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STABILIZED IRON PENTACARBONYL AND MOTOR FUEL CONTAINING THE SAME

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This invention relates to liquid fuels suitable for use in internal combustion engines. More particularly, it relates to the use of iron pentacarbonyl as an anti-knock agent in motor fuels and to iron pentacarbonyl of improved stability to light and air.

It is known that iron pentacarbonyl possesses the property of raising the octane value of gasoline. It is ideal in many respects as an anti-knock, a very small amount, less than 0.1% by volume, being sufficient to raise the octane rating of gasoline to a high value. It is very soluble in gasoline, substantially inert with respect to the parts of the engine with which it comes in contact, and in concentrated or diluted form does not cause poisoning on contact with the skin.

Despite its many advantages, iron pentacarbonyl $Fe(CO)_5$, has not attained commercial success as an anti-knock agent due to its inherent instability to light by which it is rapidly decomposed, this decomposition being most rapid in sunlight or blue light and least so in red light. The decomposition is a progressive change, the first product being iron enneacarbonyl, $Fe_2(CO)_9$, which comes down in the form of glistening golden-yellow plates according to the following reaction,

$$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$$

followed by a further decomposition with production of a voluminous black precipitate of ferrous oxide and other iron compounds.

This decomposition not only results in loss of octane value from the initially high level obtained in the gasoline with the freshly dissolved iron pentacarbonyl but also renders the gasoline unfit as a motor fuel due to the propensity of the precipitate to clog the gasoline line or the carburetor.

I have now found that motor fuels of high quality, which in the presence of sunlight and air exhibit a high degree of permanency in respect to anti-knock characteristics and freedom from formation of precipitates derived from the anti-knock agent, may be obtained from gasoline of low octane value and iron pentacarbonyl by employing in conjunction with the latter certain compounds, hereinafter more particularly defined, which act as stabilizers for the iron pentacarbonyl.

The present invention resides in my discovery that iron pentacarbonyl may be rendered substantially permanently resistant to decomposition by light and air when there is intimately associated therewith a hydrocarbon-soluble saturated aliphatic hydroxy polycarboxylic acid partial aliphatic amide. These compounds are acid-reacting by virtue of the presence therein of one or more free carboxyl groups.

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The term partial, as used herein, is employed in the usual sense to define aliphatic amides in which only part of the carboxyl groups of the hydroxy polycarboxylic portion thereof are amidified, the remainder being free.

For improving the stability of iron pentacarbonyl to light and air, the partial aliphatic amides may be employed in widely varying amounts, ranging from about 1% to about 50% by volume on the iron pentacarbonyl. The amount necessary in each instance to render the iron pentacarbonyl substantially permanently stable to light and air may vary with the individual partial aliphatic amides, but, in general, it will be about 5 to 10% by volume on the iron pentacarbonyl.

In the practice of the invention for the preparation of motor fuels of increased anti-knock characteristics the iron pentacarbonyl, which is a liquid, and the stabilizer are simply dissolved in the gasoline or other liquid base fuel to be treated, the mixture being stirred to insure uniformity in dispersion of the iron pentacarbonyl and the stabilizer therein. The iron pentacarbonyl, itself, is employed in amounts of 1 to 4 cc. or more per gallon of the liquid motor fuel, a preferred proportion based on a gasoline of 60–65 octane number being from 3 to 4 cc. per gallon of the gasoline. It will be understood, of course, that the proportion of iron pentacarbonyl used will depend on the initial octane value of the liquid fuel to be treated and as well on the level to which this value is to be lifted by the treatment. Generally, the lower the octane rating of the liquid fuel, the greater should be the proportion of iron pentacarbonyl added thereto.

The iron pentacarbonyl and stabilizer may be added separately to the liquid fuel or, as is preferred, they are added together from a concentrate which is a blend of the iron pentacarbonyl, the stabilizer, and a small proportion of a mutual organic solvent therefor which is compatible as an ingredient of the liquid motor fuel, suitably, a portion of the liquid fuel of the kind to be treated. The stabilized concentrate may be stored over long periods of time without loss in iron pentacarbonyl through decomposition.

Concentrates of stabilized iron pentacarbonyl may be conveniently, and are preferably, prepared by first dissolving the partial aliphatic amide in a relatively small quantity of gasoline, kerosene, benzol or other solvent appropriate to the motor fuel and then adding the iron pentacarbonyl to

this solution with stirring to effect a homogeneous mixture. A suitable proportion of solvent and iron pentacarbonyl in the concentrates is about equal volumes of the two, although this proportion may be varied somewhat where particular concentrations of iron pentacarbonyl are desired.

The motor fuels which may be treated with the stabilized anti-knock agent for improvement in octane value may be any of the usual liquid hydrocarbon fuels such as kerosene, gasoline, straight-run, cracked or so-called "poly" gasoline, or blends of these with benzol, alcohol or the like, Diesel fuels of the Fischer-Tropsch type, or other types, such as alcohols, in which the iron pentacarbonyl and stabilizer are soluble.

By the term hydrocarbon-soluble as used herein is meant that the substance so-designated is soluble in kerosene, gasoline, benzol and the like liquid hydrocarbons.

As a specific example of stabilized anti-knock concentrates which may be prepared in accordance with the invention is the following composition in which was blended in the preferred manner, by volume,

2 parts dioleyl citramide
22 parts gasoline
20 parts iron pentacarbonyl

When mixed with a gasoline of octane number 65 in the proportion of 8.8 cc. to the gallon of gasoline, the mixture represents a motor fuel of 75 octane number which retains its high anti-knock quality over long periods of time on exposure to air or sunlight.

Further illustrative of the partial aliphatic amides which may be employed in accordance with the invention for improving the stability of iron pentacarbonyl to light and air, are, for example, the hydrocarbon-soluble partial aliphatic amides of saturated aliphatic hydroxy polycarboxylic acids having three or more carboxyl groups, such as citric acid, isocitric acid, hydroxy citric acid, 1-hydroxy-1-carboxysuccinic acid, 1-hydroxybutane-1,2,3-tricarboxylic acid, 1-hydroxybutane-1,2,4-tricarboxylic acid, 3-hydroxybutane-1,1,5-tricarboxylic acid, 2-hydroxy-4-methylpentane-1,1,2,4-tetracarboxylic acid and 1,6-dihydroxyhexane-2,2,5,5-tetracarboxylic acid, where the amide group or groups are derived from a primary or secondary aliphatic amine, the alkyl radical of which contains four or more carbon atoms and may contain substituents which do not give rise to corrosive fumes in the engine on combustion of the motor fuel, such as chlorine and bromine atoms, for example, n-dibutylamine, 2-ethyl-hexylamine, di-2-ethyl-hexylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, oleylamine, cyclohexylamine, β-chlorobutylamine, β-bromobutylamine, β-ethoxybutylamine, etc.

Preferably, the amido groups of the aliphatic amides contain the longer chain hydrocarbon radicals, for example, of about 10 or more carbon atoms, as the longer the hydrocarbon chain thereof, generally the greater the hydrocarbon solubility of the aliphatic amide molecule.

The partial aliphatic amides of the saturated aliphatic hydroxy polycarboxylic acids may be prepared by heating an acid ester of these acids with a solution of the amine following known procedure (Karrer, Organic Chemistry, New York, 1938, page 199). For example, citric acid dimethyl ester may be heated with a solution of two mols of oleylamine to obtain the partial amide, dioleyl citramide. Obviously, the temperature to which the reactants are heated should be kept below that at which dehydration of the hydroxy acid occurs. A preferred group of the hydroxy polycarboxylic acids for the preparation of the aliphatic amides are citric, malic, tartaric and tartronic acids, preferred, however, only from the standpoint of ready availability from natural sources. Other preferred hydroxy polycarboxylic acids of the class described are those containing a plurality of hydroxy groups, such as hydroxy citric acid.

In addition to their action as stabilizers for the iron pentacarbonyl in the motor fuel, the herein-defined partial aliphatic amides favorably influence the removal of the residue of the iron pentacarbonyl from the internal combustion engine. In this respect, it has been observed that the residue is almost completely removed from the combustion areas of the engine and emerges from the exhaust as a light, fluffy red powder.

As various other embodiments of the invention will occur to those skilled in the art, it is not intended that the scope of the patent be limited except as is required by the prior art and the appended claims.

I claim:

1. A composition comprising iron pentacarbonyl blended with a minor proportion of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

2. A composition comprising iron pentacarbonyl blended with a minor proportion of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid of at least 3 carboxyl groups, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

3. A composition comprising iron pentacarbonyl blended with a minor proportion of a hydrocarbon-soluble partial alkylamide of citric acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

4. A composition comprising iron pentacarbonyl blended with a minor proportion of a hydrocarbon-soluble partial alkylamide of malic acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

5. A composition comprising iron pentacarbonyl blended with a minor proportion of a hydrocarbon-soluble partial alkylamide of tartaric acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

6. A composition comprising iron pentacarbonyl blended with a minor proportion of dioleyl citramide, the amount of the latter being sufficient to increase the stability to light of the iron pentacarbonyl.

7. A motor fuel comprising a liquid base fuel and dissolved therein a minor proportion of iron

pentacarbonyl and of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

8. A motor fuel comprising a liquid base fuel and dissolved therein a minor proportion of iron pentacarbonyl and of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid of at least 3 carboxyl groups, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

9. A motor fuel comprising a liquid hydrocarbon fuel and dissolved therein a minor proportion of iron pentacarbonyl and of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

10. A motor fuel comprising a liquid hydrocarbon fuel and dissolved therein a minor proportion of iron pentacarbonyl and of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid of at least 3 carboxyl groups, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

11. A motor fuel comprising a liquid hydrocarbon fuel and dissolved therein a minor proportion of iron pentacarbonyl and of a hydrocarbon-soluble partial alkylamide of citric acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

12. A motor fuel comprising a liquid hydrocarbon fuel and dissolved therein a minor proportion of iron pentacarbonyl and of a hydrocarbon-soluble partial alkylamide of malic acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

13. A motor fuel comprising a liquid hydrocarbon fuel and dissolved therein a minor proportion of iron pentacarbonyl and of a partial alkylamide of tartaric acid wherein the alkyl radical of the amide group in each instance contains at least four carbon atoms, the amount of the alkylamide being sufficient to increase the stability to light of the iron pentacarbonyl.

14. A motor fuel comprising a liquid hydrocarbon fuel and dissolved therein a minor proportion of iron pentacarbonyl and of dioleyl citramide, the amount of the latter being sufficient to increase the stability to light of the iron pentacarbonyl.

15. A stabilized iron pentacarbonyl concentrate consisting essentially of iron pentacarbonyl, from about 1 to about 50% by volume on the pentacarbonyl of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, and an amount of a liquid hydrocarbon solvent sufficient to dissolve the pentacarbonyl and the partial alkylamide.

16. A stabilized iron pentacarbonyl concentrate consisting essentially of iron pentacarbonyl, from about 1 to about 50% by volume on the pentacarbonyl of a hydrocarbon-soluble partial alkylamide of a saturated aliphatic hydroxy polycarboxylic acid of at least 3 carboxyl groups, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, and an amount of a liquid hydrocarbon solvent sufficient to dissolve the pentacarbonyl and the partial alkylamide.

17. A stabilized iron pentacarbonyl concentrate consisting essentially of iron pentacarbonyl, from about 1 to about 50% by volume on the pentacarbonyl of a hydrocarbon-soluble partial alkylamide of citric acid, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, and an amount of a liquid hydrocarbon solvent sufficient to dissolve the pentacarbonyl and the partial alkylamide.

18. A stabilized iron pentacarbonyl concentrate consisting essentially of iron pentacarbonyl, from about 1 to about 50% by volume on the pentacarbonyl of a hydrocarbon-soluble partial alkylamide of malic acid, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, and an amount of a liquid hydrocarbon solvent sufficient to dissolve the pentacarbonyl and the partial alkylamide.

19. A stabilized iron pentacarbonyl concentrate consisting essentially of iron pentacarbonyl, from about 1 to about 50% by volume on the pentacarbonyl of a hydrocarbon-soluble partial alkylamide of tartaric acid, wherein the alkyl radical of the amide group in each instance contains at least 4 carbon atoms, and an amount of a liquid hydrocarbon solvent sufficient to dissolve the pentacarbonyl and the partial alkylamide.

20. A stabilized iron pentacarbonyl concentrate consisting essentially of iron pentacarbonyl, from about 1 to about 50% by volume on the pentacarbonyl of dioleyl citramide, and an amount of a liquid hydrocarbon solvent sufficient to dissolve the pentacarbonyl and the dioleyl citramide.

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No references cited.