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MOTOR FUELS AND PREPARATION THEREOF

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This invention relates to novel motor fuels, particularly high anti-knock aviation engine fuels, and to methods of preparing same.

It is known that aromatic amines such as toluidine, xylidines, etc. are especially good anti-knock agents for motor fuels, even when used in relatively small amounts in the range of ½%, 1% or 2%, but considerable difficulty has been experienced from the point of view that motor fuels to which such aromatic amines have been added tend to go off color, i. e., to darken during storage, much more than similar fuels without such aromatic amines. Some stabilizers have been found which tend to prevent or to reduce the discoloration of the aromatic amines per se during storage, but even when such stabilizers are used in fuels containing the aromatic amines substantial discoloration difficulties have still persisted.

The primary object of the present invention is to overcome these difficulties and to prepare high anti-knock motor fuels containing aromatic amines but which will be substantially stable against discoloration during storage.

It has now been found that the chief reason for the difficulties of the past in the discoloration of a motor fuel containing aromatic amines and also containing a color stabilizer for said aromatic amines, is that certain other materials which had been added to the motor fuel for preventing gum formation in the hydrocarbon fuel base stock, had reacted in some deleterious manner with either the aromatic amines per se or with the color stabilizer, or in some unknown manner had not only failed to let the color stabilizer perform its normal function in stabilizing the aromatic amine against discoloration, but in some instances actually accelerated or aggravated the discoloration of the aromatic amine. After substantial investigation it has been found that the gum inhibitors which cause this deleterious action are those which contain amino groups such as normal butyl para amino phenol, isobutyl para amino phenol, mono benzyl para amino phenol, etc. On the other hand, it has been found that alkylated hydroxy aromatic compounds free from amino groups may be used satisfactorily in motor fuels containing aromatic amines and a color stabilizer therefor.

Accordingly, as examples of gum inhibitors which may be used according to the present invention may be mentioned naphthols, particularly alpha naphthol, tricresol (which is a mixture of the three isomeric, ortho, meta and para cresols), tertiary butyl phenol, wood tar distillate (which contains monohydric phenols with or

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without partially etherized polyhydric phenols), xylenols, tertiary butyl para cresol, hydroquinone, tertiary butyl ether of ortho tertiary butyl para cresol, or other tertiary alkyl ethers of alkyl phenols, diamyl phenol, petroleum phenols or alkylated products thereof, etc.

The amount of such gum inhibitor need only be a very small amount such as about 0.1 to 1.0 lbs./1000 gallons of fuel, the exact amount to be used depending primarily upon the gum forming tendencies of the hydrocarbon fuel base stock used and the intended storage conditions of time, temperature, etc.

The hydrocarbon fuel base stock may consist of any suitable gasoline base stock such as straight run or cracked petroleum distillates from paraffinic, naphthenic, mixed base, or other suitable crude petroleums, products made by special processes such as polymerization, alkylation, isomerization, hydrogenation, etc., or mixtures of any of the above, or any products obtained therefrom after various refining treatment such as acid treating, clay treating, solvent extraction, etc.

In addition to the above mentioned types of hydrocarbon liquids, the motor fuel base stock may also contain 5, 10, 20, 30% or more of the various oxygenated or other derivatives of hydrocarbons as blending agents for improving octane number or for other purposes. Such blending agents may include, for example, one or more of the various alcohols such as methanol, ethanol, isopropyl alcohol, tertiary butyl alcohol, etc.; or various anti-knock ethers such as di-isopropyl ether, ethyl isopropyl ether, methyl tertiary butyl ether, etc.; or ketones such as acetone, methyl isopropyl ketone, etc.

Although broadly the invention applies to any of the above types of base stocks suitable for motor fuel, regardless of octane number, the invention is particularly applicable to base stocks having an A. S. T. M. octane number of at least 70.

The aromatic amine which is to be used according to this invention may be any one which is sufficiently soluble in the gasoline base stock and which has a suitable boiling point or boiling range and is otherwise suitable as a potent anti-knock agent. Although the invention is intended to apply broadly to any such aromatic amines, it is believed particularly applicable to alkaryl amines, especially those having from 1 to 3 carbon atoms such as one or more of the xylidines which have the chemical formula: $(CH_3)_2C_6H_3NH_2$; either the pure separate isomer may be used or mixtures thereof. Other alkaryl amines which may be

used include the toluidines, ortho, meta or para, or mixtures thereof, the several ethyl anilines, cumidine (which is isopropyl aniline), etc. Although it is preferred to use such alkaryl amines, other aromatic amines may be used such as aniline, the various naphthylamines such as isopropyl or tertiary butyl naphthylamine, and the various derivatives of aniline in which either or both of the hydrogens of the amino group are substituted by hydrocarbons, i. e., either alkyl or aryl groups, e. g., N-monomethyl aniline, N-dimethyl aniline, N-monoethyl aniline, etc. Thus the aromatic amines may be primary, secondary, or tertiary amines.

The amount of such aromatic amines to be used will depend primarily upon the desired increase in octane number, but normally will range from about 0.5 to 5.0%, generally about 1 or 2% being found satisfactory.

The susbtance to be added for the primary purpose of stabilizing the aromatic amine against discoloration during storage may be selected from a fairly large group of materials such as the various organic sulfur compounds, particularly of the aryl mercaptan type, such as p-thiocresol, or other alkyl aromatic mercaptans, preferably having one to six alkyl carbon atoms, or heterocyclic organic compounds containing sulfur, such as thiophene or carbon disulfide, or even elemental sulfur. These various materials may be classed broadly as sulfur-containing stabilizers. The amount of such stabilizer to be used may range from about .0005% to .1% or preferably about .002 to .05% based on the total volume of motor fuel.

The invention also contemplates the use of metallo organic anti-knock agents, especially of the tetraethyl lead (T. E. L.) type, particularly in preparing high octane aviation motor fuels, and the amount of such addition agent may range from about 0.5 to 4 or even 6 cc. or more per gallon of motor fuel. In place of tetraethyl lead one may use other lead alkyl anti-knock agents such as tetramethyl lead, dimethyl diethyl lead, etc.

For the sake of illustration, the following specific examples are given:

Example I

A high octane aviation motor fuel was prepared by blending together the following material:

50% naphtha base stock having an octane number of 75,
49% high anti-knock hydrocarbon blending agent, e. g., alkylate, having an octane number of about 91,
1% commercial xylidine (mixture of isomeric xylidines),
4 cc. T. E. L./gal.,
1 lb./5000 gals. tricresol,
1 lb./5000 gals. of carbon disulfide.

Example II

Same as Example I, except for the last two items which are as follows:

0.5 lb./5000 gals. tricresol,
0.5 lb./5000 gals. carbon bisulfide.

Example III

Same as Example I, except for the last two items which are as follows:

0.5 lb./5000 gals. tricresol,
0.5 lb./5000 gals. p-thiocresol.

Example IV

Same as Example I, except for the last two items which are as follows:

1 lb./5000 gals. alkylated cresols,
1 lb./5000 gals. carbon disulfide.

It is not intended that this invention be limited to the particular materials which have been given merely for the sake of illustration, nor necessarily by any theory suggested as to the mechanism of the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as well as all modifications coming within the scope and spirit of the invention.

I claim:

1. A motor fuel composition comprising gasoline hydrocarbons, a knock reducing amount of aromatic amine, a gum inhibiting amount of alkylated hydroxy aromatic oxidation inhibitor free from any amino substituents and a sufficient amount of carbon disulfide to stabilize the aromatic amine present in said fuel against discoloration during storage.

2. A motor fuel according to claim 1 containing at least 50% by volume of hydrocarbon base stock and about 0.5 to 5.0% of alkaryl amine anti-knock agent containing 1 to 3 alkyl carbon atoms.

3. A motor fuel according to claim 1 in which the carbon disulfide is present in an amount less than 0.1%.

4. A motor fuel composed essentially of the following ingredients: about 90–99% of hydrocarbon fuel base stock of the gasoline boiling range and having an octane number of at least 70; 0.5 to 2% of xylidine; about 0.1 to 1.0 lb./1000 gallons of alkylated hydroxy aromatic gum inhibitor free of any amino substituent; about .0005% to .1% of carbon disulfide, and 0.5 to 6.0 cc. of tetraethyl lead per gallon of fuel.

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