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MOTOR FUEL

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This invention relates to high-compression spark-ignition engine motor fuels and valuable high boiling point anti-knock ingredients therefor. It is particularly concerned with diketones having pronounced effectiveness in suppressing detonation and other advantageous fuel blending qualities.

Combustible oxygen-containing organic compounds of anti-knock value in spark-ignition engine fuels have been developed mainly in the alcohol and ether classes of compounds. More recently, it was found that certain compounds containing oxygen are enhanced in anti-knock value when they contain branched alkyl terminals, but the relation between branching and anti-knock value has not been found regular for all oxygen-containing compounds, especially not for those compounds that contain more than one oxygen constituent, such as diketones, hydroxy ketones, and ester ketones. Unfortunately, alcohols and ethers of high anti-knock blending value which are readily obtainable are for the most part relatively low boiling and therefore not helpful for improving the anti-knock value of the higher boiling portions of motor fuels, these higher boiling portions being usually poorest in octane number.

In studying the operation of multicylinder engines, it has been found that the best fuels are those which possess uniformly high octane numbers throughout the complete boiling range of the fuel. It appears that a fractionation of the fuel tends to occur in the intake manifold of the engine, resulting in uneven distribution of the motor fuel fractions to the various cylinders, so that with a fuel composed of a plurality of ingredients having octane blending values varying with their boiling points, some cylinders in the engine tend to knock whereas others are entirely free of this difficulty.

One of the objects of the present invention is to enhance the octane number of relatively high boiling motor fuel fractions. Another object is to provide motor fuel blending agents which remain stably blended with hydrocarbon base fuels. Still another object is to provide blending agents which are particularly adapted for high flash "safety" and injection fuels, i. e. fuels boiling in the range of about 300° F. to 400° F. and up to 600° F., such blending agents having no substantial detrimental effect upon the specifications of the fuel, such as flash point, spontaneous ignition temperature, resistance to oxidation or gum forming, and being beneficial for the carburetion and injection of the fuel.

The present invention involves the addition to motor fuels of ketonic compounds containing at least two oxygen atoms per molecule. In general, these compounds have the type compositions represented by:

$$R\cdot CO\cdot R^1\cdot CO\cdot R^2$$

wherein R and R^2 represent terminal hydrocarbon groups linked to carbon atoms in functional groups characterized by an oxygen atom joined to a single carbon atom, as in a carbonyl or keto function, and R^1 represents an aliphatic group, such as an alkylene group separating these functional groups. Regardless of whether the terminal groups are branched or non-branched, a significant structural feature of these compounds which now has been found to affect their anti-knock value is the intervening group R^1 that separates the oxygen-containing functional groups. It has been observed that the anti-knock value of this class of compounds markedly increases with the number of carbon atoms of this intervening group, particularly when both oxygen constituents are in keto groups and the terminal hydrocarbon groups are primary. Moreover, this same principle has been noted to apply to compounds containing terminal aromatic, naphthenic, and branched aliphatic, groups and compounds in which a hydroxyl group is one of the functional groups in addition to a keto group.

The preferred types of blending compounds provided by this invention are more specifically characterized by the structural formula:

$$R\overset{O}{\overset{\|}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}R_2$$

wherein R and R^2, as before, represent terminal hydrocarbon groups, $(CH_2)_n$ stands for the intervening alkylene group, i. e., a number of methylene groups taken n times, or an alkyl substituted methylene group and n is preferably an integer greater than 1. Specific examples of these blending agents are the gamma diketones, such as acetonyl acetone, in which the carbonyl groups are in a 1:4 position, or further apart.

Ketonic compounds containing cyclic hydrocarbon radicals are likewise indicated to have improved anti-knock blending values in so far as they have structures conforming with those found best for the aliphatic compounds. An example of these compounds is benzoyl acetone.

However, these cyclic compounds are considered, in general, less useful because of their higher melting points and relatively lower solubility in hydrocarbon fuels.

In the practice of this invention, the selected relatively high boiling ketonic compounds, of which the lower molecular weight members generally begin to boil at about 300° F., may be blended with low boiling blending agents, such as isopropyl ether, alcohols, branched monoketones, branched hydrocarbons, aromatic hydrocarbons, etc., although in the case of most

high octane number fuels this is not necessary, since the low boiling ends of the fuel generally possess sufficiently high octane number values. Various organo-metallic anti-knock blending agents such as lead alkyl compounds may be employed therewith. But it is important to note that the diketones of the present invention are particularly suitable for improving high flash "safety" fuels which have been difficult to improve. It might be pointed out, also, that the preferred diketone blending agents featured herein appear to enhance the functioning of the fuel feed system. Furthermore, these compounds are relatively stable for they do not readily form peroxides as do many lower boiling oxygen-containing aliphatic compounds.

The best results are obtained with the preferred ketonic compounds mentioned when several of them are employed in minor amounts together with higher boiling fractions of cracked and/or synthetic gasolines, or with naphthas which include polymers of hydrogenated polymers and similar materials boiling in the range of 300° F. to 600° F. However, ordinary straight run gasoline and gasoline hydrocarbon fuel bases obtained by any of the known commercial methods are subject to improvement by these ketonic compounds used individually or combined. When used with these base stocks, proportions on a volumetric basis of 5%, 10%, or even 50% or more of the ketonic compounds may be employed, although there is generally no advantage in over 50%. In substantially all cases, even one or a few per cent is sufficient to show an appreciable improvement in motor fuel qualities. The following examples are presented to illustrate some of the many phases involved in the practice of this invention and to demonstrate the basis on which the most effective agents are selected:

Blends prepared with each addition agent in a hydrocarbon base reference fuel were tested by the Cooperative fuel research motor method (C. F. R. M. M.) for evaluation of their anti-knock value improvement. The results of these tests were made comparable and were evaluated on a common basis for comparison, that is, the A. S. T. M. octane blending value of each agent was determined with respect to the improvement which would be gained by using the same concentration of iso-octane as blending agent, the octane number of iso-octane being regarded as 100. Thus, a blending agent with an octane blending value above 100 is considered to have an excellent anti-knock rating as a fuel ingredient, and even more so as this value increases. From the data obtained in a series of tests, the results are summarized as follows:

Addition agent	Structure	Boiling point °F.	A.S.T.M. octane blending value
Diacetyl	$H_3C-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$	190	+20
Acetyl acetone	$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	285	+97
Acetonyl acetone	$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	376	+150

The foregoing table has been arranged to illustrate how the diketones in an unusual manner increase in octane blending value with lengthening of the intermediate alkylene group and increase of boiling point. This relation of structure to octane blending value is novel and peculiar because from what is known about hydrocarbons, alcohols, and ethers in general, the blending value decreases as the molecular weight of the compound is increased, and it is this feature of these ketonic compounds which proves valuable in selecting more satisfactory compounds, in that it permits desired improvement of high anti-knock value in higher boiling fuel fractions, and also because it permits selection of compounds with lower melting points, higher solubility in fuels, and greater stability. For higher melting point and solubility, the aliphatic compounds are preferred, but diketones containing cyclic radicals are useful in other respects, such as for their cold appreciation, i. e. their capacity to improve the anti-knock value of a fuel used in an engine having a low intake manifold temperature.

It can be readily appreciated that this invention makes available new sources of valuable motor fuel blending agents comprising a series of ketonic compounds having satisfactory volatility characteristics. A somewhat limited list of these compounds is as follows:

Name	Composition formula	Boiling point, °F.
Acetyl-propionyl-methane.	$CH_3COCH_2COC_2H_5$	316
Diacetyl-methyl-methane.	$CH_3COCH(CH_3)COCH_3$	340
Isobutyryl-acetone	$CH_3COCH_2COCH(CH_3)_2$	334
Methyl-propionyl-acetone.	$CH_3COCH(CH_3)COC_2H_5$	334
Diacetyl-dimethyl-methane.	$CH_3COC(CH_3)_2COCH_3$	360
Diacetyl-diethyl-methane.	$CH_3COC(C_2H_5)_2COCH_3$	397
Dipivaloyl-dimethyl-methane.	$(CH_3)_3COC(CH_3)_2CO(CH_3)_3$	436
Diacetyl-acetone	$CH_3COCH_2COCH_2COCH_3$	428
2·3 Diaceto-butane	$CH_3COCH(CH_3)CH(CH_3)COCH_3$	410
Diaceto-butylene	$(\cdot CO\cdot C_2H_4\cdot CO\cdot)CHCH_2CH=CH_2$	

Accordingly, several of these suitable diketones may be combined with the fuel to increase the blending value uniformly over a desired range of distillation points above 300° F. It might be pointed out that to some extent analogous hydroxy ketones respond to the same method of selection based on their structures although they appear to do so to a lesser degree.

The preferred diketones which have been described may be synthesized by a number of well known methods. For example, they may be formed by a Claisen condensation involving the elimination of an alcohol molecule in the condensation of an ester with a monoketone or another ester molecule. A general method for producing the higher ketones may be carried out by reacting diacyl halides with alkyl zince iodide. For the commercial manufacture of mixed diketones, a number of practical methods may be employed, for example, a controlled ozonization or oxidation of diolefinic hydrocarbons, hydration of diacetylenes, or a Friedel-Crafts condensation of acyl halides.

The preferred ketonic compounds which have been described are miscible with hydrocarbon fuels in proportions extending over a wide range. They have a high solvency for nitrogen and oxygen-containing compounds, such as aromatic amines and alcohols, which adapts them for use together with such blending agents. They are relatively resistant to oxidation and can be preserved for extended periods with small amounts

of oxidation inhibitors, such as aromatic amines or aromatic hydroxy compounds, e. g. beta, phenyl alpha-naphthyl amine, alpha-naphthol, or similar known inhibitors. They may also be used with other known addition agents such as gum fluxes, corrosion inhibitors, color stabilizers, dyes, lubricants, etc.

Various modifications may be made within the scope of this invention which is not intended to be limited by the specific examples given for the sake of illustration.

I claim:

1. A motor fuel composition comprising mostly hydrocarbons adapted as a fuel for spark-ignition engines blended with a minor but effective octane improving amount of at least 1% by volume of a ketonic compound boiling in the boiling range of said fuel and having the formula:

$$R \cdot CO \cdot R^1 \cdot CO \cdot R^2$$

wherein R and R^2 are terminal organic groups, and R^1 represents an aliphatic hydrocarbon radical separating carbon atoms linked to oxygen, each oxygen atom being bound to only one carbon atom, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

2. A motor fuel composition comprising mainly hydrocarbons adapted as a fuel for spark-ignition engines blended with a minor but effective octane improving amount of at least 1% by volume of an aliphatic diketone boiling in the range of 300° F. to 600° F., the keto groups in said diketone being separated by an alkylene group, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

3. A motor fuel composition comprising mainly a hydrocarbon fuel adapted for spark-ignition engines blended with a substantial anti-knock value improving amount of at least 1% by volume of a diketone boiling in the range of about 300° F. to 600° F. and having the formula:

$$R \cdot CO \cdot (CH_2)_n \cdot CO \cdot R^2$$

wherein R and R^2 are terminal alkyl groups and $(CH_2)_n$ represents an alkylene group containing at least 2 carbon atoms, n being an integer greater than 1, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

4. A motor fuel composition comprising motor fuel hydrocarbons boiling in the range of 300° F. to 600° F. and a minor but effective octane improving amount of at least 1% by volume of polyketones boiling in said range, said polyketones having alkylene groups separating keto functions, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

5. A motor fuel composition comprising gasoline hydrocarbons and a minor but effective octane improving amount of at least 1% by volume of a diketone boiling in the range of 300° F. to 600° F. and belonging to the homologous series of diacetyl-alkyl-methanes, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

6. A motor fuel composition comprising gasoline hydrocarbons blended with a minor but effective octane improving of at least 1% by volume amount of diacetyl-dimethyl-methane, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

7. A motor fuel composition comprising naphtha hydrocarbons boiling in the range of 300° F. to 600° F. blended with a minor but effective octane improving amount of at least 1% by volume of an alkyl-acetonyl-acetone boiling in the range of 300° F. to 600° F., said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

8. A motor fuel composition comprising naphtha hydrocarbons boiling in the range of 300° F. to 600° F. blended with a minor but effective octane improving amount of at least 1% by volume of methyl-propionyl-acetone, said fuel composition being free of any substantial amount of other oxygen-containing organic compounds.

9. A motor fuel composition consisting essentially of naphtha hydrocarbons blended with at least 1% by volume of acetonyl acetone to substantially increase the octane number of the fuel, said composition being free of any substantial amount of other oxygen-containing organic compounds.

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