different. These aromatic compounds are excellent retarders of the decomposition of tetraalkyl lead, both in concentrated solutions (containing at least 25 per cent by weight of tetraalkyl lead), such as "ethyl fluid," and in dilute solutions in hydrocarbon motor fuels.

The action of the N,N'-di-secondary alkyl-p-phenylenediamines and N,N'-di-tertiary alkyl-p-phenylenediamines in retarding haze formation is entirely unexpected since the corresponding simple primary alkyl derivatives, e. g. N,N'-dimethyl-p-phenylenediamine do not have this effect and, in fact, tend to promote the formation of haze, especially in motor fuels.

The N,N'-di-secondary alkyl-p-phenylenediamines exert an additional effect on hydrocarbon motor fuels, if the motor fuels are of a character which tend to deteriorate and form gum. These secondary alkyl derivatives have a high gum inhibiting effect. Very often when gasolines, which are only relatively stable to oxygen absorption and consequent gum formation, are treated with tetraalkyl lead compounds, a decrease in stability results. The compounds known to the prior art for the stabilization of concentrated tetraalkyl lead solutions have no ability to prevent this decrease. Conversely, the majority of potent compounds which can be added to motor fuels to

retard or inhibit oxygen absorption and gum formation are incompatible with concentrated tetraalkyl lead solutions. It is unusual to find a compound which is both a good stabilizing agent for concentrated tetraalkyl lead solution and also a potent gum inhibitor. When this dual role is desired of the N,N'-di-alkyl-p-phenylenediamine, the amount incorporated in the "ethyl fluid" is somewhat greater than is required for stabilization of the concentrated solution so that by the addition of the usual amount of the concentrate to motor fuels, a suitable stabilizing amount of N,N'-di-alkyl-p-phenylenediamine will be incorporated in the motor fuel. Usually from 1 to 10 per cent by weight, based on the tetraalkyl lead, of N,N'-di-alkyl-p-phenylenediamine is sufficient, to stabilize the concentrated solutions of lead tetraalkyl against haze formation and precipitation; and this concentration will give in the motor fuel a concentration of phenylenediamine derivative of from 0.001 per cent to 0.01 per cent by weight, based on the motor fuel, depending upon the amount of lead tetraalkyl solution which is added to the motor fuel. A concentration of 0.001 per cent to 0.01 per cent of phenylenediamine derivative in the motor fuel is ordinarily sufficient to retard haze formation induced by the lead tetraalkyl, as well as to retard gum formation.

In practicing our invention, we add an amount of the phenylenediamine derivative to the tetraalkyl lead compound itself, or to a mixture of the tetraalkyl lead compound and one or more halogenated hydrocarbons. In some instances it is desirable to replace a portion of the halogenated hydrocarbon with a solvent, such as benzol or naphtha, to enhance the solubility of the N,N'-di-alkyl-p-phenylenediamine in the concentrated tetraalkyl lead solution. In the case of N,N'-di-secondary butyl-p-phenylenediamine the use of such solvents is not necessary. Or, we can add the phenylenediamine derivative to a motor fuel containing a tetraalkyl lead compound or we can add the phenylenediamine derivative to a motor fuel to which is then added the tetraalkyl lead compound.

By the term "hydrocarbon motor fuel," we mean not only motor fuels consisting entirely of hydrocarbons, but also motor fuels containing hydrocarbons and appreciable amounts of other combustible substances, such as alcohols. By way of description of our invention, the following illustrative examples are given, but it will be understood that other embodiments exist and may be practiced without departing from the spirit of the invention:

Example I

In an accelerated storage test, in which the samples were exposed to diffuse sunlight, to 99 grams of commercial "ethyl fluid" (60 per cent by weight of lead tetraethyl in ethylene dibromide) was added 1 gram of N,N'-di-secondary butyl-p-phenylenediamine. This amount of base will be found sufficient to prevent the development of haze or precipitate indefinitely. A similar sample of "ethyl fluid" containing no N,N'-di-secondary butyl-p-phenylenediamine developed an appreciable amount of yellow precipitate in 9 days storage in a closed container.

Example II

Two samples of commercial gasoline were treated with "ethyl fluid" (60 per cent by weight of lead tetraethyl in ethylene dibromide) to yield a concentration of 0.1 per cent tetraethyl lead. These samples were subjected to an accelerated storage test in the oxygen bomb for 16 hours, a length of time insufficient to cause any appreciable oxygen absorption and gum formation with these relatively stable gasolines. One sample (A) contained no tetraalkyl lead stabilizing agent; one sample (B) contained 0.01 per cent N,N'-di-secondary butyl-p-phenylenediamine; one sample (C) contained 0.01 per cent N,N'-di-isopropyl-p-phenylenediamine. The effectiveness of these compounds in preventing lead precipitation is shown in the table.

Table

Gasoline	Time	Precipitation		
		A	B	C
	Hrs.			
Pennsylvania Straight Run	16	Heavy	None	None.
Texas Aviation Base Stock	16	do	do	Do.

Likewise, other concentrated or dilute solutions of lead tetraalkyl compounds in solvents, such as benzene (benzol), toluene, naphtha, hexanes, heptanes, octanes, nonanes, carbontetrachloride, chloroform, isopropyl benzene or di-isopropyl ether, for example, or in gasoline which is substantially stable and does not tend to form appreciable gum upon storage, or in cracked gasoline, can be stabilized against haze formation or precipitation by means of N,N'-di-secondary alkyl-p-phenylenediamines or N,N'-di-tertiary alkyl-p-phenylenediamines. Either symmetrical or unsymmetrical phenylenediamine derivatives can be employed. Thus, the symmetrical derivative N,N'-di-tertiary butyl-p-phenylenediamine or the unsymmetrical derivative N-secondary butyl-N'-isopropyl-p-phenylenediamine can be employed instead of N,N'-di-secondary butyl-p-phenylenediamine. N-secondary butyl-N'-isopropyl-p-phenylenediamine is described in the copending application of H. Von Bramer and L. G. Davy, Serial No. 493,762, filed July 7, 1943, now Patent No. 2,381,015, dated August 7, 1945.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing a tetraalkyl lead compound, a halogenated hydrocarbon lead scavenger and, as a haze retarder, a small amount of an aromatic compound which is a derivative of a p-phenylenediamine in which one hydrogen atom of each amino group is replaced by an alkyl group selected from the group consisting of secondary and tertiary alkyl groups.

2. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing tetraethyl lead, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 0.001 to 0.01 percent based on the weight of the hydrocarbon motor fuel of an aromatic compound which is a derivative of a p-phenylenediamine in which one hydrogen atom of each amino group is replaced by an alkyl group selected from the group consisting of secondary and tertiary alkyl groups.

3. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing a tetraalkyl lead compound, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 0.001 to

0.01 percent based on the weight of the hydrocarbon motor fuel of N,N'-di-secondary butyl-p-phenylenediamine.

4. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing tetraethyl lead, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 0.001 to 0.01 percent based on the weight of the hydrocarbon motor fuel of N,N'-di-secondary butyl-p-phenylenediamine.

5. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing lead tetraethyl, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 0.001 to 0.01 percent based on the weight of the hydrocarbon motor fuel of N,N'-di-tertiary butyl-p-phenylenediamine.

6. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing lead tetraethyl, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 0.001 to 0.01 percent based on the weight of the hydrocarbon motor fuel of N,N'-di-isopropyl-p-phenylenediamine.

7. A tetraalkyl lead compound containing, as a haze retarder, from 1 to 10 percent based on the weight of the tetraalkyl lead compound of an aromatic compound which is a derivative of a p-phenylenediamine in which one hydrogen atom of each amino group is replaced by an alkyl group selected from the group consisting of secondary and tertiary alkyl groups.

8. Tetraethyl lead containing, as a haze retarder, from 1 to 10 percent based on the weight of the tetraethyl lead of an aromatic compound which is a derivative of a p-phenylenediamine in which one hydrogen atom of each amino group is replaced by an alkyl group selected from the group consisting of secondary and tertiary alkyl groups.

9. A tetraalkyl lead compound containing, as a haze retarder, from 1 to 10 percent based on the weight of the tetraethyl lead of N,N'-di-secondary butyl-p-phenylenediamine.

10. Tetraethyl lead containing, as a haze retarder, from 1 to 10 percent based on the weight of the tetraethyl lead of N,N'-di-secondary butyl-p-phenylenediamine.

11. A composition consisting of tetraethyl lead, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 1 to 10 percent based on the weight of the lead tetraethyl of an aromatic compound which is a derivative of a p-phenylenediamine in which one hydrogen atom of each amino group is replaced by an alkyl group selected from the group consisting of secondary and tertiary alkyl groups.

12. A composition consisting of tetraethyl lead, a halogenated hydrocarbon lead scavenger and, as a haze retarder, from 1 to 10 percent based on the weight of the lead tetraethyl of N,N'-di-secondary butyl-p-phenylenediamine.

13. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing tetraethyl lead and, as a haze retarder, from 0.001 to 0.01 percent based on the weight of the hydrocarbon motor fuel of an aromatic compound which is a derivative of a p-phenylenediamine in which one hydrogen atom of each amino group is replaced by an alkyl group selected from the group consisting of secondary and tertiary alkyl groups.

14. A hydrocarbon motor fuel which is substantially stable and does not tend to form appreciable gum upon storage containing tetraethyl lead and, as a haze retarder, from 0.001 to 0.01 percent based on the weight of the hydrocarbon motor fuel of N,N'-di-secondary butyl-p-phenylenediamine.

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